

Chapter 9

Stable isotope geochemistry

9.1 INTRODUCTION

Stable isotope geochemistry is concerned with variations in the isotopic compositions of elements arising from physicochemical processes rather than nuclear processes. Fractionation[†] of the isotopes of an element might at first seem to be an oxymoron. After all, in the last chapter we saw that the value of radiogenic isotopes was that the various isotopes of an element had identical chemical properties and therefore that isotope ratios such as $^{87}\text{Sr}/^{86}\text{Sr}$ are not changed measurably by chemical processes. In this chapter we will find that this is not quite true, and that the very small differences in the chemical behavior of different isotopes of an element can provide a very large amount of useful information about chemical (both geochemical and biochemical) processes.

The origins of stable isotope geochemistry are closely tied to the development of modern physics in the first half of the 20th century. The discovery of the neutron in 1932 by H. Urey and the demonstration of variable isotopic compositions of light elements by A. Nier in the 1930s and 1940s were the precursors to this development. The real history of stable isotope geochemistry begins in 1947 with the publication of Harold Urey's paper, *The Thermodynamic Properties of Isotopic Substances*, and Bigeleisen and Mayer's paper *Calculation of Equilibrium Constants for Isotopic Exchange Reactions*. These works not

only showed why, on theoretical grounds, isotope fractionations could be expected, but also suggested that these fractionations could provide useful geologic information. Urey then set up a laboratory to determine the isotopic compositions of natural substances and the temperature dependence of isotopic fractionations, in the process establishing the field of stable isotope geochemistry.

What has been learned in the 65 years since those papers were published would undoubtedly astonish even Urey. Stable isotope geochemistry, like radiogenic isotope geochemistry, has become an essential part of not only geochemistry, but also the earth sciences as a whole. In this chapter, we will attempt to gain an understanding of the principles underlying stable isotope geochemistry and then briefly survey its many-fold applications in the earth sciences. In doing so, we add the final tool to our geochemical toolbox.

9.1.1 Scope of stable isotope geochemistry

Traditionally, the principal elements of interest in stable isotope geochemistry were H, C, N, O, and S. Over the last two decades, Li and B have also become "staples" of isotope geochemistry. These elements have several common characteristics:

1. They have low atomic mass.
2. The relative mass difference between their isotopes is large.

[†]Fractionation in this context refers to the change in an isotope ratio that arises as a result of some chemical or physical process.

3. They form bonds with a high degree of covalent character.
4. The elements exist in more than one oxidation state (C, N, and S), form a wide variety of compounds (O), or are important constituents of naturally occurring solids and fluids.
5. The abundance of the rare isotope is sufficiently high (generally at least tenths of a percent) to facilitate analysis.

It was once thought that elements not meeting these criteria would not show measurable variation in isotopic composition. However, as new techniques offering greater sensitivity and higher precision have become available (particularly use of the MC-ICP-MS), geochemists have begun to explore isotopic variations of many more elements, including Mg, Si, Cl, Ca, Ti, Cr, Fe, Zn, Cu, Ge, Se, Mo, Tl, and U. The isotopic variations observed in these elements have generally been quite small. Nevertheless, some geologically useful information has been obtained from isotopic study of these metals and exploration of their isotope geochemistry continues. We will not have space to consider these isotopes here; their application is reviewed in a recent book (Johnson *et al.*, 2004).

The elements of interest in radiogenic isotope geochemistry are heavy (Sr, Nd, Hf, Os, Pb), most form dominantly ionic bonds, generally exist in only one oxidation state, and there is only small relative mass differences between the isotopes of interest. Thus isotopic fractionation of these elements is quite small. More importantly, with the exception of Pb, natural fractionation is routinely corrected for in the process of correcting much larger fractionations that typically occur during analysis. Thus is it that one group of isotope geochemists make their living by measuring isotope fractionations while the other group makes their living by ignoring them!

Stable isotope geochemistry has been applied to a great variety of problems, and we will see a number of examples in this chapter. One of the most common is geothermometry.

Another is process identification. For instance, plants that produce “C₄” hydrocarbon chains (that is, hydrocarbon chains 4 carbons long) as their primary photosynthetic product will fractionate carbon differently to plants that produce C₃ chains. This fractionation is retained up the food chain. This allows us, for example, to draw some inferences about the diet of fossil mammals from the stable isotope ratios in their bones. Sometimes stable isotope ratios are used as “tracers”, much as radiogenic isotopes are. So, for example, we can use oxygen isotope ratios in igneous rocks to determine whether they have assimilated crustal material, as crust generally has different O isotope ratios than does the mantle. One of the most important and successful applications has been in paleoclimatology, where fractionation of O and H isotopes in the hydrologic cycle has left a record of climate change in marine sediments and glacial ice.

9.1.2 Some definitions

9.1.2.1 The δ notation

As we shall see, variations in stable isotope ratios are typically in the parts per thousand to parts per hundred range and are most conveniently and commonly reported as *per mil* deviations, δ , from some standard. For example, O isotope ratios are often reported as per mil deviations from SMOW* (standard mean ocean water) as:

$$\delta^{18}\text{O} = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sam}} - (^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}} \right] \times 10^3 \quad (9.1)$$

Unfortunately, a dual standard developed for reporting O isotopes. While O isotopes in most substances are reported relative to SMOW, the oxygen isotope composition of carbonates is reported relative to the Pee Dee Belemite (PDB) carbonate standard.[†] This value is related to SMOW by:

$$\delta^{18}\text{O}_{\text{PDB}} = 1.03086 \delta^{18}\text{O}_{\text{SMOW}} + 30.86 \quad (9.2)$$

* In practice, this and other standards are artificially prepared and distributed by the International Atomic Energy Commission in Vienna. These working standards are sometimes referred to as “V-SMOW”, “V-CDT”, and so on.

[†] There is, however, a good historical reason for this: analytical difficulties in the measurement of carbonate oxygen prior to 1965 required it be measured against a carbonate standard.

A similar δ notation is used to report other stable isotope ratios. Hydrogen isotope ratios, δD , are also reported relative to SMOW, carbon isotope ratios relative to PDB, nitrogen isotope ratios relative to atmospheric nitrogen (denoted ATM), and sulfur isotope ratios relative to troilite in the Canyon Diablo iron meteorite (denoted CDT). Boron and lithium isotope ratios are reported relative to laboratory standards. Table 9.1 lists the isotopic composition of these standards.

9.1.2.2 The fractionation factor

The *fractionation factor*, α , is the ratio of isotope ratios in two phases:

$$\alpha_{A-B} \equiv \frac{R_A}{R_B} \quad (9.3)$$

The fractionation of isotopes between two phases is also often reported as $\Delta_{A-B} = \delta_A - \delta_B$. The relationship between Δ and α is:

$$\Delta \approx (\alpha - 1) \times 10^3 \quad \text{or} \quad \delta \approx 10^3 \ln \alpha \quad (9.4)^*$$

As we will see, *at equilibrium*, α may be related to the equilibrium constant of thermodynamics by:

$$\alpha_{A-B} = (K/K_\infty)^{1/n} \quad (9.5)$$

where n is the number of atoms exchanged, K_∞ is the equilibrium constant at infinite temperature, and K is the equilibrium constant written in the usual way (except that concentrations are used rather than activities because the ratios of the activity coefficients are equal to 1, i.e., there are no isotopic effects on the activity coefficient).

9.2 THEORETICAL CONSIDERATIONS

Isotope fractionation can originate from both *kinetic* effects and *equilibrium* effects. The former may be intuitively expected, but the latter may at first seem somewhat surprising. After all, we have been taught that the chemical properties of an element are dictated by its electronic structure, and that the nucleus plays no real role in chemical interactions. In

Table 9.1 Isotope ratios of stable isotopes.

Element	Notation	Ratio	Standard	Absolute ratio
Hydrogen	δD	D/H ($^2\text{H}/^1\text{H}$)	SMOW	1.557×10^{-4}
Lithium	$\delta^7\text{Li}$	$^7\text{Li}/^6\text{Li}$	NIST 8545 (L-SVEC)	12.285
Boron	$\delta^{11}\text{B}$	$^{11}\text{B}/^{10}\text{B}$	NIST 951	4.044
Carbon	$\delta^{13}\text{C}$	$^{13}\text{C}/^{12}\text{C}$	PDB	1.122×10^{-2}
Nitrogen	$\delta^{15}\text{N}$	$^{15}\text{N}/^{14}\text{N}$	Atmosphere	3.613×10^{-3}
Oxygen	$\delta^{18}\text{O}$	$^{18}\text{O}/^{16}\text{O}$	SMOW, PDB	2.0052×10^{-3}
	$\delta^{17}\text{O}$	$^{17}\text{O}/^{16}\text{O}$	SMOW	3.76×10^{-4}
Sulfur	$\delta^{34}\text{S}$	$^{34}\text{S}/^{32}\text{S}$	CDT	4.416×10^{-2}
	$\delta^{33}\text{S}$	$^{33}\text{S}/^{32}\text{S}$	CDT	7.877×10^{-3}
	$\delta^{36}\text{S}$	$^{36}\text{S}/^{32}\text{S}$	CDT	1.535×10^{-4}

* To derive this, we rearrange eqn. 9.1 to obtain: $R_A = (\delta_A + 10^3)R_{STD}/10^3$. Note that Δ is sometimes defined as $\Delta \equiv 10^3 \ln \alpha$, in which case $\Delta_{AB} \approx \delta_A - \delta_B$. So that α may be expressed as:

$$\alpha = \frac{(\delta_A + 10^3)R_{STD} / 10^3}{(\delta_B + 10^3)R_{STD} / 10^3} \approx \frac{(\delta_A + 10^3)}{(\delta_B + 10^3)}$$

Subtracting 1 from each side and rearranging, we obtain:

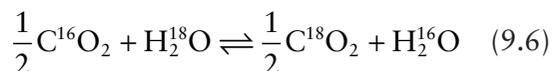
$$\alpha - 1 = \alpha - 1 = \frac{(\delta_A - \delta_B)}{(\delta_B + 10^3)} \approx \frac{(\delta_A - \delta_B)}{10^3} \approx 2 \times 10^{-3}$$

Since δ is small, the second equation in 9.4 results from the approximation that for $x \approx 1$, $\ln x \approx x - 1$.

the following sections, we will see that quantum mechanics predicts that the mass of an atom affects its vibrational motion, and therefore the strength of chemical bonds. It also affects rotational and translational motions. From an understanding of these effects of atomic mass, it is possible to predict the small differences in the chemical properties of isotopes quite accurately.

