CHAPTER 29

READING THE SEDIMENTARY RECORD: THE USE OF STABLE ISOTOPES IN THE STUDY OF PALEOCEANOGRAPHY

INTRODUCTION

Isotopes of an element react at different rates due to the slight difference in their atomic masses. Favorable energetics usually cause the lighter isotope to react faster and to a greater extent. In the case of the stable isotopes, this causes the reaction products to be relatively enriched in the light isotope. The degree of this enrichment is dependent upon such factors as (1) the reaction mechanism, (2) the degree to which the reaction has proceeded, (3) the isotopic composition of the reactants, and (4) environmental conditions, such as temperature and pressure. As a result, there is considerable spatial and temporal variability in the relative abundances of the naturally occurring stable isotopes.

The factors that control this variability have been quantified for some of the stable isotopes present in the ocean. This information has been used in a variety of applications, such as to (1) trace the fate or source of various materials in the ocean, (2) determine the type and extent of biogeochemical reactions that have acted on these materials, and (3) assess past environmental conditions in the ocean. As a result, the relative abundances of the naturally occurring stable isotopes have provided a vast amount of very important information on the biogeochemistry of the ocean. As with the radionuclides, many of the conclusions presented in earlier chapters are based on stable isotope data. Some examples are discussed below.

STABLE ISOTOPES

Most studies of the naturally occurring stable isotopes have focused on the elements carbon, hydrogen, oxygen, sulfur, and nitrogen. As shown in Table 29.1, carbon, nitrogen, and hydrogen have only two stable isotopes, while oxygen has three and sulfur has four. For each element, one isotope is most abundant, (i.e., ^{12}C, ^{1}H, ^{16}O, ^{14}N, and ^{32}S). The heavy isotope of H, ^{2}H, is called deuterium and is usually represented as D.

TABLE 29.1
Relative Abundances of Some Stable Isotopes[a]

Atomic Number	*Symbol*	*Mass Number*	*Abundance (%)*
1	H	1	99.99
		2	0.01
6	C	12	98.9
		13	1.1
		14[b]	10^{-10}
7	N	14	99.6
		15	0.4
8	O	16	99.8
		17	0.04
		18	0.2
16	S	32	95.0
		33	0.8
		34	4.2
		36	0.2

[a]These values are averages that are representative of Earth's crust, ocean, and atmosphere. They have been rounded to the nearest 0.1 percent, except for the very rare isotopes.

[b]Radioactive.

The relative abundances of the stable isotopes in Earth's crust, ocean, and atmosphere have been used to define the atomic weights of the elements. These atomic weights are a weighted average of the mass numbers of an element's naturally occurring isotopes. The weighting reflects the average natural abundance of each of the isotopes on the outer earth. The similarity of oxygen's atomic weight, 15.9994 amu, to the mass number of ^{16}O indicates that this is the most abundant naturally occurring isotope of oxygen on Earth's surface.

The relative abundances of the stable isotopes are usually expressed as ratios. As shown in Table 29.2, the most abundant isotope is in the denominator. Slight deviations from these average ratios are observed in many marine materials. For example, the $^{13}C/^{12}C$ ratio in most marine organic matter ranges between 0.000921 to 0.001098. These small differences are detected with a Nier-type ratio mass spectrometer, which measures only one isotope ratio at a time. (The mass spectra generated by the GC-MS systems are produced by mass spectrometers that sequentially measure the relative abundance of each mass fragment, or isotope.)

This type of mass spectrometer is very sensitive to changes in environmental conditions and the performance of various electronic components. As a result, absolute ratios cannot be determined with a high level of accuracy. On the

TABLE 29.2
Average Stable Isotope Ratios

$\frac{^{2}H}{^{1}H} = 0.0016$
$\frac{^{13}C}{^{12}C} = 0.001123$
$\frac{^{15}N}{^{14}N} = 0.00677$
$\frac{^{18}O}{^{16}O} = 0.00200$
$\frac{^{34}S}{^{32}S} = 0.0443$

other hand, excellent accuracy and precision are obtained by analyzing the sample and a standard as concurrently as possible. Thus the isotope ratio of a sample is always measured relative to a standard. This relative difference is reported as a **del value**, which is defined as

$$\delta \text{ in } ‰ = \left[\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}}\right] \times 1000 \qquad (29.1)$$

where R is the isotope ratio with the most abundant isotope in the denominator. Since the ratio difference is multiplied by 1000, del values have units of parts per thousand, which are also called parts per mil (‰).

A del value of 0‰ means that the isotopic composition of the sample is equal to that of the standard. Positive del values indicate that the sample is enriched in the heavy (rare) isotope relative to the standard. Negative del values indicate isotope depletion; the sample has relatively less of the heavy (rare) isotope than the standard.

The internationally accepted stable isotope standards for C, H, N, O, and S are listed in Table 29.3. All meet the following criteria: (1) a reasonably abundant supply of this material exists; (2) the material is isotopically homogeneous; and (3) it is relatively easy to prepare for isotope analysis (e.g., the carbon and oxygen must be quantitatively converted to $CO_2(g)$, the hydrogen to $H_2(g)$, the nitrogen to $N_2(g)$ and the sulfur to $SO_2(g)$).

Most of these standards are materials that are active and abundant in the crustal-ocean factory. Thus del values represent a convenient comparison with a geochemically relevant benchmark. For example, a sample of limestone with a $\delta^{13}C$ value of +6‰ is relatively enriched in ^{13}C as compared to PDB, which is an ancient carbonate fossil of a marine invertebrate. The original fossils used as the PDB isotope standard have long since been used up. Thus other working standards, such as NBS-20 ($\delta^{13}C[PDB] = -1.06‰$), are presently used though the $\delta^{13}C$ results are still reported with respect to PDB.

TABLE 29.3
Internationally Accepted Stable Isotope Standards for Hydrogen, Carbon, Oxygen, Nitrogen, and Sulfur

Element	*Standard*	*Abbreviation*
H	Standard Mean Ocean Water	SMOW
C	*Belemnitella americana* from the Cretaceous Peedee formation, South Carolina	PDB
N	Atmospheric N_2	—
O	Standard Mean Ocean Water	SMOW
	Belemnitella americana from the Cretaceous Peedee formation, South Carolina	PDB
S	Troilite (FeS) from the Canyon Diablo iron meteorite	CD

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FRACTIONATIONS

Variations in relative isotope abundance are caused by the preferential reaction or transport of one of the isotopes. Isotopic segregation, or **fractionation**, can occur during a variety of physicochemical processes, such as chemical reactions, phase changes, and molecular diffusion. For example, $H_2{}^{16}O(l)$ is more likely to evaporate than $H_2{}^{18}O(l)$. Thus the resulting water vapor will be relatively depleted in ^{18}O as compared to its parent liquid. The degree to which isotopes become segregated as a result of a particular process is usually expressed as a fractionation factor (α), which is defined as

$$\alpha = \frac{R_{\text{products}}}{R_{\text{reactants}}} \tag{29.2}$$

Since $\alpha \approx 1$, Eq. 29.2 can be rewritten as

$$(\alpha - 1)1000 \approx \delta_{\text{products}} - \delta_{\text{reactants}} \tag{29.3}$$

Fractionation is caused by the slight physicochemical differences that exist among the isotopes of an element. As discussed below, α's are dependent on the reaction mechanism and environmental conditions.

Although isotopes in a given compound form the same kinds of chemical bonds, their bond energies differ. This is due to the effect of the slight mass differences on the vibrational energy of molecules and their chemical bonds. Molecules that contain an atom of the light isotope have a higher vibrational energy than those that contain an atom of the heavier isotope. As a result, the chemical bonds in the lighter molecule are more apt to react, causing the products to become enriched in the light isotope.*

Most biologically mediated processes occur as a series of enzyme-catalyzed reaction steps. Each of these steps is reversible and thus has the potential to attain equilibrium. But when combined in a series, they cause an overall unidirectional transformation of reactants into products, such as in the bacterially mediated reduction of nitrate to N_2. In these processes, fractionations can arise from differences in the rates at which the isotopes are transformed from reactants into products. Since the light isotope reacts faster, it tends to become enriched in the products. In the case of denitrification, this causes N_2 to become relatively enriched in ^{14}N. This type of isotope segregation is rate dependent, so it is termed a **kinetic fractionation**. In many such reactions, the isotopes react at rates that are concentration dependent. Thus kinetic fractionation factors also tend to be concentration dependent.

