Water-Quality Principles
QW1022–TEL

Lesson 11—Environmental Isotopes

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Isotopes

Isotopes of a particular element have the same number of protons in the atomic nucleus but different numbers of neutrons. Thus they have the same atomic number but different atomic weights. Oxygen, for example, occurs as ^{16}O with an atomic weight of 16 (99.76 percent of the total), ^{18}O with an atomic weight of 18 (0.2 percent), and as ^{17}O (0.04 percent) with an atomic weight of 17. Isotopes are called *stable* if they are not involved in any natural radioactive decay scheme, *radioactive* if they undergo radioactive decay, and *radiogenic* if they are formed by radioactive decay but do not themselves decay. Radioactive isotopes are used primarily to measure age. Stable isotopes are used to understand the sources of a water, or processes that have affected a water since it was "formed" (since it entered an aquifer, for example). Radiogenic isotopes are less widely used in water studies; they are used primarily for determining the source of specific elements, particularly strontium.

STABLE ISOTOPES

The chemical properties of an element are determined by the atomic number, so that the chemical behavior of different isotopes of the same element is almost identical. There are, however, minor differences that result solely from the differences in mass. The differences are significant only among isotopes of the lighter elements, in which the difference in mass is a significant fraction of the total mass of the atom. The differences in mass cause isotopic fractionation in nature. *Fractionation* is any process that causes the isotopic ratios in particular phases or regions to differ from one another. For example, the ratio of $^{16}O/^{18}O$ in rain is different from the ratio in the oceans, which is different again from the ratio in carbonate shells forming in the ocean.

The ratio of ^{18}O to ^{16}O in nature averages about 1:500. It is not particularly convenient to use (or easy to measure) absolute isotopic ratios, and the δ (delta) notation is used instead. With oxygen, for example, $\delta^{18}O$ is defined by

$$\delta^{18}O = \frac{\left(^{18}O/^{16}O\right)_{sample} - \left(^{18}O/^{16}O\right)_{standard}}{\left(^{18}O/^{16}O\right)_{standard}} \times 1000$$

$\delta^{18}O$ represents the relative difference in parts per thousand [called per mil (‰) by analogy with percent (%)] between the ratio in a sample and the ratio in some standard. For $\delta^{18}O$, the normal reference standard is V-SMOW, an acronym for "Vienna Standard Mean Ocean Water." In practice, each laboratory has its own standard or set of standards which have been calibrated against the V-SMOW scale. During a measurement, the isotopic ratio of the sample is compared to that of the laboratory standard (by means of a mass spectrometer), and the result is recalculated to the SMOW scale. Oxygen isotopes in carbonates all used to be reported on the PDB scale, which has a marine calcite (a belemnite from the Pee Dee Formation of South Carolina) as its reference point rather than SMOW. The PDB (or V-PDB) scale for $\delta^{18}O$ is now used only in paleoclimatic studies. $^{13}C/^{12}C$ ratios are reported as $\delta^{13}C$, with the PDB calcite as the reference standard, $^{34}S/^{32}S$ ratios are reported as $\delta^{34}S$, with the Canyon Diablo troilite (an iron sulfide in the Canyon Diablo meteorite) as the reference standard, and $^{15}N/^{14}N$ ratios are reported as $\delta^{15}N$, with atmospheric N_2 as the reference standard.

Fractionation Processes

Fractionation may be caused by chemical processes, such as reaction between a solid and solution, or by physical processes such as evaporation and diffusion. Biological processes can be regarded as special cases of chemical and physical processes.

Equilibrium Chemical Processes. Consider the exchange of ^{18}O between water and carbon monoxide (carbon monoxide was chosen for simplicity; the same principles apply for carbon dioxide and calcium carbonate):

$$H_2^{18}O + C^{16}O = H_2^{16}O + C^{18}O \tag{14–1}$$

$$K_{equilib} = \frac{a_{C^{18}O}a_{H_2^{16}O}}{a_{C^{16}O}a_{H_2^{18}O}}$$

The activity coefficients will be the same for each isotope, so,

$$K_{equilib} = \frac{\left(^{18}O/^{16}O\right)_{CO}}{\left(^{18}O/^{16}O\right)_{H_2O}} \tag{14–2}$$

$K_{equilib}$ here is called the *fractionation factor,* usually represented by the symbol α. When reactants or products contain more than one oxygen atom (CO_2, for example), $K_{equilib}$ can be written in more than one way. The fractionation factor α is always simply the isotopic ratio in one compound divided by the ratio in the other compound.

If the chemical behavior of the two isotopes were identical, the ΔG_R° value for Eq. (14–1) would be zero, and α would have a value of unity. Because of the way the vibrational energy of molecules is quantized, however, the energy of the C—^{18}O bond is slightly different from the energy of the C—^{16}O bond, and the energy of the H—^{18}O bond is different from that of the

H—^{16}O bond. The difference in bond energy for the C—O bond is slightly less than that for the H—O bond, and, as a consequence, the total free energy of the system is minimized when the ratio $^{18}O/^{16}O$ is slightly higher in the CO than in the H_2O. This means that the ΔG_R° value for Eq. (14–1) has a small negative value, and α is slightly greater than 1 (for calcite-water, α is 1.028 at 25°C). Thus when carbon monoxide (or calcite) is in isotopic equilibrium with water, the carbon monoxide (or calcite) will be slightly enriched in ^{18}O relative to the water, or, in the commonly used jargon, it will be isotopically heavier. The value of α for all isotopic exchange reactions approaches unity as temperature increases; that is, fractionation increases as temperature decreases.