9.2.1 Equilibrium isotope fractionations

Most isotope fractionations arise from *equilibrium* effects. *Equilibrium fractionations arise from translational, rotational and vibrational motions of molecules in gases and liquids and atoms in crystals because the energies associated with these motions are mass-dependent.* Systems tend to adjust themselves so as to minimize energy. Thus isotopes will be distributed so as to minimize the vibrational, rotational, and translational energy of a system. Of the three types of energies, vibrational energy makes by far the most important contribution to isotopic fractionation. Vibrational motion is the only mode of motion available to atoms in a solid. These effects are, as one might expect, small. For example, the equilibrium constant for the reaction:



is only about 1.04 at 25°C and the ΔG of the reaction, given by $-RT \ln K$, is only -100J/mol (you'll recall most ΔG s for reactions are typically in the kJ/mol range).

9.2.1.1 The quantum mechanical origin of isotopic fractionations

It is fairly easy to understand, at a qualitative level at least, how some isotope fractionations can arise from vibrational motion. Consider the two hydrogen atoms of a hydrogen molecule: they do not remain at a fixed distance from one another; rather they continually oscillate toward and away from each other, even at absolute zero. The frequency of this oscillation is quantized, that is, only discrete frequency values are possible. Figure 9.1 is a schematic diagram of energy as a function of interatomic distance in the hydrogen molecule. As the atoms vibrate back and forth,

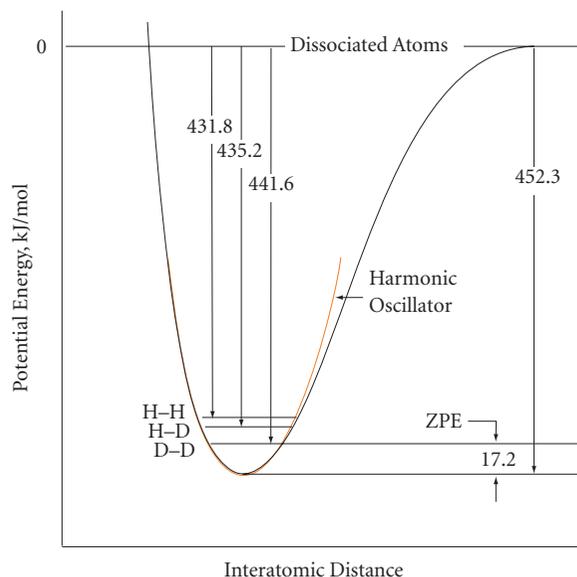


Figure 9.1 Energy-level diagram for the hydrogen molecule. Fundamental vibration frequencies are 4405 cm^{-1} for H_2 , 3817 cm^{-1} for HD , and 3119 cm^{-1} for D_2 . The zero point energy of H_2 is greater than that of HD , which is greater than that of D_2 . Arrows show the energy, in kJ/mol , required to dissociate the three species. After O'Neil (1986). With permission from the Mineralogical Society of America.

their potential energy varies as shown by the curved line. The *zero point energy* (ZPE) is the energy level at which the molecule will vibrate in its ground state, which is the state in which the molecule will be at low temperature. The zero point energy is always some finite amount above the minimum potential energy of an analogous harmonic oscillator.

The potential energy curves for various isotopic combinations of an element are identical, but as the figure shows, the zero point vibrational energies differ, as do vibration energies at higher quantum levels, being lower for the heavier isotopes. Vibration energies and frequencies are directly related to bond strength. Because of this, the energy required for the molecule to dissociate will differ for different isotopic combinations. For example, 440.6 kJ/mol is necessary to dissociate a D_2 ($^2\text{H}_2$) molecule, but only 431.8 kJ/mol is required to dissociate the $^1\text{H}_2$ molecule. Thus the bond formed by the two deuterium atoms is 9.8 kJ/mol stronger than the H-H bond. The differences in bond strength can also lead

to kinetic fractionations, since molecules that dissociate more easily will react more rapidly. We will discuss kinetic fractionations later.

9.2.1.2 Predicting isotopic fractionations from statistical mechanics

Now let's attempt to understand the origin of isotopic fractionations on a more quantitative level. We have already been introduced to several forms of the *Boltzmann distribution law* (e.g., eqn. 2.84), which describes the distribution of energy states. It states that the probability of a molecule having internal energy E_i is:

$$\mathcal{P}_i = \frac{g_i e^{-E_i/kT}}{\sum_n g_n e^{-E_n/kT}} \quad (9.7)$$

where g is a statistical weight factor,* k is Boltzmann's constant, and the sum in the denominator is taken over all possible states. The average energy (per molecule) is:

$$\bar{E} = \sum_i E_i \mathcal{P}_i = \frac{\sum_i g_i E_i e^{-E_i/kT}}{\sum_i g_i e^{-E_i/kT}} \quad (9.8)$$

As we saw in Chapter 2, the *partition function*, Q , is the denominator of this equation:

$$Q = \sum_n g_n e^{-E_n/kT} \quad (9.9)$$

The partition function is related to thermodynamic quantities U and S (eqns. 2.90 and 2.91). Since there is no volume change associated with isotope exchange reactions, we can use the relationship:

$$\Delta G = \Delta U - T\Delta S \quad (9.10)$$

and eqns. 2.120 and 2.124 to derive:

$$\Delta G_r = -RT \ln \prod_i Q_i^{v_i} \quad (9.11)$$

and comparing with eqn. 3.86, that the equilibrium constant is related to the partition function as:

$$K = \prod_i Q_i^{v_i} \quad (9.12)$$

for isotope exchange reactions. In the earlier exchange reaction (eqn. 9.6) this is simply:

$$K = \frac{Q_{\text{C}^{18}\text{O}_2}^{0.5} Q_{\text{H}_2^{16}\text{O}}}{Q_{\text{C}^{16}\text{O}_2}^{0.5} Q_{\text{H}_2^{18}\text{O}}} \quad (9.13)$$

The usefulness of the partition function is that it can be calculated from quantum mechanics, and from it we can calculate equilibrium fractionations of isotopes.

There are three modes of motion available to gaseous molecules: vibrational, rotational, and translational (Figure 9.2). The partition function can be written as the product of the

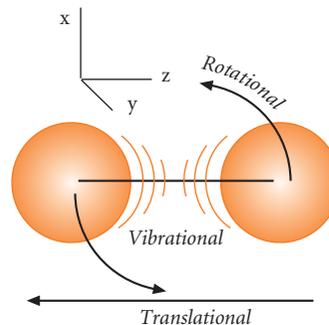


Figure 9.2 The three modes of motion, illustrated for a diatomic molecule. Rotations can occur about both the y - and x -axes; only the rotation about the y -axis is illustrated. Since radial symmetry exists about the z -axis, rotations about that axis are not possible according to quantum mechanics. Three modes of translational motion are possible: in the x , y , and z directions. Possible vibrational and rotational modes of motion of polyatomic molecules are more complex.

* This factor comes into play where more than one state corresponds to an energy level E_i (the states are said to be “degenerate”). In that case g_i is equal to the number of states having energy level E_i .

translational, rotational, vibrational, and electronic partition functions:

$$Q_{total} = Q_{vib} Q_{trans} Q_{rot} Q_{elec} \quad (9.14)$$

The electronic configurations and energies of atoms are unaffected by the isotopic differences, so the last term can be ignored in the present context.

The vibrational motion is the most important contributor to isotopic fractionations, and it is the only mode of motion available to atoms in solids. So we begin by calculating the vibrational partition function. We can approximate the vibration of atoms in a simple diatomic molecule such as CO or O₂ by that of a harmonic oscillator. The energy of a “quantum” oscillator is:

$$E_{vib} = (n + 1/2)h\nu_0 \quad (9.15)$$

where ν_0 is the ground-state vibrational frequency, h is Planck’s constant and n is the vibrational quantum number. The partition function for vibrational motion of a diatomic molecule is given by:

$$Q_{vib} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/2kT}} \quad (9.16)^*$$

Vibrations of atoms in molecules and crystals approximate those of harmonic oscillators. For an ideal harmonic oscillator, the relation between frequency and reduced mass is:

$$\nu = \frac{1}{2} \sqrt{\frac{k}{\mu}} \quad (9.17)$$

* Polyatomic molecules have many modes of vibrational motion available to them. The partition function is calculated by summing the energy over all available modes of motion; since energy occurs in the exponent, the result is a product:

$$Q_{vib} = \prod_i \frac{e^{-h\nu_i/2kT}}{1 - e^{-h\nu_i/2kT}} \quad (9.16a)$$

† Equation 9.21 also holds for linear polyatomic molecules such as CO₂. The symmetry factor is 1 if it has plane symmetry, and 2 if it does not. For non-linear polyatomic molecules, eqn. 9.21 is replaced by:

$$Q_{rot} = \frac{8\pi^2(8\pi^3 ABC)^{1/2} (kT)^{3/2}}{\sigma h^3} \quad (9.21a)$$

where A , B , and C are the three principle moments of inertia.

where k is the forcing constant, which depends upon the electronic configuration of the molecule, but not the isotope involved, and μ is reduced mass:

$$\mu = \frac{1}{1/m_1 + 1/m_2} = \frac{m_1 m_2}{m_1 + m_2} \quad (9.18)$$

Hence we see that the vibrational frequency, and therefore also vibrational energy and partition function, depends upon the mass of the atoms involved in the bond.