Physical processes, such as diffusion and phase changes, can cause kinetic fractionations in chemical systems which are not at equilibrium. For example, the net evaporation of water produces vapor that is relatively depleted in ^{18}O as compared to its parent liquid.

The relative isotope composition of reactants and products can also differ even if equilibrium is achieved. The resulting isotope segregation is termed **thermodynamic fractionation** and can usually be described as a type of isotope exchange, such as illustrated below:

$$H_2{}^{18}O(g) + H_2{}^{16}O(l) \rightleftharpoons H_2{}^{16}O(g) + H_2{}^{18}O(l) \qquad (29.4)$$

In this reaction, the products are favored over the reactants at equilibrium because $H_2{}^{16}O$ requires less energy to maintain in the gas phase than $H_2{}^{18}O$. Equilibrium isotope exchange can also occur during chemical reactions as illustrated below.

$$H_2{}^{16}O(l) + C^{18}O^{16}O(aq) \rightleftharpoons H_2{}^{18}O(l) + C^{16}O^{16}O(aq) \qquad (29.5)$$

The fractionation factors for such simple systems can be calculated from theoretical principles. Less success has been achieved for processes that involve solids, as these fractionations are also dependent on differences in lattice energy. Kinetic fractionation factors for most naturally occurring chemical reactions are also difficult to calculate due to their multistep nature. As a result, most fractionation factors are determined experimentally.

All fractionation factors decrease with increasing reaction temperature. The addition of heat increases the total energy of the molecules, including their vibrational energy. At high enough temperatures, the vibrational energy of a

*A "reverse" isotope fractionation can occur during bond formation if the energy of the transition state complex is closer to that of the products than that of the reactants. Because the heavier isotope has a lower activation energy than the lighter one, less energy is required to form its new bond.

molecule is increased to a level such that differences due to dissimilar isotopic composition are insignificant. At these temperatures, $\alpha = 1$.

SOME APPLICATIONS OF THE STABLE ISOTOPES TO THE STUDY OF MARINE BIOGEOCHEMICAL PROCESSES

The Hydrogen and Oxygen Isotopes

The relative abundances of the hydrogen and oxygen isotopes in various natural materials are given in Figures 29.1 and 29.2, respectively. This type of diagram, in which the isotopic compositions of the various materials are reported as a range of del values, is called a Caltech Plot.

δD and $\delta^{18}O$ of Natural Waters

The range of del values seen in natural waters is largely the result of fractionations which occur during evaporation and condensation. The fractionation factor for this process (Eq. 29.4) is defined as

$$\alpha = \frac{R_{\text{liquid}}}{R_{\text{gas}}} \tag{29.6}$$

where $\alpha_D = (^2H/^1H)_{\text{liquid}}/(^2H/^1H)_{\text{gas}}$ and $\alpha_{18} = (^{18}O/^{16}O)_{\text{liquid}}/(^{18}O/^{16}O)_{\text{gas}}$. More energy

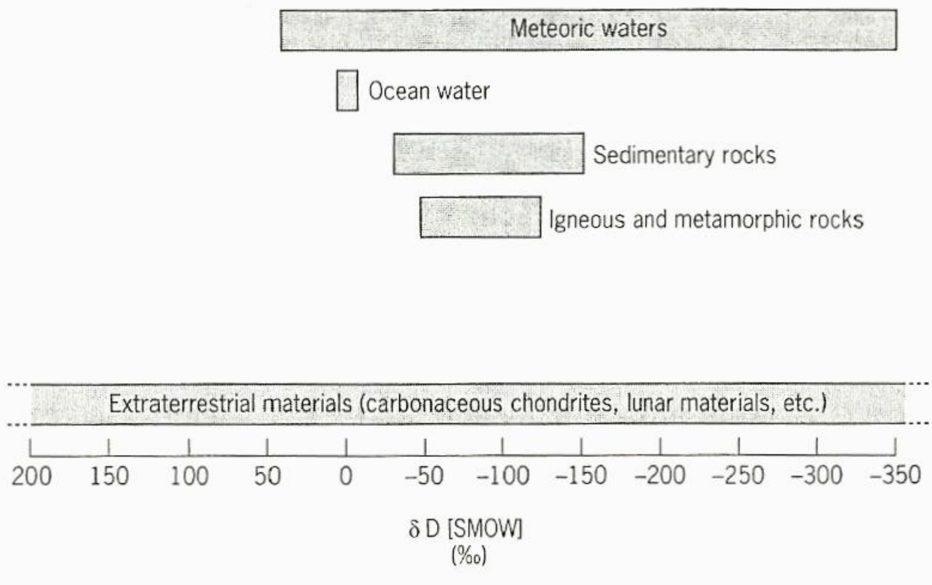

FIGURE 29.1. δD [SMOW] of some geologically important materials. Meteoric waters are produced by meteorological processes, such as rain and snow. They include all liquid and solid water on land and in underground aquifers. They do not include water in the ocean, sediments or below the crust. *Source*: From *Stable Isotope Geochemistry*, J. Hoefs, copyright © 1980 by Springer-Verlag, Heidelberg, Germany, p. 23. Reprinted by permission.

is required to keep the heavy isotope in the gaseous phase, so these fractionation factors are always greater than 1 and decrease with increasing temperature as shown below (Figure 29.3).

The del values of natural waters are also affected by the extent to which evaporation or condensation have occurred. As shown in Figure 29.4, an isotope distillation occurs as moisture-laden clouds produced by evaporation at low latitudes travel poleward and lose water via condensation.

At low latitudes, net evaporation of water from the ocean produces vapor which is depleted in ^{18}O. Atmospheric circulation transports this vapor poleward. The decline in temperature causes water vapor to condense en route. Since ^{18}O is more likely to condense than ^{16}O, the remaining water vapor becomes progressively depleted in ^{18}O. This causes the relative abundance of ^{18}O in the cloud to decrease, so that the ^{18}O content of any further condensate also declines. In other words, the $\delta^{18}O$ of the condensate is a function of the fraction of water vapor that remains in the atmosphere.

This process, in which the isotopic composition of the product varies as a result of the extent of reaction, is called a **Rayleigh Distillation**. Its effect on the isotopic composition of the remaining reactant is given by

$$\frac{R_f}{R_o} = f^{(\alpha - 1)} \tag{29.7}$$

where f is the fraction of remaining reactant, R_f is the del value of the reactant at some f and R_o is the del value when $f = 1$ (i.e., prior to the removal of any reactant). This expression can also be written in terms of del values as illustrated below for the Rayleigh Distillation of ^{18}O and ^{16}O in water vapor as it undergoes condensation.

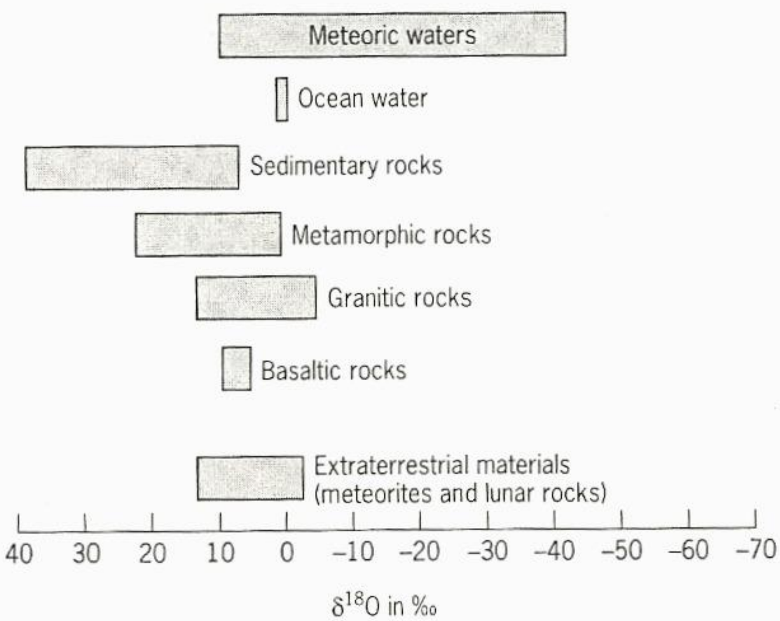

FIGURE 29.2. $\delta^{18}O$ [SMOW] of some geologically important materials. *Source*: From *Stable Isotope Geochemistry*, J. Hoefs, copyright © 1980 by Springer-Verlag, Heidelberg, Germany, p. 36. Reprinted by permission.