When the δ notation is used, Eq. (14–2) becomes (since α is close to 1)

$$\delta^{18}O_{CO} = \delta^{18}O_{H_2O} + \Delta \tag{14–3}$$

where Δ is approximately 1000 ln α, which is approximately equal to $(1 - \alpha) \times 1000$. Δ values approach zero as temperature increases. Although α and Δ can in principle be calculated by statistical mechanics, uncertainties in the calculation make this approach impractical. The fractionation factors used in geochemistry are either measured experimentally or calculated from natural systems that are assumed to be in isotopic equilibrium. Eq. (14–3) is the basis of the use of isotopes to measure temperatures (discussed later in this chapter). If the isotopic compositions of two coexisting compounds are known, Δ can be calculated, and one can look up (e.g., Friedman and O'Neil, 1977) the temperature at which the fractionation between the two compounds has the magnitude of the measured Δ.

Nonequilibrium Chemical Processes. In the discussion above it was assumed that isotopic equilibrium existed between the compounds being considered. This is generally the case for precipitates growing from solution by inorganic processes, but is often not the case for reactions involving biological systems. When equilibrium is not maintained, the process causing fractionation is usually the *kinetic isotope effect*. The principle of this effect is as follows: the strength of a chemical bond—meaning the energy that must be supplied to break the bond—is different for different isotopes because of the way molecules vibrate. In CO_2, for example, the ^{12}C—O bond is weaker than the ^{13}C—O bond (^{12}C is the common isotope of carbon making up 98.89 percent of the total carbon in nature; ^{13}C is a stable isotope that makes up 1.11 percent of natural carbon). In a chemical reaction in which the C—O bond is broken—photosynthesis, for example—the activation energy (Chapter 11) for the reaction is largely determined by the energy needed to break the C—O bond. The activation energy is thus lower for ^{12}C—O bonds than for ^{13}C—O bonds. The reaction rate is related to activation energy by the Arrhenius equation [Eq. (11–3)]:

$$\text{Rate} = A \exp\left(-\frac{\text{activation energy}}{RT}\right)$$

Thus molecules with ^{12}C—O bonds will react more rapidly than molecules with ^{13}C—O bonds. The organic matter produced by photosynthesis is enriched in ^{12}C relative to (is isotopically lighter than) the CO_2 source. In the oceans, for example, dissolved CO_2 species have a δ^{13}C of about zero per mil, whereas marine organic matter (mostly photosynthetic phytoplankton) has a δ^{13}C of about –20 per mil. The kinetic isotope effect is most important in reactions involving isotopic fractionation of carbon and sulfur, whose low-temperature chemistry

in nature is dominated by biological processes. The direction of the effect is always to cause enrichment of the light isotope in the reaction product, and the magnitude of the effect may be variable. In an equilibrium process, the isotopic fractionation between two particular compounds is constant at a particular temperature, but in a nonequilibrium process the amount of fractionation may depend on reaction rate and environmental factors in addition to temperature.

Physical Processes. Isotopic fractionation can also be caused by physical processes. The most important such process in nature is vapor–liquid fractionation during evaporation and condensation. The vapor pressure of water containing the light isotopes (^{1}H and ^{16}O) is greater than that of water containing the heavier isotopes, deuterium (D) and ^{18}O. When liquid water and water vapor are in equilibrium, the vapor is isotopically lighter with respect to both D/H and $^{18}O/^{16}O$ than the liquid, and hence water vapor in the atmosphere is isotopically lighter than water in the ocean.

If evaporation is rapid, fractionation between liquid and vapor is greater than the equilibrium value. The reason for the kinetic effect is probably the different rates of diffusion of light and heavy isotopes to the surface of the liquid (Dansgaard, 1964).

$^{18}O/^{16}O$ and D/H

The important stable isotopes of oxygen are ^{16}O and ^{18}O, and the stable isotopes of hydrogen are ^{1}H and ^{2}H, the latter commonly written as D from the name deuterium. There is about one D atom per 6700 H atoms in the hydrosphere. Tritium (^{3}H), the radioactive isotope of hydrogen, is discussed in a separate section.

The isotopic composition of seawater is, by the definition of the SMOW scale, zero per mil for both $\delta^{18}O$ and δD. Variations from place to place in the oceans are relatively small, except where there is a large influx of fresh water.

Source of Waters. Water vapor in equilibrium with liquid water at 20°C would be depleted by about 80‰ in deuterium and about 10‰ in ^{18}O. The water formed by evaporation at the ocean surface is not completely in equilibrium with seawater and has a $\delta^{18}O$ value of about −13‰ (Siegenthaler, 1979). When water vapor condenses to form rain, fractionation takes place in the reverse direction, with the liquid being isotopically heavier than the vapor. If the fraction during condensation is about 10‰, then the first rain to fall from water vapor over the ocean would have a $\delta^{18}O$ value of about −3‰; the fractionation during evaporation is largely reversed during condensation.

If a rain of $\delta^{18}O = -3‰$ forms from a vapor of $\delta^{18}O = -13‰$, ^{18}O is being selectively removed from the vapor phase. As rain continues to fall, the $\delta^{18}O$ of the vapor will become progressively more negative. The difference between vapor and liquid will remain about 10‰, and so the rain will become progressively lighter in $\delta^{18}O$. This process, in which material is progressively removed from a system without subsequent reequilibration, is called *Rayleigh fractionation*. Similar fractionation processes affect the hydrogen isotopes, so rain becomes progressively lighter in both δD and $\delta^{18}O$ as it occurs farther from the ocean source. The δD and $\delta^{18}O$ values in precipitation and hence in fresh waters generally plot close to a straight line, $\delta D = 8\delta^{18}O + 10$ (Fig. 14-1). The position along this line (the *meteoric water line*) of a particular rainfall depends, in the simplest view, on the amount of precipitation that has occurred between the time the air mass left the ocean and the time of the particular rainfall. This is somewhat of an oversimplification, as we are ignoring the complexities of atmospheric processes and the