Rotational motion of molecules is also quantized. We can approximate a diatomic molecule as a dumbbell rotating about the center of mass. The rotational energy for a quantum rigid rotator is:

$$E_{rot} = \frac{j(j+1)b^2}{8\pi^2 I} \quad (9.19)$$

where j is the rotational quantum number and I is the moment of inertia, $I = \mu r^2$, where r is the interatomic distance. The statistical weight factor, g , in this case is equal to $(2j + 1)$ since there 2 axes about which rotations are possible. For example, if $j = 1$, then there are $j(j + 1) = 2$ quanta available to the molecule, and $(2j + 1)$ ways of distributing these two quanta: all to the x-axis, all to the y-axis or one to each. Thus:

$$Q_{rot} = \sum (2j + 1) e^{-j(j+1)b^2/8\pi^2 I kT} \quad (9.20)$$

Because the rotational energy spacings are small, eqn. 9.20 can be integrated to yield:

$$Q_{rot} = \frac{8\pi^2 I kT}{\sigma h^2} \quad (9.21)^\dagger$$

where σ is a symmetry factor whose value is 1 for heteronuclear molecules such as $^{16}\text{O}-^{18}\text{O}$ and 2 for homonuclear molecules such as $^{16}\text{O}-^{16}\text{O}$. This arises because in homonuclear molecules, the quanta must be equally distributed between the rotational axes, i.e., the j s must be all even or all odd. This restriction does not apply to heterogeneous molecules, hence the symmetry factor.

Finally, translational energy associated with each of the three possible translational motions (x , y , and z) is given by the solution to the Schrödinger equation for a particle in a box:

$$E_{\text{trans}} = \frac{n^2 h^2}{8ma^2} \quad (9.22)$$

where n is the translational quantum number, m is mass, and a is the dimension of the box. This expression can be inserted into eqn. 9.8. Above about 2K, spacings between translational energy levels are small, so eqn. 9.8 can also be integrated. Recalling that there are 3 degrees of freedom, the result is:

$$Q_{\text{trans}} = \frac{(2\pi mkT)^{3/2}}{h^3} V \quad (9.23)$$

where V is the volume of the box (a^3). Thus the full partition function is:

$$\begin{aligned} Q_{\text{total}} &= Q_{\text{vib}} Q_{\text{trans}} Q_{\text{rot}} \\ &= \frac{e^{-hv/2kT}}{1 - e^{-hv/2kT}} \frac{8\pi^2 I kT}{\sigma h^2} \frac{(2\pi mkT)^{3/2}}{h^3} V \end{aligned} \quad (9.24)$$

It is the ratio of partition functions that occurs in the equilibrium constant expression, so that many of the terms in eqn. 9.24 eventually cancel. Thus the partition function ratio for two different isotopic species of the same diatomic molecule, A and B, reduces to:

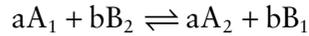
$$\begin{aligned} \frac{Q_A}{Q_B} &= \frac{e^{-hv_A/2kT}}{1 - e^{-hv_A/2kT}} \frac{I_A}{\sigma_A} m_A^{3/2} \\ &= \frac{e^{-hv_B/2kT}}{1 - e^{-hv_B/2kT}} \frac{I_B}{\sigma_B} m_B^{3/2} \\ &= \frac{e^{-hv_A/2kT} (1 - e^{-hv_B/2kT}) I_A \sigma_B m_A^{3/2}}{e^{-hv_B/2kT} (1 - e^{-hv_A/2kT}) I_B \sigma_A m_B^{3/2}} \end{aligned} \quad (9.25)$$

Since bond lengths are essentially independent of the isotopic composition, this further reduces to:

$$\begin{aligned} \frac{Q_A}{Q_B} &= \frac{e^{-hv_A/2kT} (1 - e^{-hv_B/2kT}) \mu_A \sigma_B m_A^{3/2}}{e^{-hv_B/2kT} (1 - e^{-hv_A/2kT}) \mu_B \sigma_A m_B^{3/2}} \\ &= \frac{e^{-h(v_A - v_B)/2kT} (1 - e^{-hv_B/2kT}) \mu_A \sigma_B m_A^{3/2}}{(1 - e^{-hv_A/2kT}) \mu_B \sigma_A m_B^{3/2}} \end{aligned} \quad (9.26)$$

Notice that all the temperature terms cancel except for those in the vibrational contribution. Thus vibrational motion alone is responsible for the temperature dependency of isotopic fractionations. This ratio is sometimes called the reduced partition function.

As we see from eqn. 9.5, we need to calculate K_∞ to calculate the fractionation factor α from the equilibrium constant. For a reaction such as:



where A_1 and A_2 are two molecules of the same substance differing only in their isotopic composition, and a and b are the stoichiometric coefficients, the equilibrium constant is:

$$K_\infty = \frac{(\sigma_{A_2} / \sigma_{A_1})^a}{(\sigma_{B_1} / \sigma_{B_2})^b} \quad (9.27)$$

Thus for a reaction where only a single isotope is exchanged, K_∞ is simply the ratio of the symmetry factors.

9.2.1.3 Temperature dependence of the fractionation factor

As we noted earlier, the temperature dependence of the fractionation factor depends only on the vibrational contribution. At temperatures where $T \ll hv/k$, the $1 - e^{-hv/kT}$ terms in eqns. 9.16 and 9.26 tend to 1 and can therefore be neglected, so the vibrational partition function becomes:

$$Q_{\text{vib}} \cong e^{-hv/2kT} \quad (9.28)$$

In a further simplification, since Δv is small, we can use the approximation $e^x \approx 1 + x$ (valid for $x \ll 1$), so that the ratio of vibrational energy partition functions at low temperature becomes:

$$Q_{\text{vib}}^A / Q_{\text{vib}}^B \cong 1 - h\Delta v / 2kT$$

Since the translational and rotational contributions are temperature-independent, we expect a relationship of the form:

$$\alpha \cong A + \frac{B}{T} \quad (9.29)$$

In other words, α should vary inversely with temperature at low temperature.

At higher temperature, the $1 - \exp(-h\nu/kT)$ term differs significantly from 1. Furthermore, at higher vibrational frequencies, the harmonic oscillator approximation breaks down (as suggested in Figure 9.1), as do several of the other simplifying assumptions we have made, so that *at high temperature* the relation between the fractionation factor and temperature approximates:

$$\ln \alpha \propto \frac{1}{T^2} \quad (9.30)$$

Since α is generally small, $\ln \alpha \approx 1 + \alpha$, so that $\alpha \propto 1 + 1/T^2$. At infinite temperature, the fractionation is unity, since $\ln \alpha = 0$. This is illustrated in Figure 9.3 for distribution of ^{18}O and ^{16}O between CO_2 and H_2O . The $\alpha \propto 1/T$ relationship breaks down around 200°C ; above that temperature, the relationship follows $\alpha \propto 1/T^2$.

It must be emphasized that the simple calculations performed in Example 9.1 are applicable only to a gas whose vibrations can be approximated by a simple harmonic oscillator. Real gases often show fractionations that

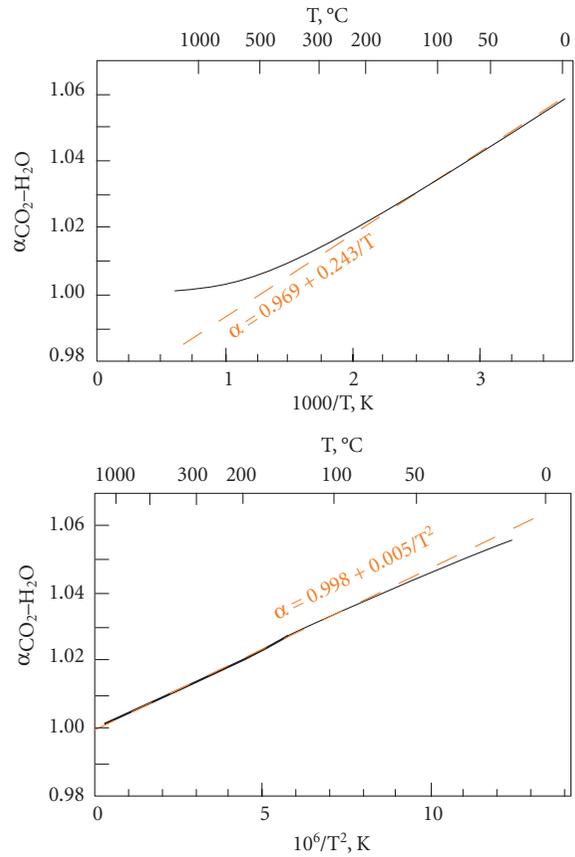
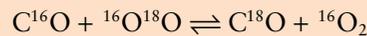


Figure 9.3 Calculated value of $\alpha^{18}\text{O}$ for $\text{CO}_2\text{--H}_2\text{O}$, shown vs. $1/T$ and $1/T^2$. Dashed lines show that up to $\sim 200^\circ\text{C}$, $\alpha \approx 0.969 + 0.0243/T$. At higher temperatures, $\alpha \approx 0.9983 + 0.0049/T^2$. Calculated from the data of Richet *et al.* (1977).