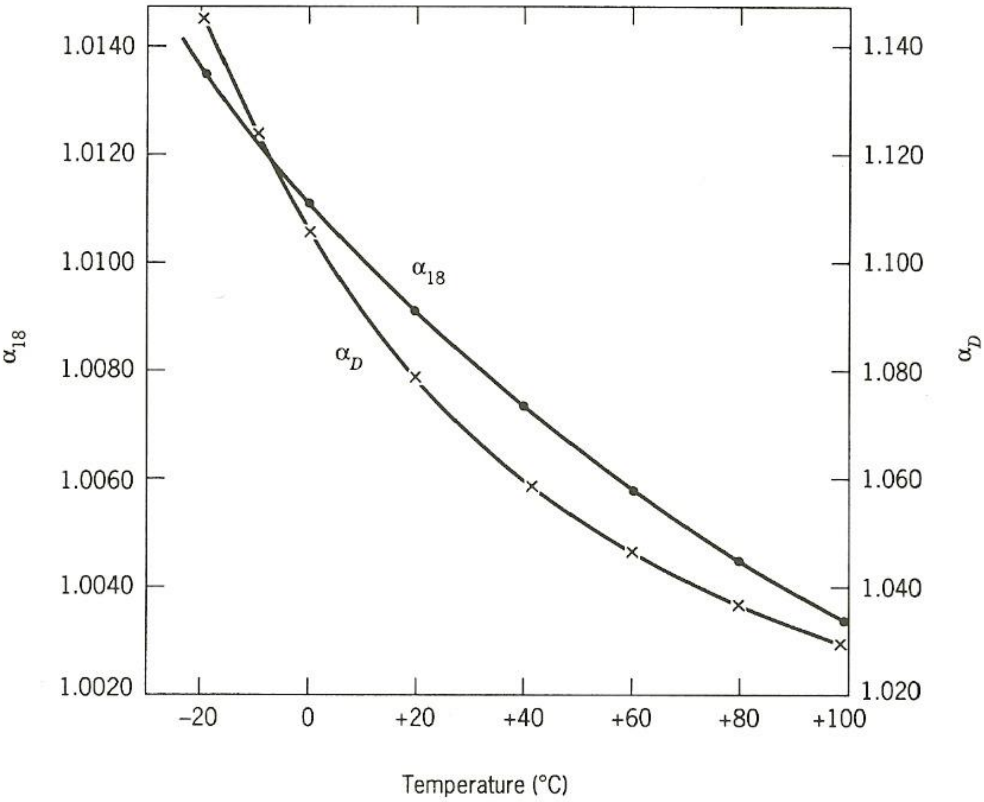

FIGURE 29.3. Temperature variation of isotope fractionation factors for the condensation of water where $\alpha_D = (^2H/^1H)_{liquid}/(^2H/^1H)_{gas}$ and $\alpha_{18} = (^{18}O/^{16}O)_{liquid}/(^{18}O/^{16}O)_{gas}$. These fractionation factors are for the case where isotopic equilibrium is achieved between the liquid and gas phases. *Source*: From *Principles of Isotope Geology*, 2nd ed., G. Faure, copyright © 1986 by John Wiley & Sons, Inc., New York, p. 433. Reprinted by permission. Data from W. Dansgaard, reprinted with permission from *Tellus*, vol. 16, p. 438, copyright © 1965 by Munksgaard International Publishers, Ltd., Copenhagen, Denmark.

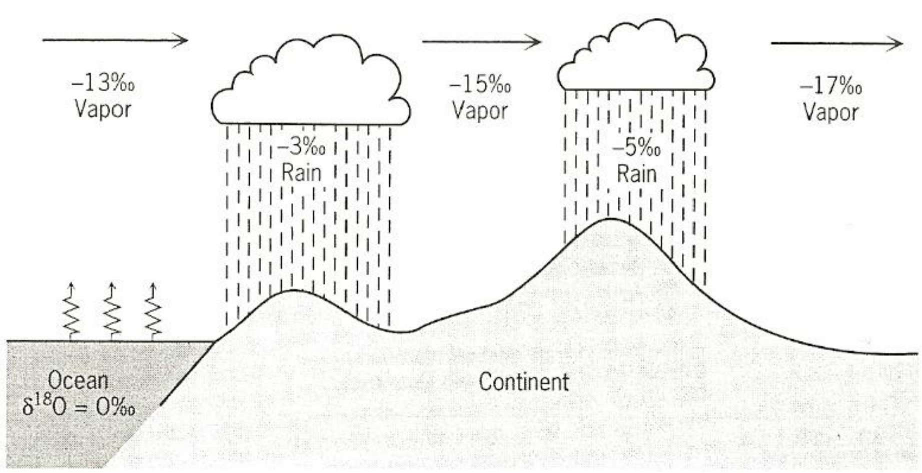

FIGURE 29.4. Schematic fractionation in the atmospheric water cycle. *Source*: From *Lectures in Isotope Geology*, U. Siegenthaler (eds.: E. Jager and J. C. Hunziker), copyright © 1979 by Springer-Verlag, Heidelberg, Germany, p. 266. Reprinted by permission.

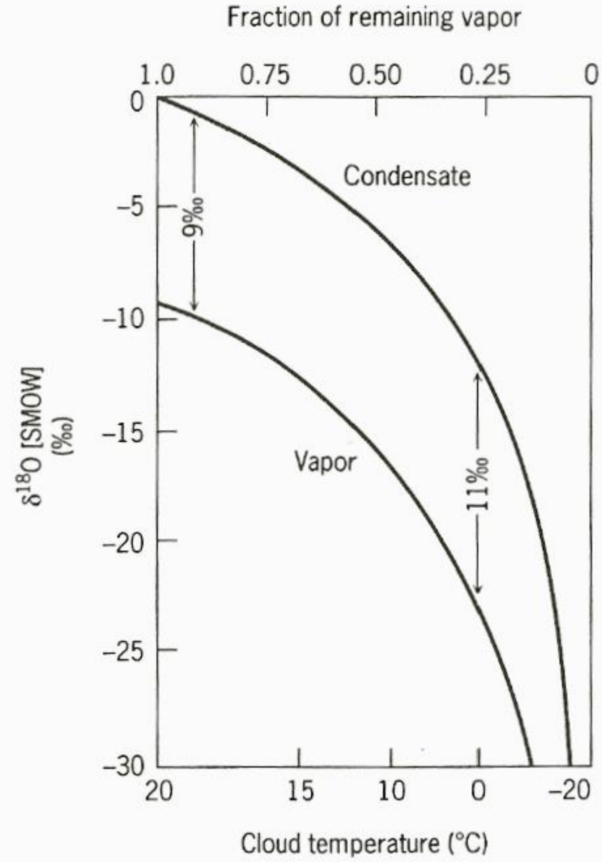

FIGURE 29.5. $\delta^{18}O$ [SMOW] in cloud vapor and condensate plotted as a function of the fraction of remaining vapor for a Rayleigh process. The temperature of the clouds is shown on the lower axis. As indicated, the increase in fractionation with decreasing temperature is taken into account. *Source*: From *Stable Isotope Geochemistry*, J. Hoefs, copyright © 1980 by Springer-Verlag, Heidelberg, Germany, p. 12. Reprinted by permission. After W. Dansgaard, reprinted with permission from *Tellus*, vol. 16, p. 440, copyright © 1964 by Munksgaard International Publishers, Ltd., Copenhagen, Denmark.

$$\delta^{18}O_f = [\delta^{18}O_o + 1000]f^{(\alpha-1)} \tag{29.8}$$

A similar equation can be generated to describe the effect of this Rayleigh Distillation on the isotopic composition of the resulting condensate.