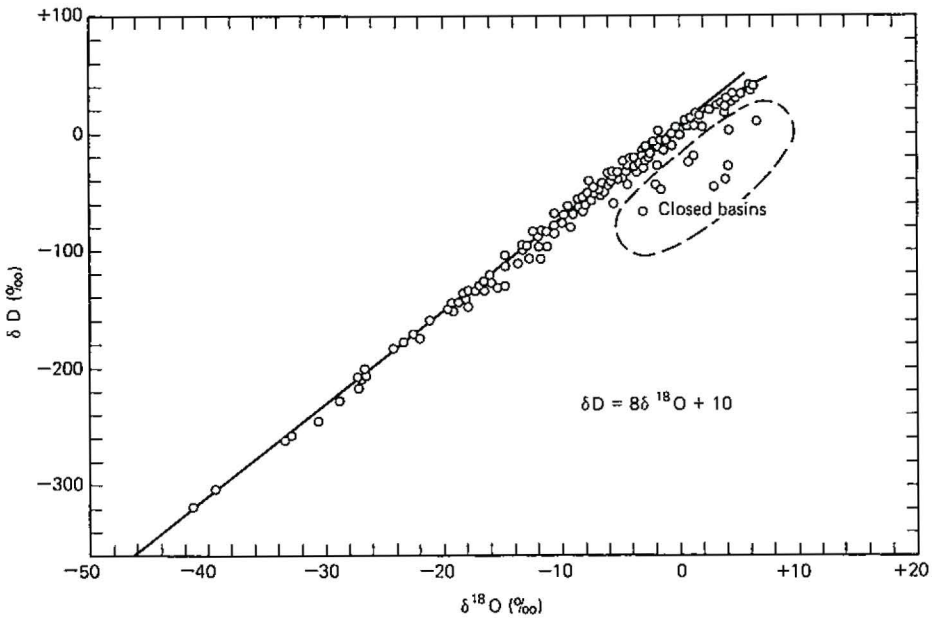

FIGURE 14-1 Deuterium and $\delta^{18}O$ variations in rivers, lakes, rain, and snow. (Craig, 1961. Copyright 1961 by the American Association of Science.)

effect of temperature on fractionation. In general, rain becomes progressively lighter in δD and $\delta^{18}O$ from the equator toward the poles, from the coast inland, and from lower to higher elevations (Fig. 14-2). The isotopically lightest precipitation occurs at the poles both because of temperature effects and because almost all the water vapor originally present in the air has been removed as precipitation before the air reaches polar regions.

When water undergoes evaporation, the residual water becomes progressively enriched in the heavier isotopes, ^{18}O and D. However, the composition of the residual water does not follow the meteoric water line. It evolves along a line that is less steep than the meteoric water line, the precise slope being determined by the temperature and relative humidity at which the evaporation takes place (Gonfiantini, 1986). The deviations of the points labeled "Closed basins" on Fig. 14-1 from the meteoric water line illustrate the effect of evaporation.

Analyses of δD and $\delta^{18}O$ can be used in conjunction with Fig. 14-1 to identify the probable source of an underground water. δD is generally unaffected by reaction with aquifer materials at low temperatures. $\delta^{18}O$ is generally unaffected by reaction with silicates at low temperatures for short periods of time (less than 1 million years or so), but exchange with $CaCO_3$ in limestone aquifers may cause a significant shift toward heavier $\delta^{18}O$ values (Clayton et al., 1966). Thus if the isotopic composition of an underground water plots close to the meteoric water line in a position similar to that of present-day precipitation in the same region, the water is almost certainly meteoric. If it has the same δD value as local precipitation but a slightly heavier $\delta^{18}O$ value, the water is probably meteoric, but has been affected by exchange with calcite. If it plots close to the seawater value, and the seawater value is far from the local precipitation range, the water is not meteoric, and may perhaps be connate. Because of shifts in climatic patterns, precipitation during the Pleistocene (about 10,000 to 2,000,000 years ago) and the Tertiary (the time before the Pleistocene) differed cyclically in isotopic composition

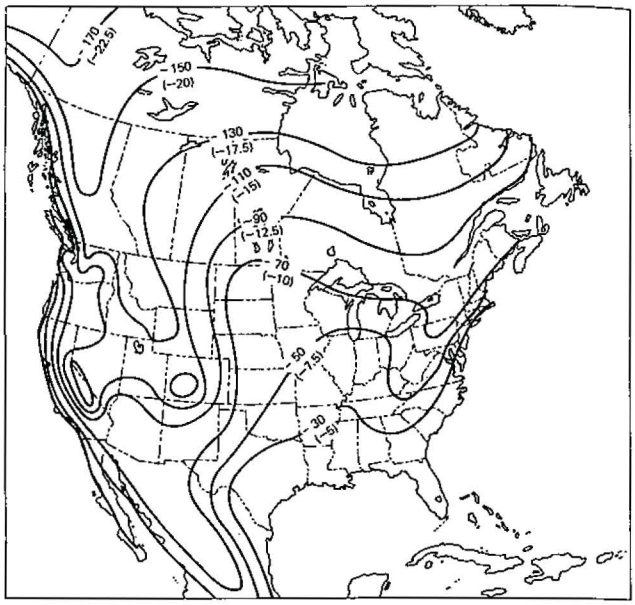

FIGURE 14-2 Distribution of δD and corresponding $\delta^{18}O$ (in parentheses) in meteoric waters in North America (adapted from Sheppard et al., 1969).

from present-day precipitation. Thus isotopes may indicate that a water is meteoric but was formed sometime in the geological past.