Example 9.1 Predicting isotopic fractionations

Consider the exchange of ^{18}O and ^{16}O between carbon monoxide and oxygen:



The frequency for the $\text{C-}^{16}\text{O}$ vibration is $6.505 \times 10^{13} \text{sec}^{-1}$, and the frequency of the $^{16}\text{O}_2$ vibration is $4.738 \times 10^{13} \text{sec}^{-1}$. How will the fractionation factor, $\alpha = (^{18}\text{O}/^{16}\text{O})_{\text{CO}} / (^{18}\text{O}/^{16}\text{O})_{\text{O}_2}$, vary as a function of temperature?

Answer: The equilibrium constant for this reaction is:

$$K = \frac{Q_{\text{C}^{18}\text{O}} Q_{^{16}\text{O}_2}}{Q_{\text{C}^{16}\text{O}} Q_{^{18}\text{O}^{16}\text{O}}} \quad (9.31)$$

The rotational and translational contributions are independent of temperature, so we calculate them first. The rotational contribution is:

$$K = \left(\frac{Q_{C^{18}O} Q_{^{16}O_2}}{Q_{C^{16}O} Q_{^{18}O^{16}O}} \right)_{rot} = \frac{\mu_{C^{18}O} \sigma_{C^{16}O} \mu_{^{16}O_2} \sigma_{^{18}O^{16}O}}{\mu_{C^{16}O} \sigma_{C^{18}O} \mu_{^{18}O^{16}O} \sigma_{^{16}O_2}} = \frac{1}{2} \frac{\mu_{C^{18}O} \mu_{^{16}O_2}}{\mu_{C^{16}O} \mu_{^{18}O^{16}O}} \quad (9.32)$$

(the symmetry factor, σ , is 2 for $^{16}O_2$ and 1 for the other molecules). Substituting values $\mu_{C^{16}O} = 6.857$, $\mu_{C^{18}O} = 7.20$, $\mu_{^{18}O^{16}O} = 8.471$, $\mu_{^{16}O_2} = 8$, we find: $K_{rot} = 0.9917/2$.

The translational contribution is:

$$K_{trans} = \frac{m_{C^{18}O}^{3/2} m_{^{16}O_2}^{3/2}}{m_{C^{16}O}^{3/2} m_{^{18}O^{16}O}^{3/2}} \quad (9.33)$$

Substituting $m_{C^{16}O} = 28$, $m_{C^{18}O} = 30$, $m_{^{18}O^{16}O} = 34$, $m_{^{16}O_2} = 32$ into eqn. 9.33, we find $K_{trans} = 1.0126$.

The vibrational contribution to the equilibrium constant is:

$$K_{vib} = \frac{e^{-h(v_{C^{18}O} - v_{C^{16}O} + v_{^{16}O_2} - v_{^{18}O^{16}O})/2kT} (1 - e^{-hv_{^{16}O_2}/kT}) (1 - e^{-hv_{^{18}O^{16}O}/kT})}{(1 - e^{-hv_{C^{18}O}/kT}) (1 - e^{-hv_{^{16}O_2}/kT})} \quad (9.34)$$

To obtain the vibrational contribution, we can assume the atoms vibrate as harmonic oscillators and, using experimentally determined vibrational frequencies for the ^{16}O molecules, solve eqn. 9.20 for the forcing constant, k and calculate the vibrational frequencies for the ^{18}O -bearing molecules. These turn out to be $6.348 \times 10^{13} \text{ sec}^{-1}$ for $C^{18}O$ and $4.605 \times 10^{13} \text{ sec}^{-1}$ for $^{18}O^{16}O$, so that eqn. 9.34 becomes:

$$K_{vib} = \frac{e^{-5.580/T} (1 - e^{-3119/T}) (1 - e^{-2208/T})}{(1 - e^{-3044/T}) (1 - e^{-2272/T})}$$

If we carry the calculation out at $T = 300 \text{ K}$, we find:

$$K = K_{rot} K_{trans} K_{vib} = \frac{1}{2} \times 0.9917 \times 1.0126 \times 1.1087 = \frac{1.0229}{2}$$

To calculate the fractionation factor α from the equilibrium constant, we need to calculate K_{∞}

$$K_{\infty} = \frac{(1/1)^1}{(2/1)^1} = \frac{1}{2}$$

so that

$$\alpha = K / K_{\infty} = 2K$$

At 300 K , $\alpha = 1.0233$. The variation of α with temperature is shown in Figure 9.4.

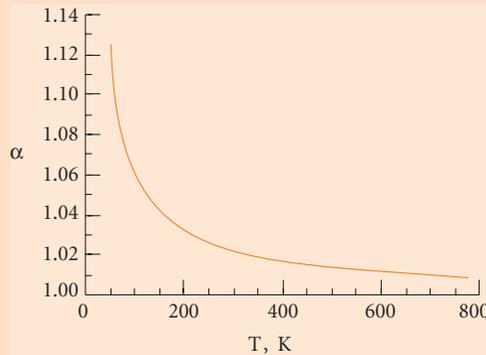


Figure 9.4 Fractionation factor, $\alpha = (^{18}O/^{16}O)CO/(^{18}O/^{16}O)O_2$, calculated from partition functions as a function of temperature.

are complex functions of temperature, with minima, maxima, inflections, and crossovers. Vibrational modes of silicates, on the other hand, are relatively well behaved.

9.2.1.4 Composition and pressure dependence

The nature of the chemical bonds in the phases involved is most important in determining isotopic fractionations. *A general rule of thumb is that the heavy isotope goes into the phase in which it is most strongly bound.* Bonds to ions with a high ionic potential and low atomic mass are associated with high vibrational frequencies and have a tendency to incorporate the heavy isotope preferentially. For example, quartz, SiO_2 , is typically the most ^{18}O rich mineral and magnetite the least. Oxygen is dominantly covalently bonded in quartz, but dominantly ionically bonded in magnetite. The O is bound more strongly in quartz than in magnetite, so the former is typically enriched in ^{18}O .

Substitution of cations in a dominantly ionic site (typically the octahedral sites) in silicates has only a secondary effect on the O bonding, so that isotopic fractionations of O isotopes between similar silicates are generally small. Substitutions of cations in sites that have a strong covalent character (generally tetrahedral sites) result in greater O isotope fractionations. Thus, for example, we would expect the fractionation between the end-members of the alkali feldspar series and water to be similar, since only the substitution of K^+ for Na^+ is involved. We would expect the fractionation factors between end-members of the plagioclase series and water to be greater, since this series involves the substitution of Al for Si as well as Ca for Na, and the bonding of O to Si and Al in tetrahedral sites has a large covalent component.

Carbonates tend to be very ^{18}O rich because O is bonded to a small, highly charged atom, C^{4+} . The fractionation, $\Delta^{18}\text{O}_{\text{cal-water}}$, between calcite and water is about 30 per mil at 25°C . The cation in the carbonate has a secondary role (due to the effect of the mass of the cation on vibrational frequency). The $\Delta^{18}\text{O}_{\text{carb-H}_2\text{O}}$ decreases to about 25 when Ba replaces Ca (Ba has about three times the mass of Ca).

Crystal structure plays a secondary role. The $\Delta^{18}\text{O}$ between aragonite and calcite is of

the order of 0.5 per mil. However, there is apparently a large fractionation (10 per mil) of C between graphite and diamond.

Pressure effects on fractionation factors turn out to be small, no more than 0.1 per mil over 0.2 GPa. We can understand the reason for this by recalling that $\partial\Delta G/\partial P = \Delta V$. The volume of an atom is entirely determined by its electronic structure, which does not depend on the mass of the nucleus. Thus the volume change of an isotope exchange reaction will be small, and hence there will be little pressure dependence. There will be a minor effect because vibrational frequency and bond length change as crystals are compressed. The compressibility of silicates is of the order of 1 part in 10^4 , so we can expect effects on the order of 10^{-4} or less, which are generally insignificant.

9.2.2 Kinetic isotope fractionations

Kinetic isotope fractionations are normally associated with fast, incomplete, or unidirectional processes like evaporation, diffusion, dissociation reactions, and biologically mediated reactions. As an example, recall that temperature is related to the average kinetic energy. In an ideal gas, the average kinetic energy of all molecules is the same. The kinetic energy is given by:

$$E = \frac{1}{2}mv^2 \quad (9.35)$$

Consider two molecules of carbon dioxide, $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$, in such a gas. If their energies are equal, the ratio of their velocities is $(45/44)^{1/2}$, or 1.011. Thus $^{12}\text{C}^{16}\text{O}_2$ can diffuse 1.1% further in a given amount of time than $^{13}\text{C}^{16}\text{O}_2$. This result, however, is largely limited to ideal gases, with low pressures where collisions between molecules are infrequent and intermolecular forces negligible. For the case where molecular collisions are important, the ratio of their diffusion coefficients is the inverse ratio of the square roots of the reduced masses of CO_2 and air (mean molecular weight 28.8):

$$\frac{D_{^{12}\text{CO}_2}}{D_{^{13}\text{CO}_2}} = \frac{\sqrt{\mu_{^{12}\text{CO}_2\text{-air}}}}{\sqrt{\mu_{^{13}\text{CO}_2\text{-air}}}} = \frac{4.1906}{4.1721} = 1.0044 \quad (9.36)$$

Hence we predict that gaseous diffusion will lead to a 4.4‰ rather than 11‰ fractionation.