As clouds move from low to high latitudes, α increases due to decreasing temperature. The effect of this temperature change on the Rayleigh Distillation of water vapor is shown in Figure 29.5. Assuming that isotopic equilibrium is achieved in the clouds, the initial condensate will be enriched in ^{18}O by 9‰ relative to its parent vapor. As the remaining vapor moves to higher latitudes, the preferential removal of ^{18}O causes it to become progressively depleted in ^{18}O and hence its $\delta^{18}O$ becomes more negative. The $\delta^{18}O$ of the resulting condensate also decreases, but by less than would have been achieved at low latitudes due to the effect of temperature on the fractionation factor. For example, the condensate produced at 0°C is enriched in ^{18}O by 11‰ relative to its parent vapor. This increase in enrichment counters some of the depletion caused by the Raleigh Distillation Effect.

This process causes the $\delta^{18}O$ and δD of meteoric water* to be linearly related and generally decrease with increasing latitude, as illustrated in Figure 29.6. Deviations from these trends are caused by processes, such as an excess of evaporation over precipitation, that occur in some semi-isolated basins.

In comparison, the $\delta^{18}O$ and δD of seawater are not nearly as variable. The small differences that do exist are related to salinity, as shown in Figure 29.7. In the surface waters, evaporation causes a concurrent enrichment in salt

*See Figure 29.1 for a definition of meteoric water.

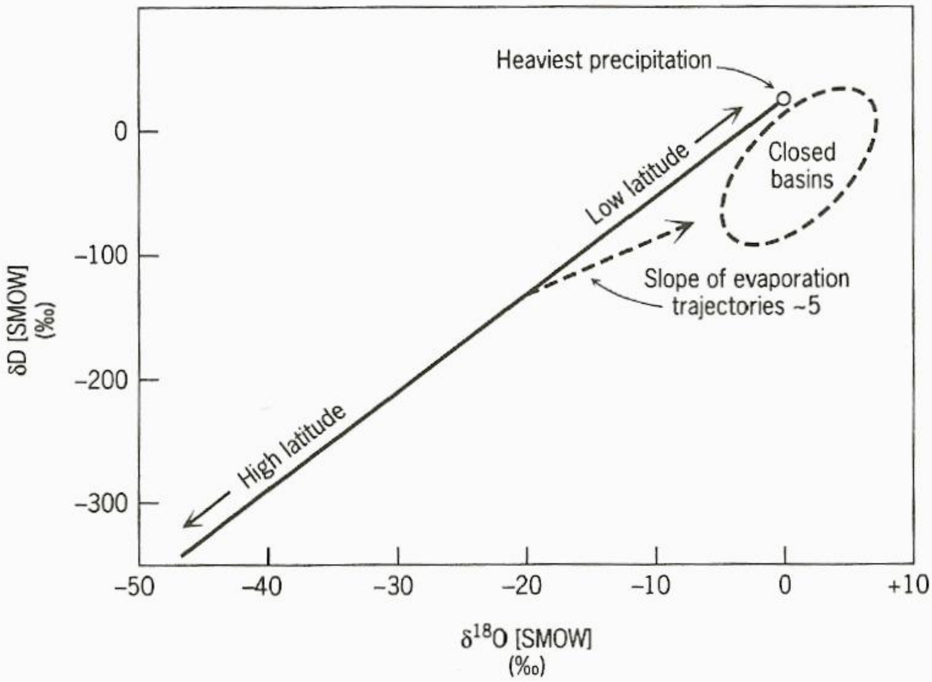

FIGURE 29.6. Relationship between δD [SMOW] and $\delta^{18}O$ [SMOW] in meteoric water. *Source*: From *Principles of Isotope Geology*, 2nd ed., G. Faure, copyright © 1986 by John Wiley & Sons, Inc., New York, p. 435. Reprinted by permission. After H. Craig, reprinted with permission from *Science*, vol. 133, p. 1702, copyright © 1961 by the American Academy of Sciences, Washington, DC.

and the heavy isotopes of oxygen and hydrogen. The latter is the result of the preferential evaporation of ^{16}O. Since deep water is created from the sinking of surface waters, the source of a deep-water mass can be determined from its isotopic composition and salinity. As shown in Figure 29.7, the isotopic composition and salinity of NADW is very different from that of AABW. The latter is a version of Weddell Sea water, whose salinity is increased by the removal of water as a result of freezing. The formation of sea ice has little impact on the isotopic composition of the remaining seawater.

The $\delta^{18}O$ and salinity of the waters that would be produced from the conservative mixing of AABW and NADW is shown by the dashed line. Since Indian and Pacific bottom water lie slightly off this trend, they appear to be produced by the mixing of AABW, NADW, and a small amount of some other water mass whose identity has not yet been established. This "unknown" water is likely some version of Weddell Sea water that has not been as intensely affected by freezing as pure AABW. These data support the conclusion that deep-water masses are currently being formed only in the North Atlantic and Southern oceans.

$\delta^{18}O$ of Igneous and Metamorphic Rocks

During the crystallization process, igneous and metamorphic rocks acquire oxygen from sources such as subterranean water. If the minerals solidify in

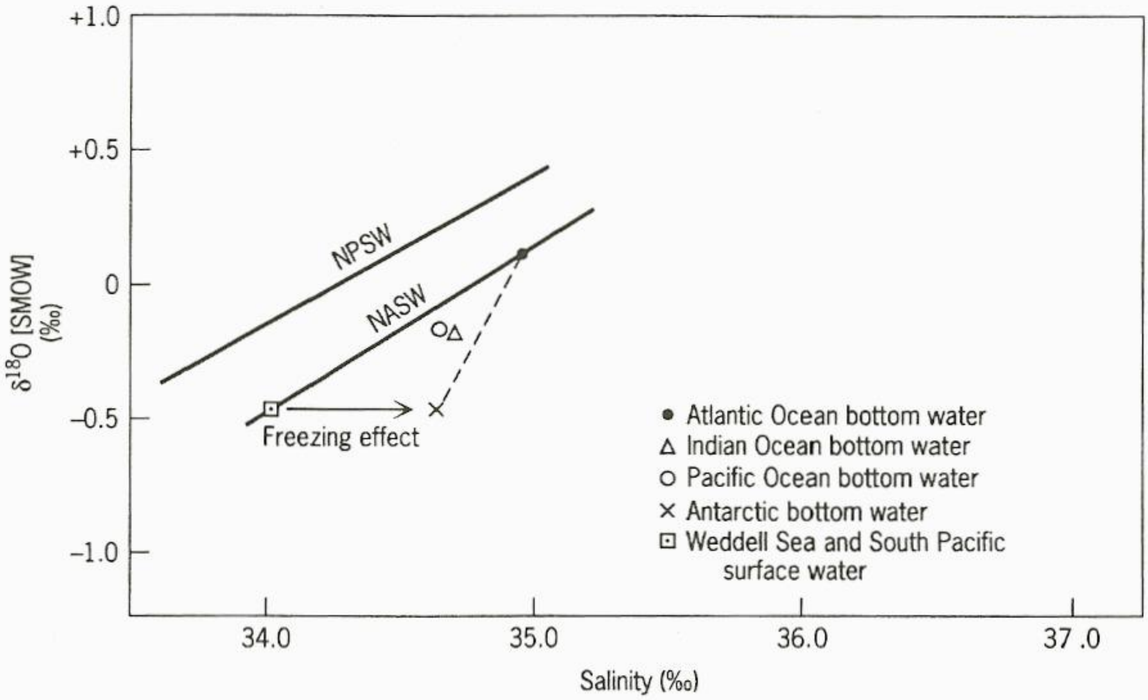

FIGURE 29.7. Relationship between $\delta^{18}O$ [SMOW] and salinity in the surface waters of the North Pacific (NPSW), the North Atlantic (NASW), and the major deep water masses. The formation of AABW from Weddell Sea water is shown by the arrow. The conservative mixing line between NADW and AABW is shown by the dashed line. *Source*: From *Principles of Isotope Geology*, 2nd ed., G. Faure, copyright © 1986 by John Wiley & Sons, Inc., New York, p. 440. Reprinted by permission. After *Stable Isotopes in Oceanographic Studies and Paleotemperatures*, H. Craig and L. I. Gordon (ed.: E. Tongiorgi), copyright © 1965 by Consiglio Nazionale delle Richerche, Laboratorio di Geologia Nucleare, Pisa, Italy, p. 39. Reprinted by permission.