Although the isotopic composition of precipitation at a particular location is approximately constant, it varies from season to season and from one rainstorm to another. The reasons for the variations include different histories for individual air masses, different atmospheric temperatures, and different amounts of evaporation from raindrops as they fall through the atmosphere. The variations can be used to identify the season at which most recharge takes place, and they have been used to identify the source of runoff associated with individual storms.

In a study of the Wilson Creek drainage basin in Manitoba, Canada, Fritz et al. (1976) found that the local groundwater and the base flow of the stream had a $\delta^{18}O$ of about −14.5‰. A storm occurred during August 1973 in which the isotopic composition of the rain was about −19‰. The variation in the isotopic composition of the runoff during the storm is shown in Fig. 14-3. The isotopic composition of the runoff can be interpreted in terms of a mixing model, in which the runoff is regarded as a mixture of rainwater ($\delta^{18}O = -19‰$) and water that was present in the basin prior to the storm ($\delta^{18}O = -14.5‰$). On this assumption, the runoff from the storm is mostly pre-storm water (Fig. 14-4), not water that arrived as rain during the storm. Similar results were obtained for headwater catchments in New Zealand (Pearce et al., 1986; Sklash et al., 1986). There, only about 3 percent of storm runoff was water that had entered the catchment during the particular storm. This sort of information would be very difficult to obtain by physical measurements, and the $\delta^{18}O$, which is a property of the water itself, can be interpreted with less ambiguity than concentrations of individual solutes whose sources are not known with certainty. It is interesting that the conclusion of this study—that most storm runoff is not simply rainwater that has flowed over the ground surface—is similar to the conclusion reached by Kennedy and Malcolm (1977) on the basis of chemical arguments (Chapter 12). The process of assigning runoff to different sources is called *hydrograph separation.*

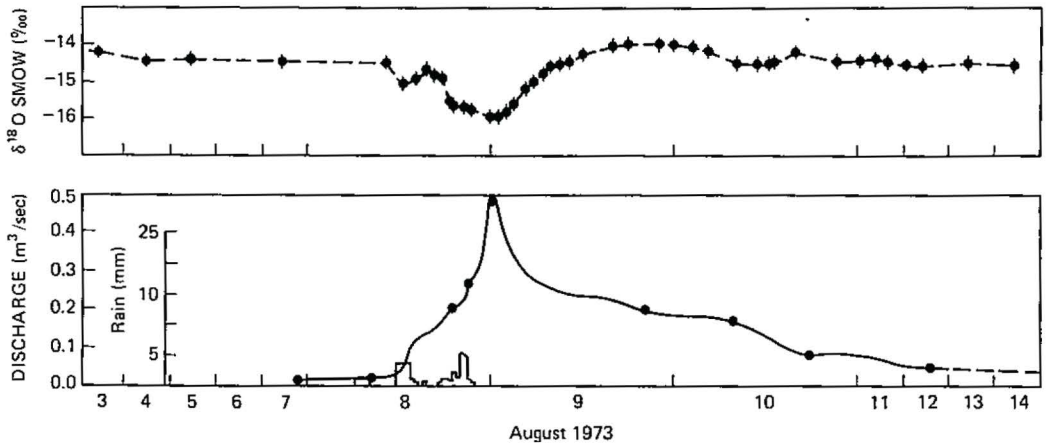

FIGURE 14-3 Variation of rainfall (lowest curve), discharge, and $\delta^{18}O$ of runoff during a storm on the Wilson Creek drainage (Fritz et al., 1976).

In many thermal (hot-spring) waters, the deuterium content of the water is the same as that of local precipitation, but the $\delta^{18}O$ is heavier than that of local precipitation (Fig. 14-5). The interpretation of these results is that the waters are meteoric, and the $\delta^{18}O$ has been shifted by isotopic exchange with rock. The reason that the $\delta^{18}O$ value is shifted but not the δD value is that rock contains a large amount of oxygen, but very little hydrogen. In a water-saturated rock, 50 percent or more of the total oxygen in the system is in the rock, but almost all the hydrogen in the system is in the water. In an isotopic exchange reaction the total mass of each isotope remains constant. In a geothermal system, some ^{18}O is transferred from the rock to the water,

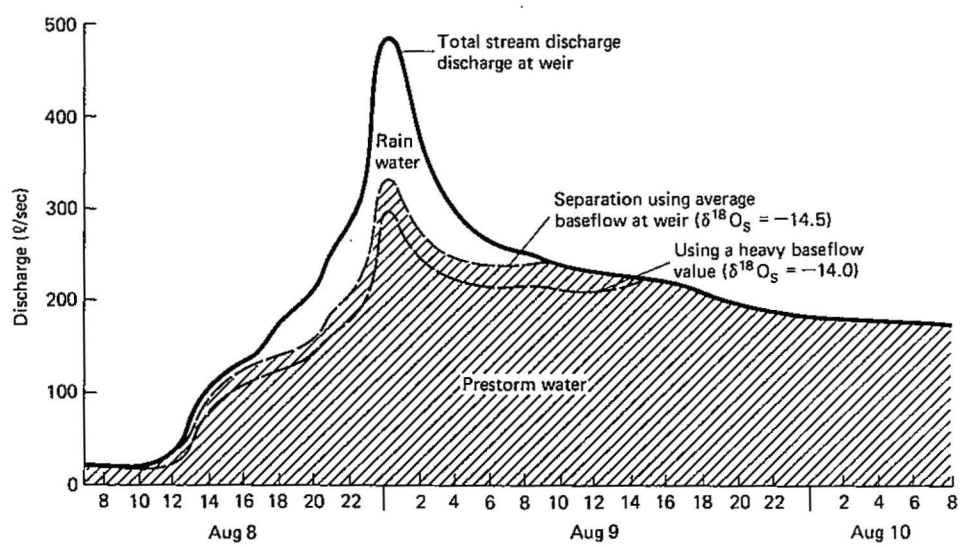

FIGURE 14-4 Discharge of Wilson Creek divided into rainwater and prestorm components on the basis of ^{18}O. Dashed line shows effect of different assumed isotopic composition for prestorm water (Fritz et al., 1976).