Molecules containing the heavy isotope are more stable and have higher dissociation energies than those containing the light isotope. This can be readily seen in Figure 9.1. The energy required to raise the D₂ molecule to the energy where the atoms dissociate is 441.6 kJ/mol, whereas the energy required to dissociate the H₂ molecule is 431.8 kJ/mol. Therefore it is easier to break the H-H than the D-D bond. Where reactions attain equilibrium, isotopic fractionations will be governed by the considerations of equilibrium discussed earlier. *Where reactions do not achieve equilibrium, the lighter isotope will usually be preferentially concentrated in the reaction products*, because of this effect of the bonds involving light isotopes in the reactants being more easily broken. Large kinetic effects are associated with biologically mediated reactions (e.g., photosynthesis, bacterial reduction), because such reactions generally do not achieve equilibrium and do not go to completion (e.g., plants do not convert all CO₂ to organic carbon). Thus ¹²C is enriched in the products of photosynthesis in plants (hydrocarbons) relative to atmospheric CO₂, and ³²S is enriched in H₂S produced by bacterial reduction of sulfate.

We can express this in a more quantitative sense. In Chapter 5, we found the reaction rate constant could be expressed as:

$$k = Ae^{-E_b/kT} \quad (5.24)$$

where k is the rate constant, A the frequency factor, and E_b is the barrier energy. For example, in a dissociation reaction, the barrier energy is the difference between the dissociation energy and the zero point energy when the molecule is in the ground state, or some higher vibrational frequency when it is not (Figure 9.1). The frequency factor is independent of isotopic composition, thus the ratio of reaction rates between the HD molecule and the H₂ molecule is:

$$\frac{k_D}{k_H} = \frac{e^{-(\epsilon-1/2h\nu_D)/kT}}{e^{-(\epsilon-1/2h\nu_H)/kT}} \quad (9.37)$$

or

$$\frac{k_D}{k_H} = e^{(\nu_H-\nu_D)h/2kT} \quad (9.38)$$

Substituting for the various constants, and using the wavenumbers given in the caption to Figure 9.1 (remembering that $\omega = c\nu$, where c is the speed of light) the ratio is calculated as 0.24; in other words, we expect the H₂ molecule to react four times faster than the HD molecule, a very large difference. For heavier elements, the rate differences are smaller. For example, the same ratio calculated for ¹⁶O₂ and ¹⁸O¹⁶O shows that the ¹⁶O₂ will react about 15% faster than the ¹⁸O¹⁶O molecule.

The greater translational velocities of lighter molecules also allow them to break through a liquid surface more readily and hence evaporate more quickly than a heavy molecule of the same composition. Thus water vapor above the ocean is typically around $\delta^{18}\text{O} = -13$ per mil, whereas at equilibrium the vapor should only be about 9 per mil lighter than the liquid.

Let's explore this a bit further. An interesting example of a kinetic effect is the fractionation of O isotopes between water and water vapor. This is an example of Rayleigh distillation (or condensation), and is similar to fractional crystallization. Let A be the amount of the species containing the major isotope, for example H₂¹⁶O, and B be the amount of the species containing the minor isotope (H₂¹⁸O). The rate at which these species evaporate is proportional to the amount present:

$$dA = k_A A \quad (9.39a)$$

and

$$dB = k_B B \quad (9.39b)$$

Since the isotopic composition affects the reaction, or evaporation, rate, $k_A \neq k_B$. Earlier we saw that for equilibrium fractionations, the fractionation factor is related to the equilibrium constant. For kinetic fractionations, the fractionation factor is simply the ratio of the rate constants, so that:

$$\frac{k_B}{k_A} = \alpha \quad (9.40)$$

and

$$\frac{dB}{dA} = \alpha \frac{B}{A} \quad (9.41)$$

Rearranging and integrating, we have:

$$\ln \frac{B}{B^0} = \alpha \ln \frac{A}{A^0}$$

or

$$\frac{B}{B^0} = \left(\frac{A}{A^0} \right)^\alpha \quad (9.42)$$

where A^0 and B^0 are the amount of A and B originally present. Dividing both sides by A/A^0 :

$$\frac{B/A}{B^0/A^0} = \left(\frac{A}{A^0} \right)^{\alpha-1} \quad (9.43)$$

Since the amount of B makes up only a trace of the total amount of H_2O present, A is essentially equal to the total water present, and A/A^0 is essentially identical to f , the fraction of the original water remaining. Hence:

$$\frac{B/A}{B^0/A^0} = f^{\alpha-1} \quad (9.44)$$

Subtracting 1 from both sides, we have:

$$\frac{B/A - B^0/A^0}{B^0/A^0} = f^{\alpha-1} - 1 \quad (9.45)$$

The left side of eqn. 9.45 is the relative deviation from the initial ratio. The per mil relative deviation is simply:

$$\Delta = 1000(f^{\alpha-1} - 1) \quad (9.46)$$

Of course, the same principle applies when water condenses from vapor. Assuming a value of α of 1.01, δ will vary with f , the fraction of vapor remaining, as shown in Figure 9.5.

Even if the vapor and liquid remain in equilibrium through the condensation process, the isotopic composition of the remaining vapor will change continuously. The relevant equation is:

$$\Delta = \left(1 - \frac{1}{(1-f)/\alpha + f} \right) \times 1000 \quad (9.47)$$

The effect of equilibrium condensation is also shown in Figure 9.5.

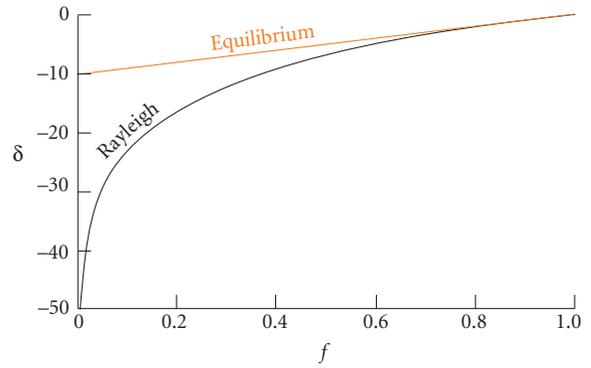


Figure 9.5 Fractionation of isotope ratios during Rayleigh and equilibrium condensation. δ is the per mil difference between the isotopic composition of original vapor and the isotopic composition when fraction f of the vapor remains.

9.2.3 Mass-dependent and mass-independent fractionations

Oxygen and sulfur both have more than two isotopes, as do, of course, many other elements. How do we expect the fractionations between various isotope ratios to be related? For example, if a 4‰ fractionation of $\delta^{18}O$ is observed in a particular sample, what value of $\delta^{17}O$ do we predict? A first guess might be that we would expect the difference in the fractionation to be proportional to the mass difference. In other words, if $\delta^{18}O$ increases by 4‰ in some process, we would expect $\delta^{17}O$ to increase by about 2‰. If we think about this in a little more detail, we realize that fractionation factors are more complex functions of mass. Looking at eqn. 9.26, for example, we see that mass occurs in a variety of ways, as $m^{3/2}$, as reduced mass, and in the exponential term. Consequently, the ratio of fractionation of $^{17}O/^{16}O$ to that of $^{18}O/^{16}O$ will not be exactly half. In fact, in most cases the ratio is about 0.52. Nevertheless, the fractionation between isotopes predicted by this equation is proportional to the difference in mass – this is referred to as *mass-dependent fractionation*.

There are, however, some exceptions where the ratio of fractionation of $^{17}O/^{16}O$ to that of $^{18}O/^{16}O$ is close to 1. Since the extent of fractionation in these cases seems independent of the mass difference, this is called *mass-independent fractionation*. Mass-independent

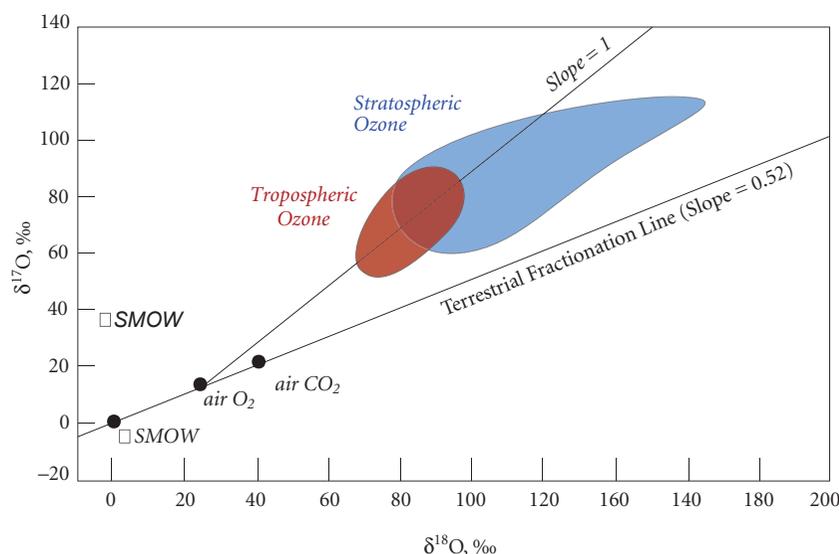


Figure 9.6 Oxygen isotopic compositions in the stratosphere and troposphere show the effects of mass-independent fractionation. A few other atmospheric trace gases show similar effects. Essentially all other material from the Earth and Moon plot on the *terrestrial fractionation line*. From Johnson *et al.* (2001). Reproduced with permission of the American Geophysical Union.

fractionation is rare. It was first observed in oxygen isotope ratios in meteorites (we will consider these variations in Chapter 10) and has subsequently been observed in oxygen isotope ratios of atmospheric gases, most dramatically in stratospheric ozone (Figure 9.6), and most recently in sulfur isotope ratios of Archean sediments and modern sulfur-bearing aerosols in ice. The causes of mass-independent fractionation are poorly understood and it seems likely there may be more than one cause.