isotopic equilibrium with this oxygen source, their $\delta^{18}O$ can be used to determine the temperature at which this process occurred. The minerals that can be used as geothermometers are ones that experience a significant amount of fractionation as a result of equilibrium isotope exchange with the oxygen source. The relationship between the degree of this fractionation and the solidification temperature is given by the semi-empirical equation

$$1000 \ln \alpha = A(10^6/T^2) + B \tag{29.9}$$

where A and B are constants for a mineral that must be experimentally determined and $\alpha = R_{\text{rock}}/R_{\text{water}}$. Examples of geothermometer equations for various silicate minerals are plotted in Figure 29.8. Values of B are given by the y-intercept, and values of A are obtained from the slope of the line that best fits the calibration data as determined by the method of linear regression.

With values of A and B, the solidification temperature of a rock sample can be inferred from Eq. 29.9 if the isotopic compositions of the constituant mineral and its oxygen source are known. The requirement for the latter can be eliminated by combining geothermometer equations as follows. Consider two minerals whose fractionation factors are α_1 and α_2 and whose $\delta^{18}O$'s are δ_1 and δ_2, respectively. If the $\delta^{18}O$ of the oxygen source is represented by δ_o,

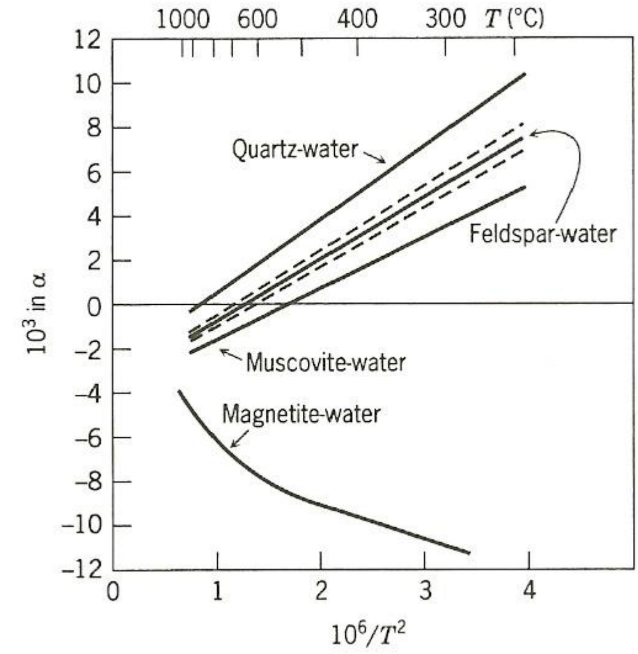

FIGURE 29.8. Schematic diagram of some experimentally determined oxygen isotope calibration curves. *Source*: From H. Friedrichsen, reprinted with permission from *Neues Jahrbuchfuer Mineralogie Monatshefte*, vol. 1, p. 29, copyright © 1971 by E. Schweizerbart'sche, Stuttgart, Germany.

then the fractionation factors can be written as follows, using the relationship given in Eq. 29.3:

$$1000\alpha_1 \approx \delta_1 - \delta_o \tag{29.10}$$

$$1000\alpha_2 \approx \delta_2 - \delta_o \tag{29.11}$$

Likewise, the geothermometer equations for minerals 1 and 2 are

$$1000 \ln \alpha_1 = A_1(10^6/T^2) + B_1 \tag{29.12}$$

$$1000 \ln \alpha_2 = A_2(10^6/T^2) + B_2 \tag{29.13}$$

α is rarely greater than 1.004 and can be thought of as $1.00X$, where $X \leq 4$. Since $\ln(1.004) = 0.00399$, $1000 \ln 1.00X \approx X$ or $1000 \ln \alpha \approx 1000(\alpha - 1)$. Thus Eqs. 29.10 and 29.12 can be equated to yield

$$\delta_1 - \delta_o = A_1(10^6/T^2) + B_1 + 1000 \tag{29.14}$$

and for mineral 2,

$$\delta_2 - \delta_o = A_2(10^6/T^2) + B_2 + 1000 \tag{29.15}$$

δ_o can be eliminated by subtracting Eq. 29.15 from Eq. 29.14 to yield

$$\delta_1 - \delta_2 = (A_1 - A_2)(10^6/T^2) + (B_1 - B_2) \tag{29.16}$$

In other words, when two solid phases have equilibrated with some common reservoir of oxygen, the difference in their δ values is a function of temperature. This assumes, of course, that no other process has altered their isotopic composition. In actuality, the isotopic compositions of most igneous and metamorphic rocks have been shown to change as they cool following crystallization. In these cases, cooling is so slow that the minerals continue to undergo isotope exchange with their oxygen sources. Thus temperatures inferred from their isotopic composition are underestimates of the crystallization temperature. As discussed below, the isotopic composition of minerals that equilibrated with oxygen sources at low temperatures can yield other useful information.

$\delta^{18}O$ and δD of Clay Minerals

Convincing evidence refuting the occurrence of reverse weathering in marine sediments has been obtained from the isotopic composition of clay minerals. During chemical weathering on land, clay minerals undergo isotopic exchange with meteoric waters. Thus the δD and $\delta^{18}O$ of a terrestrial clay mineral is determined by (1) its fractionation factor for isotope exchange, (2) the temperature at which weathering occurred, (3) the degree to which equilibrium with meteoric waters was achieved, and (4) the isotopic composition of the meteoric waters.

If the clay minerals reach isotopic equilibrium with meteoric waters, their δD and $\delta^{18}O$ should be linearly related in a fashion similar to that seen in meteoric waters (Figure 29.6). This linear relationship can be described as

$$\delta D = A\delta^{18}O + B \tag{29.17}$$

where A and B are constants for the mineral at a given temperature. Values of A and B have been determined for various terrestrial clay minerals, such as kaolinite, illite, and montmorillonite. The resulting equations, relevant for temperatures at which weathering occurs, are plotted in Figure 29.9 along with the meteoric water line.

Fractionation during equilibrium isotope exchange causes terrestrial clays to be enriched in ^{18}O relative to their meteoric waters, but depleted in δD. This fractionation is large and causes the mineral lines in Figure 29.9 to be considerably offset from the meteoric water relationship. By examining the effects of temperature on this fractionation, it appears that the clay minerals in modern soils were formed under somewhat warmer conditions than presently exist. Similar calculations can be done to determine what the isotopic composition of clay minerals should be if they are in isotopic equilibrium with seawater. Since the isotopic composition of seawater varies little, these predicted clay mineral values are represented by the small boxes in Figure 29.9.

The actual isotopic composition of clay minerals isolated from marine sediments is closer to that of terrestrial clays than of authigenic ones. This suggests that most of the clay minerals in marine sediments are detrital in origin.