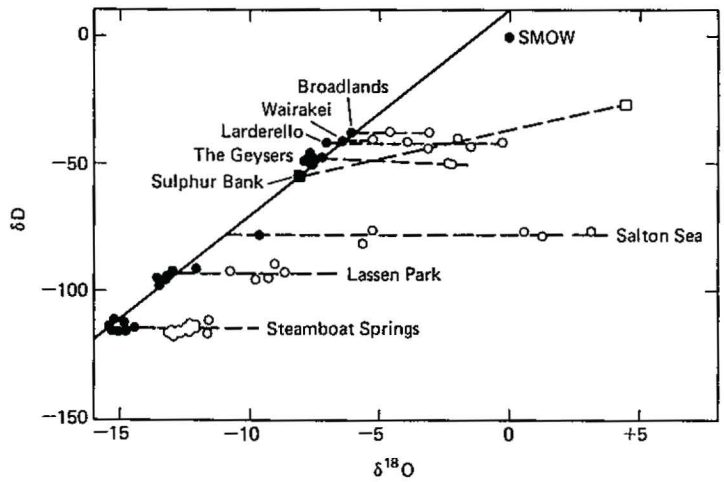

FIGURE 14-5 Values of δD and $\delta^{18}O$ for samples of thermal (open circles) and local meteoric waters (solid circles) in several areas (after Ellis and Mahon, 1977).

and some ^{16}O from the water to the rock. The rock becomes isotopically lighter and the water becomes isotopically heavier. There is so little hydrogen in the rock, however, that no change in the δD of the rock could be large enough to balance a significant change in the δD of the water. Thus alteration of rock in hydrothermal systems may cause a significant change in the $\delta^{18}O$ of the water but usually no detectable change in the δD of the water. Clayton et al. (1966) concluded on the basis of similar arguments that the water in several oilfield brines was meteoric in origin. The δD values were similar to present-day (or in some cases Pleistocene) surface waters from the same area; the $\delta^{18}O$ values were generally heavier than present-day local surface waters, which was interpreted as being a result of isotopic exchange with calcite in limestones.

Water-Rock Interaction. We mentioned above that interaction between meteoric water and limestone usually causes an increase in the $\delta^{18}O$ of the water. Limestones were generally formed in approximate isotopic equilibrium with seawater at temperatures below 20°C. Meteoric waters have $\delta^{18}O$ values lower than that of seawater, and aquifer temperatures are often higher than the original temperature of formation of the limestone. As a result of both the $\delta^{18}O$ difference and the temperature difference, recrystallization of calcite in an aquifer generally results in a net transfer of ^{16}O to the calcite and ^{18}O to the water. The magnitude of the shift in the water value depends on the mass ratio of water to reacting calcite in addition to temperature and initial isotopic compositions. If a water is flowing rapidly through an aquifer, the effective ratio of water to reacting calcite is likely to be high, so the shift in the $\delta^{18}O$ of the water is likely to be small. Conversely, if the water is almost stagnant, the effective water-rock ratio will be high, and larger isotopic shifts can be expected in the water.

When isotopic exchange occurs between silicates and water at low temperatures, the important reaction is conversion of one solid phase to another rather than recrystallization. Consider the water in the pores of a feldspar-containing rock. If the feldspar does not undergo alteration, the $\delta^{18}O$ of the water will not change. If the feldspar alters to a clay mineral, the clay mineral will form in isotopic equilibrium with the water, and this will normally cause a shift in the $\delta^{18}O$ of the water. The magnitude of the shift can sometimes be used to

estimate the amount of reaction that has taken place. In a sediment core taken by the Deep Sea Drilling Project from near Antarctica, for example, the $\delta^{18}O$ of the interstitial water decreased with depth (Fig. 14-6). Lawrence et al. (1979) showed that the depletion was caused by conversion of volcanic material ($\delta^{18}O = +6$ to $+10$ per mil) to smectite ($\delta^{18}O = +20$ to $+25$ per mil), but that this reaction alone was inadequate to explain the shift; alteration of the volcanic basement was also contributing to the ^{18}O depletion in the interstitial water.

In weathering zones, the ratio of water to altered rock is normally high (water in this context means total water, integrated over time, that has flowed through the weathering zone during the alteration, not the amount present at any instant), and so clay minerals and hydroxides formed during weathering are normally in isotopic equilibrium with local meteoric water (Lawrence and Taylor, 1971; Savin, 1980).

Isotopic Temperature Measurement. When two oxygen-containing compounds are in isotopic equilibrium, the fractionation between them (Δ) is a function of temperature only:

$$\delta^{18}O_A = \delta^{18}O_B + \Delta$$

If A and B are two minerals that grew together in isotopic equilibrium, and neither mineral has undergone subsequent isotopic exchange, measurement of $\delta^{18}O_A$ and $\delta^{18}O_B$ allows the