There is at least a partial theoretical explanation in the case of atmospheric ozone (Gao and Marcus, 2001). Their theory can be roughly explained as follows. Formation of ozone in the stratosphere typically involves the energetic collision of monatomic and molecular oxygen:



The ozone molecule thus formed is in a vibrationally excited state and, consequently, subject to dissociation if it cannot lose this excess energy. The excess vibrational energy can be lost either by collisions with other molecules, or by partitioning to rotational energy. In the stratosphere, collisions are infrequent, hence repartitioning of vibrational energy represents an important pathway to stability. Because there are more possible

energy transitions for asymmetric species such as $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}^{16}\text{O}^{17}\text{O}$ than symmetric ones such as $^{16}\text{O}^{16}\text{O}^{16}\text{O}$, the former can more readily repartition its excess energy and form a stable molecule. At higher pressures, such as prevail in the troposphere, the symmetric molecule can lose energy through far more frequent collisions, lessening the importance of the vibrational to rotational energy conversion. Gao and Marcus (2001) were able to closely match observed experimental fractionations, but their approach was in part empirical because a full quantum mechanical treatment is not yet possible.

Theoretical understanding of mass-independent sulfur isotope fractionations is less advanced. Mass-independent fractionations similar to those observed (discussed later) have been produced in the laboratory by photo dissociation (photolysis) of SO_2 and SO using deep ultraviolet radiation (wavelengths <220 nm). Photolysis at longer wavelengths does not produce mass-independent fractionation. Current explanations therefore focus on ultraviolet photolysis. However, as yet there is no theoretical explanation of this effect and alternative explanations, including ones that involve the role of symmetry in a manner analogous to ozone, cannot be entirely ruled out.

9.3 ISOTOPE GEOTHERMOMETRY

One of the principal uses of stable isotopes is geothermometry. Like “conventional” chemical geothermometers, stable isotope geothermometers are based on the temperature dependence of the equilibrium constant. As we have seen, this dependence may be expressed as:

$$\ln K = \ln \alpha = A + \frac{B}{T^2} \quad (9.48)$$

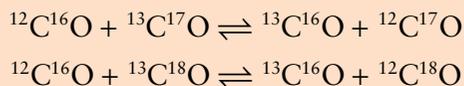
In actuality, the constants A and B are slowly varying functions of temperature, such that K tends to zero at absolute zero, corresponding to complete separation, and to 1 at infinite temperature, corresponding to no isotope separation. We can obtain a qualitative understanding of why this is so by recalling that the entropy of a system increases with temperature. At infinite temperature, there is complete disorder, hence isotopes would be mixed randomly between phases (ignoring for the

moment the slight problem that at infinite temperature there would be neither phases nor isotopes). At absolute zero, there is perfect order, hence no mixing of isotopes between phases. A and B are, however, sufficiently invariant over a limited range of temperatures that they can be viewed as constants. We have also noted that at low temperatures, the form of eqn. 9.48 changes to $K \propto 1/T$.

In principle, a temperature may be calculated from the isotopic fractionation between any two phases, provided the phases equilibrated and the temperature dependence of the fractionation factor is known. And indeed, there are too many isotope geothermometers for all of them to be mentioned here. Figure 9.7 shows some fractionation factors between quartz and other minerals as a function of temperature. Figure 9.8 shows sulfur isotope fractionation factors between various sulfur-bearing species and H_2S . Table 9.2 lists coefficients A and B for eqn. 9.48 for the oxygen isotope fractionation factor between quartz and other oxides and silicates.

Isotopic “clumping”

In Example 9.1, we calculated the distribution of ^{18}O between CO and O_2 . However, the CO and O_2 will consist of 12 isotopically distinct molecules or “isotopologues”, such as $^{12}\text{C}^{16}\text{O}$, $^{12}\text{C}^{17}\text{O}$, $^{13}\text{C}^{18}\text{O}$, $^{16}\text{O}^{17}\text{O}$, and so on. The distribution of isotopes between these species will not be random but rather some of these isotopologues will be thermodynamically favored. To understand this, consider just the isotopologues of CO and reactions relating them:



The equilibrium constant for first reaction can be calculated as:

$$K = \frac{q_{^{13}\text{C}^{16}\text{O}} q_{^{12}\text{C}^{17}\text{O}}}{q_{^{12}\text{C}^{16}\text{O}} q_{^{13}\text{C}^{17}\text{O}}}$$

and a similar equation can be written for the second reaction. The individual partition functions can be calculated as described in the previous section. Doing so, we find that the two heaviest species, $^{13}\text{C}^{17}\text{O}$ and $^{13}\text{C}^{18}\text{O}$, will be more abundant than if isotopes were merely randomly distributed among the six isotopologues: the heavy isotopes tend to “clump”. The extent of this non-random distribution will depend upon temperature, thus this effect can be used as a geothermometer, and one that is independent of the isotopic composition of other phases, which is an important advantage. Eiler (2007) reviewed the theory and use of this approach.

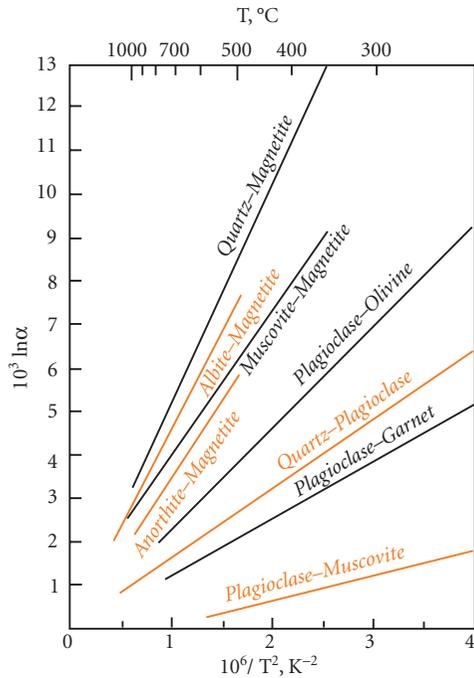


Figure 9.7 Oxygen isotope fractionation for several mineral pairs as a function of temperature.

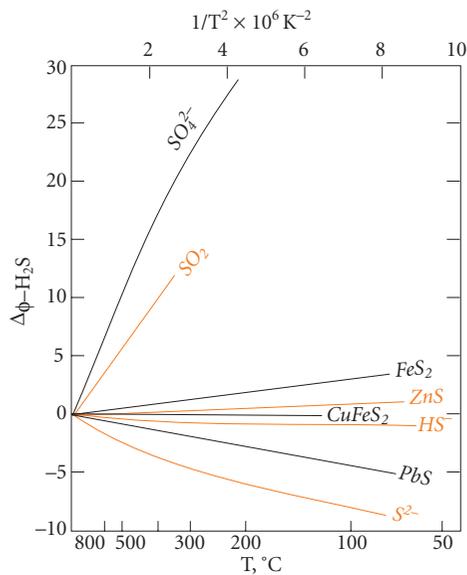


Figure 9.8 Relationship of S isotope fractionation between H_2S and other sulfur-bearing species, and temperature. After Ohmoto and Rye (1979). With permission from John Wiley & Sons.

Table 9.2 Coefficients for oxygen isotope fractionation at low temperatures: $\Delta_{\text{Qz}-\phi} = A + B' 10^6/T^2$.

ϕ	A	B
Feldspar	0	$0.97 + 1.04b^*$
Pyroxene	0	2.75
Garnet	0	2.88
Olivine	0	3.91
Muscovite	-0.60	2.2
Amphibole	-0.30	3.15
Biotite	-0.60	3.69
Chlorite	-1.63	5.44
Ilmenite	0	5.29
Magnetite	0	5.27

* b is the mole fraction of anorthite in the feldspar. This term therefore accounts for the compositional dependence discussed earlier. From Javoy (1977). Reproduced with permission of the Geological Society, London.

Table 9.3 Coefficients for oxygen isotope fractionations at elevated temperatures (600–1300°C).

	Cc	Ab	An	Di	Fo	Mt
Qz	0.38	0.94	1.99	2.75	3.67	6.29
Cc		0.56	1.61	2.37	3.29	5.91
Ab			1.05	1.81	2.73	5.35
An				0.76	1.68	4.30
Di					0.92	3.54
Fo						2.62

Coefficients are for mineral pair fractionations expressed as $1000\alpha = B \times 10^6/T^2$ where B is given in the table. For example, the fractionation between albite and diopside is $1000\alpha_{\text{An-Di}} = 1.81 \times 10^6/T^2$ (T in kelvin). Qz, quartz; Cc, calcite; Ab, albite; An, anorthite; Di, diopside; Fo, forsterite; Mt, magnetite.

From Chiba *et al.* (1989). With permission from Elsevier.

Because of the dependence of the equilibrium constant on the inverse square of temperature, stable isotope geothermometry is employed primarily at low temperatures, that is, non-magmatic temperatures. At temperatures in excess of 800°C or so, the fractionations are generally small, making accurate temperatures difficult to determine from them. However, even at temperatures of the upper mantle (1000°C or more), fractionations, although small, remain significant. Experimentally determined fractionation factors for minerals in the temperature range of 600° to 1300°C, which agree well with theoretical calculations, are given in Table 9.3.

Table 9.4 lists similar coefficients for the sulfur fractionation between H₂S and sulfur-bearing compounds. Recall that if phases α and γ and α and β are in equilibrium with each other, then γ is also in equilibrium with β . Thus these tables may be used to obtain the fractionation between any two of the phases listed (see Example 9.2).

Table 9.4 Coefficients for sulfur isotope fractionation: $\Delta_{\phi-H_2S} = A \times 10^6 / T^2 + B \times 10^3 / T$ (T in kelvin).