$\delta^{18}O$ of Marine Carbonate Minerals

The $\delta^{18}O$ of sedimentary carbonates is one of the most widely used records of paleoclimate change. The basis for this application lies in the tendency of marine organisms to deposit calcite in isotopic equilibrium with ambient seawater. This isotopic equilibrium is the result of the following isotope exchange reaction

$$CaC^{16}O^{16}O^{16}O(s) + H_2^{18}O(l) \rightleftharpoons Ca^{18}O^{16}O^{16}O(s) + H_2^{16}O(l) \tag{29.18}$$

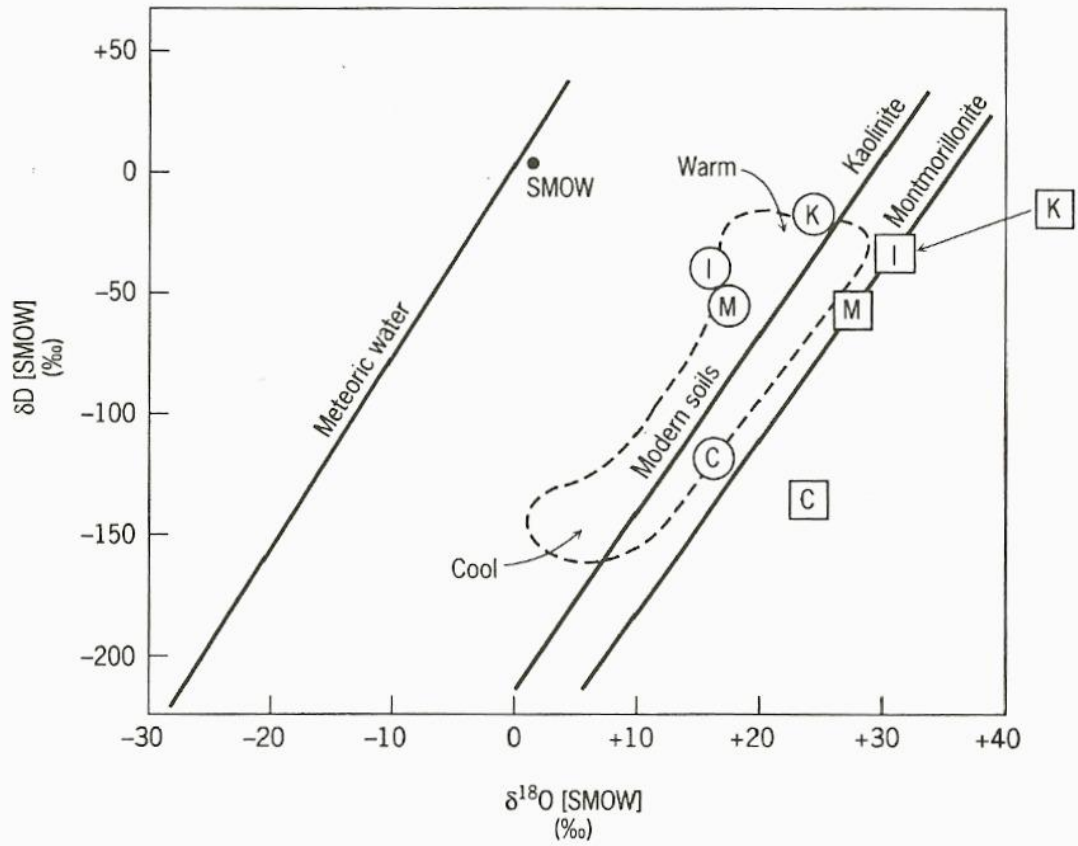

FIGURE 29.9. Relationship between δD [SMOW] and $\delta^{18}O$ [SMOW] of clay minerals. The lines represent the isotopic composition that would be achieved if the clay minerals reached isotopic equilibrium with meteoric waters at earth-surface temperatures. The boxes represent the isotopic composition that would be achieved if the clay minerals reached isotopic equilibrium with seawater at 0°C. The circles are the observed isotopic composition of clay minerals collected from marine sediment, where K = kaolinite; M = montmorillonite; C = chlorite; and I = illite. Also shown is the isotopic composition of meteoric waters. *Source*: From *Principles of Isotope Geology*, 2nd ed., G. Faure, copyright © 1986 by John Wiley & Sons, Inc., New York, p. 479. Reprinted by permission. After H. P. Taylor, Jr., reprinted with permission from *Economic Geology*, vol. 69, p. 857, copyright © 1974 by Economic Geology Publishing Co., El Paso, TX. Seawater Data from S. M. Savin and S. Epstein, reprinted with permission from *Geochimica et Cosmochimica Acta*, vol. 34, p. 55, copyright © 1971 by Pergamon Press, Elmsford, NY.

This isotope exchange causes pure calcite to be considerably enriched in ^{18}O at equilibrium. For example, calcite that has been isotopically equilibrated at 25°C is 28.6‰ enriched in ^{18}O as compared to the water. Thus calcite that is deposited in isotopic equilibrium with SMOW at this temperature will have $\delta^{18}O$ of +28.6‰ on the SMOW scale.

The $\delta^{18}O$ of marine carbonates is usually measured on the PDB scale, as this standard is also a fossil marine carbonate. The following equation relates the $\delta^{18}O$ of carbonates measured on the SMOW scale to the PDB scale.

$$\delta^{18}O[SMOW] = 1.03086\delta^{18}O[PDB] + 30.86 \qquad (29.19)$$

The small correction factor (1.03086) compensates for fractionation that occurs during the preparation of marine carbonates for mass spectrometric analysis.

The fractionation factor for the equilibrium isotope exchange given in Eq. 29.18 increases with decreasing temperature. The effect of temperature on the $\delta^{18}O$ of isotopically equilibrated calcite (δ_c) has been experimentally established as

$$T(°C) = 16.9 - 4.2(\delta_c - \delta_w) + 0.13(\delta_c - \delta_w)^2 \qquad (29.20)$$

where δ_w is the $\delta^{18}O$ of the water. Similar equations have been developed for other carbonate phases, such as aragonite. These relationships suggest that the isotopic composition of biogenic carbonates should reflect the water temperatures under which the shells were deposited. The use of $\delta^{18}O$ as a paleothermometer is complicated by several phenomena that are discussed below.

Biogenic calcites deviate slightly from the temperature relationship given in Eq. 29.20 as a result of several factors. These include (1) species differences in fractionation factors attributable to variations in mineralogy, (2) temporal changes in fractionation factors caused by variations in growth rate, (3) isotope exchange with respiratory CO_2, and (4) incomplete isotope exchange during shell deposition (i.e., isotopic disequilibrium). Some of these effects can be minimized by determining paleotemperatures from the isotopic composition of a single species. Foraminiferan tests are the biogenic carbonate of choice as they are geographically and temporarily widespread. In addition, these protozoans tend to live in narrowly defined depth ranges, with some species inhabiting the surface waters, while others live in the deep sea and on the seafloor.

In addition to the magnitude of the equilibrium fractionation factor, the $\delta^{18}O$ of biogenic calcite is also determined by the isotopic composition of ambient seawater. As described in the preceding section, the Rayleigh Distillation of atmospheric water vapor causes the $\delta^{18}O$ of surface seawater to vary geographically and is directly related to salinity. As a result, a 1‰ increase in salinity would be accompanied by a change in $\delta^{18}O$ that is equivalent to a 1°C decrease in the calculated water temperature.

The Rayleigh Distillation of water vapor also causes polar ice to be depleted in ^{18}O relative to seawater. Thus an increase in ice volume causes the ocean to become enriched in ^{18}O. During periods of maximum glaciation, the $\delta^{18}O$ of seawater increased to +0.90‰ [SMOW]. If all present-day continental glaciers melted, the $\delta^{18}O$ of seawater would decrease to −0.6‰ [SMOW]. Thus changes in temperature, ice volume, and the relative rate of local evaporation could have caused the $\delta^{18}O$ of forams to vary over time. Over the past 1 million years, the resulting variation has only amounted to 2‰.