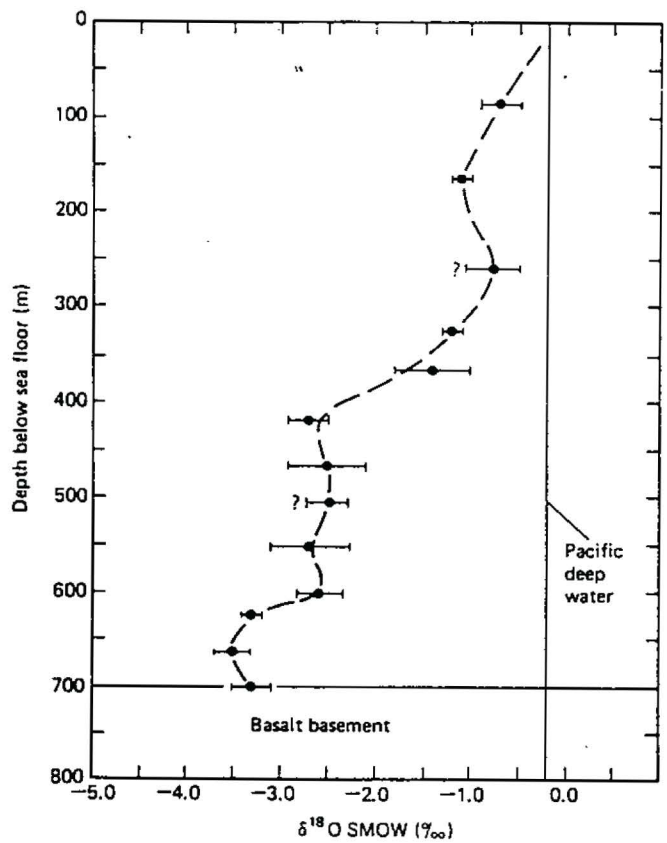

FIGURE 14-6 $\delta^{18}O$ of pore fluids from Site 323 of the Deep Sea Drilling Project. The total depletion (the area between the curve and the Pacific deep water line) can be used to estimate the amount of reaction that has taken place (Lawrence et al., 1979).

equilibration temperature to be measured: it is not necessary to know anything about the fluid from which the minerals grew.

In low-temperature environments, such as soils, the oceans, and normal aquifers, it is rare for two minerals to form at the same time in isotopic equilibrium with each other. Calcite is the most common mineral to form. When calcite is precipitated inorganically, it is usually in isotopic equilibrium with the solution. When it is precipitated by an organism, sometimes it is in equilibrium with the solution and sometimes it is not, depending on the physiology of the organism involved. The carbonate that makes a shell is normally involved in physiological processes before it is deposited as calcite, and it is not surprising that these processes sometimes cause fractionation of their own.

When calcite is precipitated in the ocean, no other suitable mineral is precipitated at the same time in isotopic equilibrium with the same water (attempts to use silica and phosphate minerals have been unsuccessful). A large number of "paleotemperature" measurements have been made by measuring the $\delta^{18}O$ of an ancient calcite shell (one phase) and assuming a value for seawater (the other phase). On this basis, curves have been published showing the variation in oceanic temperature over a time range of tens of millions of years. The main uncertainty in this approach is the isotopic composition of ancient seawater. We mentioned earlier in this chapter that precipitation in polar regions is isotopically very light (low $\delta^{18}O$). The ice caps are simply accumulated precipitation, and so the ice caps represent a large mass of isotopically light water. The isotopic composition of the total hydrosphere is constant or changing only slowly with time, so that when large ice caps are present, seawater must be isotopically heavier than average. Isotopic measurement of shells shows that during glacial maxima, $\delta^{18}O$ values are greater than during glacial minima. This could be explained by:

1. The isotopic composition of seawater being constant but temperatures lower (the absolute value of Δ increases with decreasing temperature).
2. The temperature of seawater being constant, but its isotopic composition being different because of removal of ^{16}O into ice caps.
3. Some combination of the two effects.

It is now generally agreed that both effects are important.

$^{13}C/^{12}C$

The $\delta^{13}C$ of dissolved carbonate species (mostly HCO_3^-) in the ocean is about 0‰ and of atmospheric CO_2 is about –7‰. Photosynthesis causes an enrichment of ^{12}C in the photosynthetic product. The magnitude of the fractionation depends on the biochemical pathway used for photosynthesis, particularly the C_3 versus the C_4 pathway, and on other biological and environmental factors. Marine plankton has $\delta^{13}C$ values around –20‰ in the tropical oceans and around –25 to –30‰ in the polar oceans (Deines, 1980). The values for land plants are variable, typically around –25‰. The CO_2 in the soil atmosphere, which is largely biogenic, is typically about –20‰. The $\delta^{13}C$ of meteoric waters is usually negative, but the specific values are variable. Carbonate minerals formed in the oceans have $\delta^{13}C$ values close to zero.

The $\delta^{13}C$ of a groundwater is determined by the $\delta^{13}C$ of the inflow water and the supply of carbon to, and removal of carbon from, the water during its transit through the aquifer.

There are several possible sources of carbon:

1. Dissolution of calcite, aragonite, or dolomite from limestones, which introduces relatively heavy carbon.
2. Oxidation of organic matter, which introduces relatively light carbon.
3. Transport of CO_2 gas from a soil atmosphere, which also introduces relatively light carbon.

Redox reactions involving methane (Chapter 8) can also have a large effect on $\delta^{13}C$. Methanogenesis produces an isotopically very light methane and an isotopically heavy CO_2, whereas oxidation of (typically light) methane produces light CO_2.

Carbon may be lost from the water by precipitation of a carbonate mineral or by loss of CO_2 gas. The systematics of how these processes affect the $\delta^{13}C$ of groundwater are discussed by Wigley et al. (1978). Plummer (1977) used a combination of chemical and isotopic arguments to identify the reactions involved in the chemical evolution of the water in the Floridan aquifer and showed specifically that soil zone CO_2 was being transported across the vadose zone into the groundwater.

In general, ^{13}C is used to identify sources of carbon and is particularly valuable for distinguishing between carbon derived from organic matter (isotopically light) and carbon derived from carbonate minerals (isotopically heavy). Carbon isotopes are very useful in understanding the origin of secondary carbonate minerals. Carbon isotopes are not used in low-temperature isotopic temperature determinations because there is no suitable equilibrium fractionation in nature.