ϕB	A		T (°C) range
CaSO ₄	6.0 ± 0.5	5.26	200–350
SO ₂	-5 ± 0.5	4.7	350–1050
FeS ₂		0.4 ± 0.08	200–700
ZnS		0.10 ± 0.05	50–705
CuS		-0.4 ± 0.1	
Cu ₂ S		-0.75 ± 0.1	
SnS		-0.45 ± 0.1	
MoS ₂		0.45 ± 0.1	
Ag ₂ S		-0.8 ± 0.1	
PbS		-0.63 ± 0.05	50–700

From Ohmoto and Rye (1979). With permission from John Wiley & Sons.

All geothermometers are based on the apparently contradictory assumptions that complete equilibrium was achieved between phases during, or perhaps after, formation of the phases, but that the phases did not re-equilibrate when they subsequently cooled. The reason these assumptions can be made and geothermometry works at all is the exponential dependence of reaction rates on temperature that we discussed in Chapter 5. Isotope geothermometers have the same implicit assumptions about the achievement of equilibrium as other geothermometers.

The importance of the equilibrium basis of geothermometry must be emphasized. Because most stable isotope geothermometers (though not all) are applied to relatively low-temperature situations, violation of the assumption that complete equilibrium was achieved is not uncommon. We have seen that isotopic fractionations may arise from kinetic as well as equilibrium effects. If reactions do not run to completion, the isotopic differences may reflect kinetic effects as much as equilibrium effects. There are other problems that can result in incorrect temperature as well; for example, the system may partially re-

Example 9.2 Oxygen isotope geothermometry

A granite-gneiss contains coexisting quartz, muscovite and magnetite with the following $\delta^{18}\text{O}$: quartz, 11.1; magnetite, 1.9. Find the temperature of equilibration.

Answer: According to Bottinga and Javoy (1973), the fractionation factors for these minerals can be expressed as:

$$1000 \ln \alpha_{\text{Qz-H}_2\text{O}} = -3.70 + \frac{4.10 \times 10^6}{T^2} \quad \text{and} \quad 1000 \ln \alpha_{\text{Mt-H}_2\text{O}} = -3.10 + \frac{1.9 \times 10^6}{T^2}$$

The fractionation factor $\alpha_{\text{Qz-Mt}}$ can be found as: $\alpha_{\text{Qz-H}_2\text{O}} / \alpha_{\text{Mt-H}_2\text{O}}$, or

$$\begin{aligned} 1000 \ln \alpha_{\text{Qz-Mt}} &= 1000 (\ln \alpha_{\text{Qz-H}_2\text{O}} - \ln \alpha_{\text{Mt-H}_2\text{O}}) \\ &= -3.70 + \frac{4.10 \times 10^6}{T^2} + 3.10 - \frac{1.9 \times 10^6}{T^2} \\ &= 0.6 + \frac{2.20 \times 10^6}{T^2} \end{aligned}$$

Substituting $\Delta_{\text{Qz-Mag}}$ for $1000 \ln \alpha_{\text{Qz-Mag}}$ and solving for T:

$$T = \sqrt{\frac{2.2 \times 10^6}{\Delta_{\text{Qz-Mt}} - 0.6}} \quad (9.49)$$

We calculate $\Delta_{\text{Qz-Mag}}$ as 9.2%. Substituting this into 9.49, we find T = 505 K or 232°C.

equilibrate at some lower temperature during cooling. A further problem with isotope geothermometry is that free energies of the exchange reactions are relatively low, meaning there is little chemical energy available to drive the reaction. Indeed, isotopic equilibrium probably often depends on other reactions occurring that mobilize the element involved in the exchange. Solid-state exchange reactions will be particularly slow at temperatures well below the melting point. Equilibrium between solid phases will thus generally depend on reaction of these phases with a fluid. This latter point is true of “conventional” geothermometers as well, and metamorphism, one of the important areas of application of isotope geothermometry, generally occurs in the presence of a fluid.

Isotope geothermometers do have several advantages over conventional chemical ones. First, as we have noted, there is no volume change associated with isotopic exchange reactions and hence no pressure-dependence of the equilibrium constant. However, Rumble has suggested an indirect pressure-dependence, wherein the fractionation factor depends upon fluid composition, which in turn depends upon pressure. Second, whereas conventional chemical geothermometers are generally based on solid solution, isotope geothermometers can make use of pure phases such as SiO_2 . Generally, any dependence on the composition of phases involved is of relatively second order importance (there are, however, exceptions). For example, isotopic exchange between calcite and water is independent of the concentration of CO_2 in the water. Compositional effects can be expected only where they affect bonds formed by the element involved in the exchange. For example, we noted that substitution of Al for Si in plagioclase affects O isotope fractionation factors because of the nature of the bond with oxygen.

9.4 ISOTOPIC FRACTIONATION IN THE HYDROLOGIC SYSTEM

As we noted earlier, isotopically light water has a higher vapor pressure, and hence lower boiling point, than isotopically heavy water. Let's consider this in a bit more detail. Raoult's Law (eqn. 3.8) states that the partial pressure of a species above a solution is equal to its molar concentration in the solution times the

partial pressure exerted by the pure solution. So for the two isotopic species of water (we will restrict ourselves to O isotopes for the moment), Raoult's Law is:

$$P_{\text{H}_2^{16}\text{O}} = p_{\text{H}_2^{16}\text{O}}^\circ [\text{H}_2^{16}\text{O}] \quad (9.50a)$$

and

$$P_{\text{H}_2^{18}\text{O}} = p_{\text{H}_2^{18}\text{O}}^\circ [\text{H}_2^{18}\text{O}] \quad (9.50b)$$

where p is the partial pressure and, as usual, the square brackets indicate the aqueous concentration. Since the partial pressure of a species is proportional to the number of atoms of that species in a gas, we can define the fractionation factor, α , between liquid water and vapor as:

$$\alpha_{v/l} = \frac{p_{\text{H}_2^{18}\text{O}} / p_{\text{H}_2^{16}\text{O}}}{[\text{H}_2^{18}\text{O}][\text{H}_2^{16}\text{O}]} \quad (9.51)$$

Substituting eqns. 9.50a and 9.50b into 9.51, we arrive at the relationship:

$$\alpha_{v/l} = \frac{p_{\text{H}_2^{18}\text{O}}^\circ}{p_{\text{H}_2^{16}\text{O}}^\circ} \quad (9.52)$$

Thus interestingly enough, the fractionation factor for oxygen between water vapor and liquid turns out to be just the ratio of the standard state partial pressures. The next question is how the partial pressures vary with temperature. Thermodynamics provides the answer. The temperature dependence of the partial pressure of a species may be expressed as:

$$\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2} \quad (9.53)$$

where T is temperature, ΔH is the enthalpy or latent heat of evaporation, and R is the gas constant. Over a sufficiently small temperature range, we can assume that ΔH is independent of temperature. Rearranging and integrating, we obtain:

$$\ln p = \frac{\Delta H}{RT} + \text{const} \quad (9.54)$$

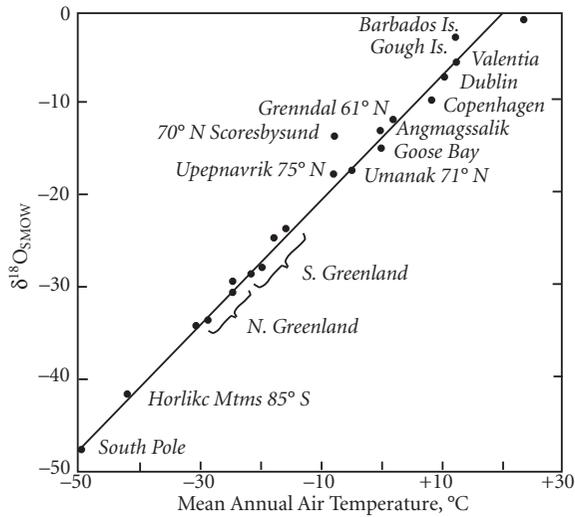


Figure 9.9 Variation of $\delta^{18}\text{O}$ in precipitation as a function of mean annual air temperature. After Dansgaard (1964). With permission from John Wiley & Sons.

We can write two such equations, one for $[\text{H}_2^{16}\text{O}]$ and one for $[\text{H}_2^{18}\text{O}]$. Dividing one by the other we obtain:

$$\ln \frac{p_{\text{H}_2^{18}\text{O}}^o}{p_{\text{H}_2^{16}\text{O}}^o} = A - \frac{B}{RT} \quad (9.55)$$

where A and B are constants. This can be rewritten as:

$$\alpha = ae^{B/RT} \quad (9.56)$$

where $a = e^A$. Over a larger range of temperature, ΔH is not constant. The log of the fractionation factor in that case depends on the inverse square of temperature, so that temperature dependence of the fractionation factor can be represented as:

$$\ln \alpha = a - \frac{B}{T^2} \quad (9.57)$$

Given the fractionation between water and vapor, we might predict that there will be considerable variation in the isotopic composition of water in the hydrologic cycle, and indeed there is. Figure 9.9 shows the global variation in $\delta^{18}\text{O}$ in precipitation.

Precipitation of rain and snow from clouds is a good example of Rayleigh condensation.

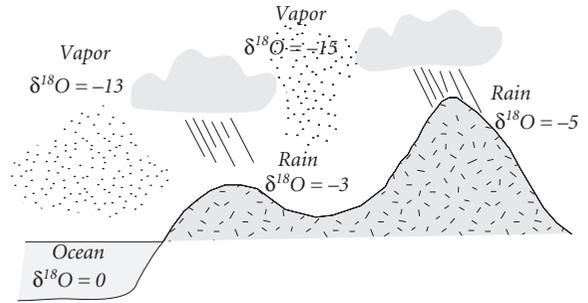


Figure 9.10 Cartoon illustrating the process of Rayleigh fractionation and the decreasing $\delta^{18}\text{O}$ in rain as it moves inland.