Although the isotopic variations have been small, similar amplitudes and frequencies have been observed in cores from many different parts of the ocean (Figure 29.10*a* and *b*). Thus the causes of these fluctuations must have had global impact and are thought to be related to periodic episodes of glaciation and deglaciation. The increases in $\delta^{18}O$ are interpreted as records of ice ages,

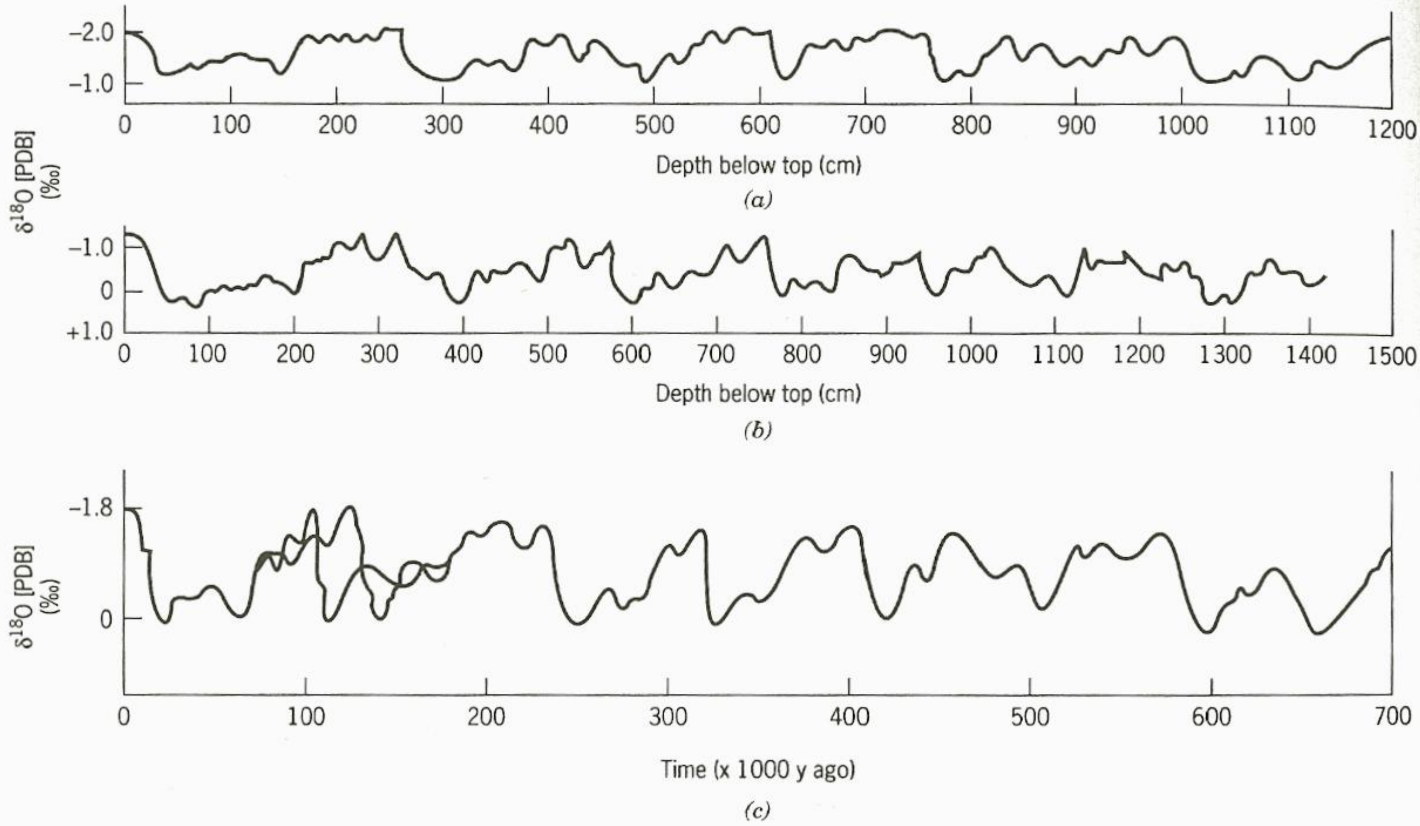

FIGURE 29.10. $\delta^{18}O$ [PDB] of tests deposited by the foraminiferan *Globigerinoides sacculifera* in cores collected from (*a*) the western equatorial Pacific and (*b*) the Caribbean Sea during the Brunhes Epoch. (*c*) Generalized isotope curve and time scales. The latter were obtained from radiometric dating. *Source*: From C. Emiliani and N. J. Shackelton, reprinted with permission from *Science*, vol. 183, pp. 511 and 513, copyright © 1974 by the American Association for the Advancement of Science, Washington, DC.

since ^{18}O enrichment is caused by both decreased temperatures and increased ice volume. Because these isotopic shifts were concurrently recorded in the sediments of all the ocean basins, they are also used as a stratigraphic marker. The timing of these events has been established by dating the sediments radiometrically, with either ^{14}C or $^{230}Th/^{231}Pa$. By averaging the isotope records from many cores, a generalized paleo-isotope curve has been constructed, as shown in Figure 29.10*c*.

The relative importance of changes in ice volume and water temperature in determining the $\delta^{18}O$ of biogenic calcite deposited over the past 1 million years has been assessed by comparing the isotopic composition of benthic and planktonic forams. The presence of polar ice caps during this period places a lower limit on the temperature of the bottom water. Since seawater can get no cooler than its freezing point, bottom-water temperatures could not have been lower than -2°C. Thus most of the variations in isotopic composition of the benthic species must have been caused by shifts in the $\delta^{18}O$ of seawater. Such shifts would have been caused by changes in ice volume.

If large changes in local surface-water temperatures occurred, the amplitude of isotopic variation in the planktonic forams should differ from that in the benthic species. For example, a greater cooling of the surface waters during an ice age would cause the planktonic species to experience a larger ^{18}O enrichment than seen in the benthic forams. In such cases, Eq. 29.20 can be used to infer δ_w from the δ_c of benthic plankton if a deep-water temperature is assumed. Since the ocean is well mixed on time scales much shorter than that of climate change, this δ_w can be used to compute a surface-water temperature from the δ_c of the planktonic tests.

As shown in Figure 29.11, the isotopic composition of the planktonic and benthic forams has fluctuated with virtually the same frequency and amplitude. This suggests that at this location, neither surface nor bottom-water temperatures varied much. This result appears applicable to most of the ocean and is supported by paleotemperatures estimated from changes in the relative abundances of surface-water species. These data indicate that surface-water temperatures varied by no more than 1.5°C. Thus the paleo-isotope curve for this time period is thought to be largely the result of changes in ice volume.

Since the surface waters are affected by short-term local variations in isotopic composition mostly as a result of meteorological events, the $\delta^{18}O$ of planktonic forams tends to be more variable than the isotopic composition of the benthic forams. Thus the $\delta^{18}O$ of benthic forams provides the least

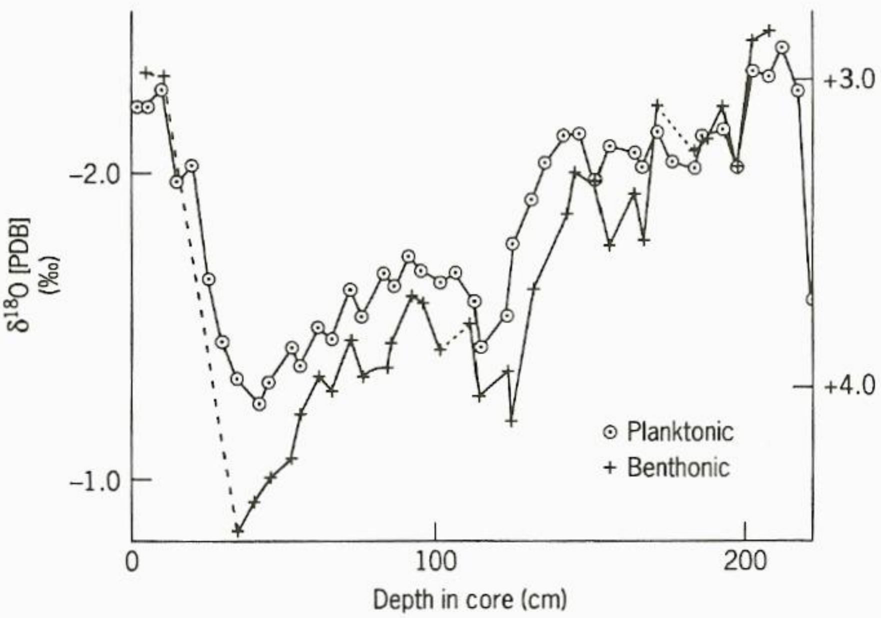

FIGURE 29.11. $\delta^{18}O$ [PDB] of planktonic and benthic foraminifera from DSDP core V28-238. The results are plotted to emphasize changes in the degree to which planktonic forams are isotopically different from the benthic species. To achieve this, the planktonic results are plotted with respect to the left vertical scale, whereas the benthic results are plotted with respect to the right vertical scale. Both are arranged such that the results overlap if the difference in their $\delta^{18}O$ is identical to that presently observed for these species (i.e., 5.3‰). *Source*: From N. J. Shackelton and N. D. Opdyke, reprinted with permission from *Quaternary Research*, vol. 3, p. 44, copyright © 1973 by Academic Press, Orlando, FL.

ambiguous record of climatic changes over the past 1 million years. Down-core variations in the $\delta^{18}O$ of benthic forams can also be interpreted as a record of paleosalinities because changes in ice volume affect the amount of water in the ocean, but not the amount of salt. The isotope data suggest that during the period of maximum glaciation, the mean salinity of the ocean was 3.5‰ higher than at present.