$^{34}S/^{32}S$

The most important natural fractionation is between oxidized sulfur (sulfate) and reduced sulfur (H_2S, sulfide minerals). The fractionation is an example of the kinetic isotope effect in a complex, multistep biological process. The Δ value varies, depending on the rate of sulfate reduction and on various biochemical factors (Kaplan and Rittenberg, 1964). The sulfate in modern seawater has a $\delta^{34}S$ of about +20‰; the $\delta^{34}S$ of pyrite in modern marine sediments varies over a wide range, from about +4 to −35‰ (Goldhaber and Kaplan, 1974). The variation is partly due to variations in the fractionation factor, and partly to the fact that pyrite does not grow from normal seawater. It grows from interstitial water in a sediment, and the $\delta^{34}S$ of the sulfate in the interstitial water increases progressively as ^{32}S is preferentially transferred into solid phases—another example of Rayleigh fractionation.

In studies of modern waters, $\delta^{34}S$ can be used to distinguish different sources of sulfur—sea salt versus atmospheric pollution in rain (Kellogg et al., 1972); recharge sources and pollution in groundwater (Holt et al., 1972; Krouse, 1980)—but the technique is not widely used in hydrologic studies.

$^{15}N/^{14}N$

Atmospheric nitrogen contains about one atom of the stable isotope ^{15}N per 273 atoms of ^{14}N. During the various biochemical reactions involving nitrogen, fractionation occurs. The fractionation processes are complex and not completely understood (Létolle, 1980; Smith, 1975).

Nitrogen isotopes have been used to identify sources, particularly anthropogenic sources, of nitrate in natural waters (e.g., Kreitler and Jones, 1975). The interpretation of such results is often ambiguous as a consequence of the large number of biological processes that may affect nitrogen compounds. Analysis of the $\delta^{18}O$ of nitrate as well as $\delta^{15}N$ may greatly increase the value of the technique for determining sources of nitrate (Aravena et al., 1993).

RADIOACTIVE ISOTOPES

The kinetics of radioactive decay and the concept of the half-life were discussed in Chapter 11.

Tritium

Tritium (^3H or T) has a half-life of 12.3 years. It is produced naturally in the atmosphere by interaction of cosmic rays with nitrogen and oxygen in the atmosphere, but by far the most important source for modern studies is thermonuclear weapons testing which took place in the atmosphere between 1952 and 1969. The natural (prebomb) level in rainwater was about 5–10 TU [one TU (tritium unit) = one T atom per 10^{18} H atoms]; the number is uncertain because few measurements were made before testing began, and the levels in old samples (notably wine) are now very low. During the 1960s, the levels in rainwater rose above 10^3 TU, and modern values are usually between 20 and 100 TU, varying considerably with time and location.

Tritium in groundwater is not significantly affected by chemical processes. Its most important use is in distinguishing between water that entered an aquifer prior to 1952 (prebomb water) and water that was in contact with the atmosphere after 1952. Prebomb water contains no tritium detectable by normal procedures; post-1952 water contains relatively high levels of tritium. Mazor (1991) summarized the interpretation of tritium values in groundwater as follows:

- Water with zero tritium (in practice <0.5 TU) has a pre-1952 age.
- Water with tritium concentrations >10 TU has a post-1952 age.
- Water with tritium concentrations between 0.5 and 10 TU represents a mixture of pre-1952 and post-1952 water.

Because of the variable source of tritium and uncertainties due to possible mixing, tritium is not used for age dating in the conventional way.

The properties of tritium make it useful in studies of mixing in the upper layers of the ocean (e.g., Rooth and Ostlund, 1972) and mixing in lakes (Imboden et al., 1977). For example, Imboden et al. found that the vertical distribution of tritium in Lake Tahoe was almost uniform, indicating that complete turnover and mixing had taken place not long before the time of sampling.

^{14}C

Like tritium, radiocarbon is produced in the atmosphere by interaction of cosmic rays with nitrogen and was introduced in large amounts by nuclear weapons testing. Unlike tritium, ^{14}C has a half-life of 5,730 years, making it a useful tool for dating waters as old as 50,000 years. Also, the amount of ^{14}C introduced by bomb testing relative to the amount naturally present is much smaller than is the case with tritium, so the distribution of ^{14}C in nature is not completely dominated by the bomb input. The ^{14}C generated in the atmosphere is carried down to the earth's

surface by precipitation and becomes incorporated into the biomass or transported into water bodies such as lakes, the ocean, and groundwater. ^{14}C undergoes radioactive decay (to ^{14}N), so once isolated from the atmosphere the amount of ^{14}C decreases with time according to the equation:

$$(^{14}C)_t = (^{14}C)_0 e^{-kt}$$

where $(^{14}C)_t$ is the amount present at time t, $(^{14}C)_0$ is the amount present at $t = 0$, and k is the decay constant, which is related to the half-life $T_{1/2}$ by the equation:

$$t_{1/2} = \frac{\ln 2}{k}$$

To determine the time since a water was last in contact with the atmosphere, it is necessary to know $(^{14}C)_0$. This is determined by tree rings for the most recent 7,000 years; there is no accurate way to determine it prior to 7,000 years, so it is generally assumed arbitrarily to have been constant. This gives rise to a time scale in "^{14}C years," which may be different from astronomical years.

Groundwater Flow Velocity. There are some complications in the behavior of ^{14}C during recharge, so the "absolute" age of a groundwater cannot be determined reliably. However, if the ^{14}C concentration is measured at several points along a flow line within an aquifer, the differences in age between the points and hence the flow velocity can be determined. One complication is that dissolution of carbonate minerals or oxidation of organic matter within the aquifer may add "old" or "dead" (no detectable ^{14}C) carbon to the water, giving an erroneously old age. The contribution of carbon from these sources can be estimated from $^{13}C/^{12}C$ measurements and chemical arguments (Wigley, 1976; Wigley et al., 1978). These calculations can be performed with the aid of the computer codes NETPATH and PHREEQC (see Chapter 16). Another complication is mixing. A low ^{14}C concentration may mean that we are looking at a relatively "old" water, or it may mean that we are looking at a mixture of relatively "young" water and "dead" water. ^{14}C measurements can be interpreted as ages only where mixing is insignificant.