Isotopic fractionations will therefore follow eqn. 9.46. Thus in addition to the temperature dependence of α , the isotopic composition of precipitation will also depend on f , the fraction of water vapor remaining in the air. The further air moves from the site of evaporation, the more water is likely to have condensed and fallen as rain, and therefore, the smaller the value of f in eqn. 9.46. Thus fractionation will increase with distance from the region of evaporation (principally tropical oceans). Topography also plays a role as mountains force air up, causing it to cool and water vapor to condense, hence decreasing f . Thus precipitation from air that has passed over a mountain range will be isotopically lighter than precipitation on the ocean side of a mountain range. These factors are illustrated in the cartoon in Figure 9.10.

Hydrogen as well as oxygen isotopes will be fractionated in the hydrologic cycle. Indeed, $\delta^{18}\text{O}$ and δD are reasonably well correlated in precipitation, as shown in Figure 9.11. The fractionation of hydrogen isotopes, however, is greater because the mass difference is greater.

9.5 ISOTOPIC FRACTIONATION IN BIOLOGICAL SYSTEMS

Biological processes often involve large isotopic fractionations. Indeed, for carbon, nitrogen, and sulfur, biological processes are the most important causes of isotopic fractionations. The largest fractionations of carbon occur during the initial production of organic matter by the so-called primary pro-

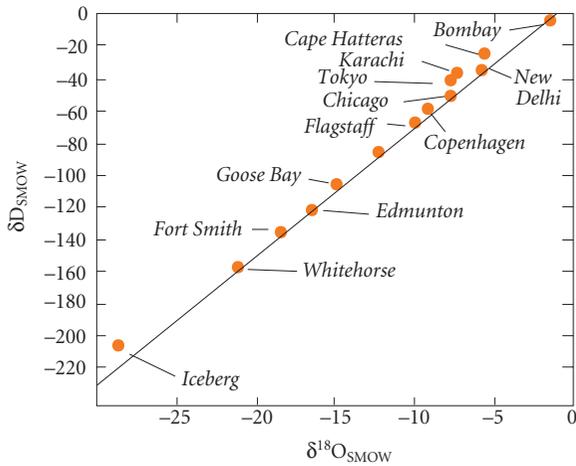


Figure 9.11 Northern hemisphere variation in δD and $\delta^{18}O$ in precipitation and meteoric waters. The relationship between δD and $\delta^{18}O$ is approximately $\delta D = 8 \times \delta^{18}O + 10$. After Dansgaard (1964). With permission from John Wiley & Sons.

ducers, or *autotrophs*. These include all plants and many kinds of bacteria. The most important means of production of organic matter is photosynthesis, but organic matter may also be produced by chemosynthesis, for example at mid-ocean ridge hydrothermal vents. Large fractionations of both carbon and nitrogen isotopes occur during primary production. Additional fractionations also occur in subsequent reactions and up through the food chain as *heterotrophs* consume primary producers, but these are generally smaller.

9.5.1 Carbon isotope fractionation during photosynthesis

Biological processes are the principal cause of variations in carbon isotope ratios. The most important of these processes is photosynthesis. As we noted earlier, photosynthetic fractionation of carbon isotopes is primarily kinetic. The early work of Park and Epstein (1960) suggested that fractionation occurred in several steps. Subsequent work has elucidated the fractionations involved in these steps, which we will consider in slightly more detail.

For terrestrial plants (those utilizing atmospheric CO_2), the first step is diffusion of CO_2 into the boundary layer surrounding the leaf,

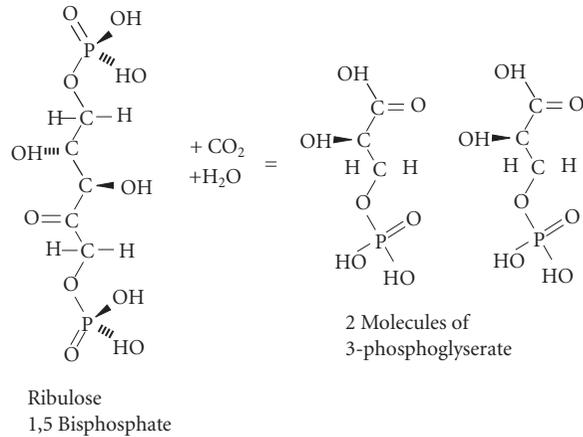
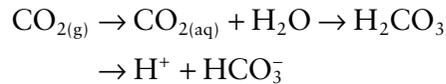


Figure 9.12 Ribulose biphosphate (RuBP) carboxylation, the reaction by which C_3 plants fix carbon during photosynthesis.

through the stomata, and internally in the leaf. On theoretical grounds, a fractionation of -4.4% is expected, as we found in eqn. 9.36. Marine algae and aquatic plants can utilize either dissolved CO_2 or HCO_3^- for photosynthesis:



An equilibrium fractionation of $+0.9\%$ is associated with dissolution ($^{13}CO_2$ will dissolve more readily), and an equilibrium $+7$ to $+8\%$ fractionation occurs during hydration and dissociation of H_2CO_3 .

At this point, there is a divergence in the chemical pathways. Most plants use an enzyme called *ribulose biphosphate carboxylase oxygenase* (RUBISCO) to catalyze a reaction in which *ribulose biphosphate carboxylase* reacts with one molecule of CO_2 to produce 2 molecules of 3-phosphoglyceric acid, a compound containing 3 carbon atoms, in a process called *carboxylation* (Figure 9.12). The carbon is subsequently reduced, carbohydrate formed, and the ribulose biphosphate regenerated. Such plants are called C_3 plants, and this process is called the Benson-Calvin Cycle, or simply the Calvin Cycle. C_3 plants constitute about 90% of all plants today and include algae and autotrophic bacteria and comprise the majority of

cultivated plants, including wheat, rice, and nuts. There is a kinetic fractionation associated with carboxylation of ribulose biphosphate that has been determined by several methods to be -29.4% in higher terrestrial plants. Bacterial carboxylation has different reaction mechanisms and a smaller fractionation of about -20% . However, for terrestrial plants a fractionation of about -34% is expected from the sum of the individual fractionations. The actual observed total fractionation is in the range of -20 to -30% . The disparity between the observed total fractionation and that expected from the sum of the steps presented something of a conundrum. The solution appears to be a model that assumes the amount of carbon isotope fractionation expressed in the tissues of plants depends on the ratio of the concentration of CO_2 inside plants to that in the external environment: the more photosynthesis depletes the CO_2 in the plant interior, the less the fractionation that occurs.

The other photosynthetic pathway is the Hatch-Slack cycle, used by the C_4 plants that include hot-region grasses and related crops such as maize and sugarcane. These plants use *phosphoenol pyruvate carboxylase* (PEP) to fix the carbon initially and form oxaloacetate, a compound that contains 4 carbons (Figure 9.13). A much smaller fractionation, about -2.0 to -2.5% , occurs during this step. In phosphoenol pyruvate carboxylation, the CO_2 is fixed in outer mesophyll cells as oxaloacetate and carried as part of a C_4 acid, either malate or aspartate, to inner bundle sheath cells where it is decarboxylated and refixed by RuBP (Figure 9.14). The environ-

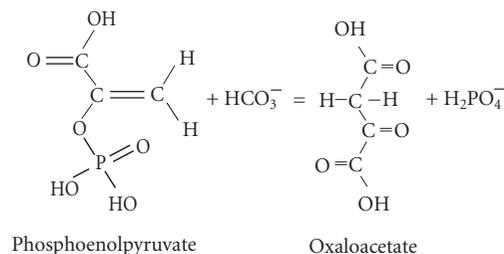


Figure 9.13 Phosphoenolpyruvate carboxylation, the reaction by which C_4 plants fix CO_2 during photosynthesis.

ment in the bundle sheath cells is almost a closed system, so that virtually all the carbon carried there is refixed by RuBP, so there is little fractionation during this step. Thus C_4 plants have average $\delta^{13}\text{C}$ of -13% , much less than C_3 plants. As in the case of RuBP photosynthesis, the fractionation appears to depend on the ambient concentration of CO_2 .

A third group of plants, the CAM plants, has a unique metabolism called the *Crassulacean acid metabolism*. These plants generally use the C_4 pathway, but can use the C_3 pathway under certain conditions. These plants are generally succulents adapted to arid environments and include pineapple and many cacti; they have $\delta^{13}\text{C}$ intermediate between C_3 and C_4 plants.

Terrestrial plants, which utilize CO_2 from the atmosphere, generally produce greater fractionations than marine and aquatic plants, which utilize dissolved CO_2 and HCO_3^- , together referred to as *dissolved inorganic carbon* or DIC. As we noted earlier, there is about a $+8\%$ equilibrium fractionation between dissolved CO_2 and HCO_3^- . Since HCO_3^- is about two orders of magnitude more abundant in seawater than dissolved CO_2 , marine algae utilize this species, and hence tend to show a lower net fractionation between dissolved carbonate and organic carbon during photosynthesis. Diffusion is slower in water than in air, so diffusion is often the rate-limiting step. Most aquatic plants have some membrane-bound mechanism to pump DIC, which can be turned on when DIC is low. When DIC concentrations are high, fractionation in aquatic and marine plants is generally similar to that in terrestrial plants. When it is low and the plants are actively pumping DIC, the fractionation is less because most of the carbon pumped into cells is fixed. Thus carbon isotope fractiona-

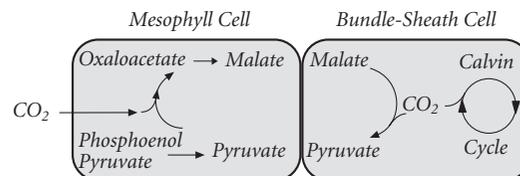


Figure 9.14 Chemical pathways in C_4 photosynthesis.