Chlorine-36

A large number of radioactive species in addition to tritium and ^{14}C are produced by cosmic ray interactions in the atmosphere. One that may be particularly useful for dating very old groundwater is ^{36}Cl (Bentley et al., 1986a, 1986b). Chloride serves as a good tracer for groundwater because it is not generally adsorbed or involved in chemical reaction, and ^{36}Cl has a half-life of 3.01×10^5 years, which is in the right range for very old groundwater. The disadvantage of the technique is that the abundance of ^{36}Cl is extremely small, and the analytical techniques required (based on tandem accelerator mass spectrometry) are complex and expensive. Bentley et al. (1986b) and Phillips et al. (1986) give examples of use of the technique to date groundwaters more than 1 million years old. Interpretations of ^{36}Cl concentrations in terms of water ages are not without controversy (Fontes and Andrews, 1993; Mazor, 1992, 1993a, 1993b; Phillips, 1993).

Radon-222

The decay of uranium and thorium to lead is one of the most widely used dating techniques in geology, but it is not directly applicable to hydrology. Several intermediate products in the decay

scheme have been used in water studies, however, particularly in oceanographic studies. One example is the use of ^{222}Rn to measure eddy diffusion in the ocean (e.g., Broecker et al., 1968) and in lakes (e.g., Imboden and Emerson, 1978). ^{222}Rn is produced by decay of ^{226}Ra (radium), which is itself a decay product of ^{238}U. ^{222}Rn is a gas, and when it is formed in sediment it diffuses into the overlying water. It has a half-life of 3.8 days, so that its concentration decreases with distance from the sediment. The profile of ^{222}Rn above the sediment depends on the rate at which it is transported upward in the water by eddy diffusion. If the eddy diffusion rate is slow, the profile will be compressed close to the sediment; if it is fast, radon will be carried to greater distances from the sediment before it disappears by decay. Knowledge of transport rates near the sediment-water interface is important, because these rates determine the rate at which other species such as nutrients are transported from the sediment into the overlying water.

^{222}Rn has also attracted a great deal of attention as a potential health hazard. It is generated in rocks and soil by decay of ^{238}U and diffuses upward into the atmosphere. In the open air, rapid dilution by mixing, coupled with the short half-life of ^{222}Rn, makes it insignificant as a health hazard. When it seeps into buildings from below, however, it may build up to dangerous concentrations. It is inhaled into the lungs, and the radiation emitted as it undergoes radioactive decay can cause cancer.

RADIOGENIC ISOTOPES: STRONTIUM-87

^{87}Sr is produced by the radioactive decay of ^{87}Rb, which has a half-life of 4.88×10^{10} years. The ratio of the concentration of ^{87}Sr to the stable, non-radiogenic ^{86}Sr can be used to deduce the source of strontium in a water. $^{87}Sr/^{86}Sr$ ratios can be measured with great precision (by mass spectrometry), which makes this a potentially sensitive technique. Since the geochemical behavior of calcium is very similar to that of strontium, strontium isotopes are often used to infer the source of calcium.

To a first approximation, rubidium behaves chemically like potassium, whereas strontium behaves like calcium. Old granitic rocks (high ratios of Rb to Sr, long time for the decay of ^{87}Rb to form of ^{87}Sr) have high $^{87}Sr/^{86}Sr$ ratios—commonly above 0.80—whereas young basalts typically have values of between 0.702 and 0.706. The present-day ratio in seawater is 0.709, reflecting a mixture of relatively radiogenic Sr derived from the continents and relatively non-radiogenic Sr derived from oceanic basalts. The value for seawater has varied in the past, increasing from about 0.7077 in the early Tertiary (50 my ago) to the present value. The exact mechanisms responsible for the changes are controversial.

The use of $^{87}Sr/^{86}Sr$ ratios to elucidate weathering reactions is well illustrated by the study of Blum et al. (1994) of weathering in the Sierra Nevada of California, the same general area as was studied by Garrels and Mackenzie (1967), a paper discussed extensively in Chapter 12. The main observation was that the Sr in runoff, particularly from glaciated terrains, was more radiogenic than the calculations of Garrels and Mackenzie would predict. They predicted that the main source of solutes was weathering of plagioclase: plagioclase contains relatively non-radiogenic strontium because it contains little rubidium. The $^{87}Sr/^{86}Sr$ of K-feldspar in the rock was not sufficiently high to explain the ratio in the water. The only mineral with a high enough ratio was biotite; the $^{87}Sr/^{86}Sr$ ratios in the water indicated that biotite was weathering much more rapidly, at least in terms of strontium release, than would be predicted by the simple mass balance calculations involving the major elements (Chapter 12).

This is another indication that the results of such mass balance calculations should be treated with caution. Strontium isotopes systematics have been incorporated into the geochemical code KINDIS (Madé and Fritz, 1992), which is a kinetic and thermodynamic model for weathering reactions.

Other uses for Sr isotopes in water studies include distinguishing between atmospherically-derived Sr and bedrock-derived Sr (Aberg et al., 1989; Graustein and Armstrong, 1983), and distinguishing between Sr derived from exchange sites in soil and Sr derived from bedrock weathering (Miller et al., 1993). Distinguishing among these sources of strontium (and by implication calcium) is particularly important in studies of the effect of acid deposition on surface waters (Chapter 13).