Biogenic calcite deposited prior to the formation of the polar ice caps must have been considerably depleted in ^{18}O relative to modern-day forams. Thus the formation of the present-day polar ice caps should have been recorded as a large increase in the $\delta^{18}O$ of benthic forams. As shown in Figure 29.12, this appears to have occurred 14 million years before present.

Interpretation of the ^{18}O record is complicated by the effects of shifts in oceanic circulation. In particular, changes in thermohaline circulation would affect bottom-water temperatures and the position of the CCD. In some cases, the impact of localized shifts can be assessed by comparing down-core variations in $\delta^{18}O$. For example, the isotope record in the subpolar North Atlantic is substantially different from that at midlatitudes and varies in such a way as to suggest that NADW was not formed in the Norwegian Sea during glacial times. Due to the variety of information obtained from the $\delta^{18}O$ record, its use as a paleoceanographic tool is considered to be the most important geochemical application of stable isotopes.

The Carbon Isotopes

The ranges of $\delta^{13}C$ in various naturally occurring substances are given in Figure 29.13. The marine chemistry of carbon is largely controlled by biological processes, many of which are accompanied by kinetic fractionations. The largest fractionation occurs during the photosynthetic fixation of carbon and

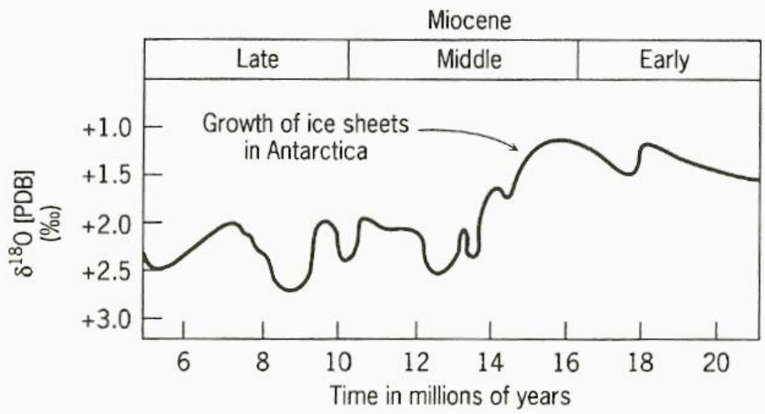

FIGURE 29.12. $\delta^{18}O$ [PDB] in the tests of the benthic foraminiferan *Cibicidoides* in a deep-sea core from the equatorial Pacific Ocean. *Source*: From *Principles of Isotope Geology*, 2nd ed., G. Faure, copyright © 1986 by John Wiley & Sons, Inc., New York, p. 446. Reprinted by permission. Data from R. Woodruff, S. M. Savin, and R. E. Douglas, reprinted with permission from *Science*, vol. 212, p. 666, copyright © 1981 by the American Association for the Advancement of Science, Washington, DC.

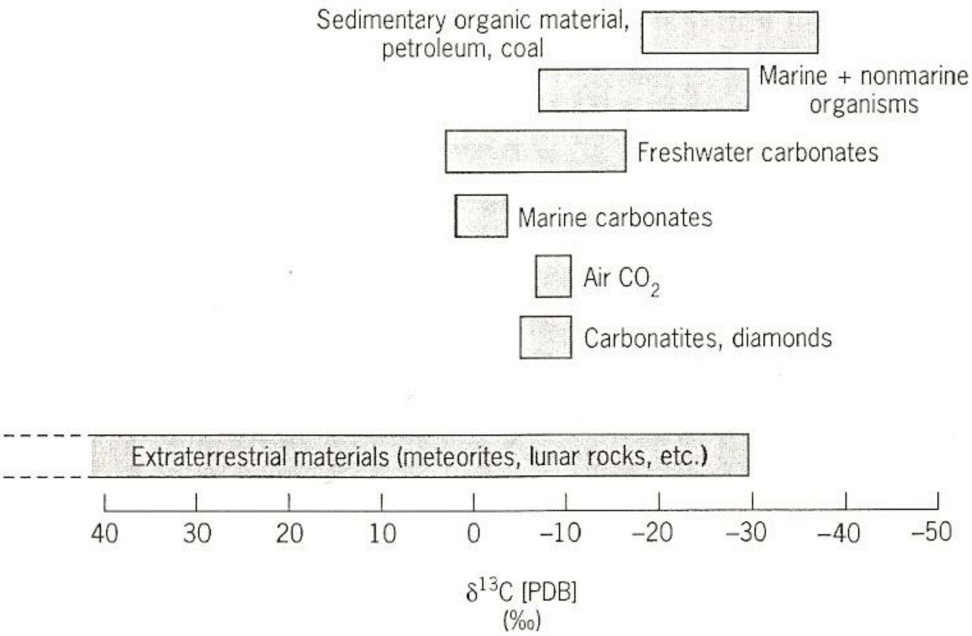

FIGURE 29.13. $\delta^{13}C$ [PDB] of some geologically important materials. *Source*: From *Stable Isotope Geochemistry*, J. Hoefs, copyright © 1980 by Springer-Verlag, Heidelberg, Germany, p. 32. Reprinted by permission.

causes most marine organic matter to be depleted in ^{13}C by approximately 20‰ relative to DIC. The magnitude of this fractionation is somewhat variable and depends on such factors as (1) the species of phytoplankton, (2) their growth rate, and (3) the temperature of ambient seawater.

As illustrated in Figure 29.14, the preferential uptake of ^{12}C by marine phytoplankton causes DIC in the euphotic zone to be relatively enriched in ^{13}C. Phytoplankton also produce O_2 that is depleted in ^{18}O. Following death, some of the ^{13}C-depleted phytoplankton biomass sinks below the euphotic zone and is remineralized. The addition of this ^{13}C-depleted CO_2 lowers the $\delta^{13}C$ of the ambient DIC. This remineralization proceeds via aerobic respiration, which involves the preferential uptake of ^{18}O-depleted O_2, thereby raising the $\delta^{18}O$ of the remaining gas.

The $\delta^{13}C$ of surface-water DIC is also influenced by isotopic equilibration with atmospheric CO_2. At 0°C, isotopic equilibration causes bicarbonate and carbonate to be 10.6‰ and 7.6‰ enriched in ^{13}C relative to atmospheric CO_2, respectively. At 30°C, bicarbonate and carbonate are 7.6‰ and 6.1‰ enriched, respectively. Isotopic equilibrium is often not achieved due to the relatively rapid preferential uptake of ^{12}C during photosynthesis. In comparison, little fractionation occurs during the deposition of biogenic calcite, so the $\delta^{13}C$ of biogenic calcite is close to that of its DIC source. Thus the $\delta^{13}C$ of biogenic calcite can be used to determine the depth or water mass in which the shell was deposited. As shown in Table 29.4, the isotopic composition of the foram tests is closest to that of surface-water bicarbonate. This isotopic similarity suggests that the tests were deposited at the surface from inorganic carbon obtained from the bicarbonate pool.

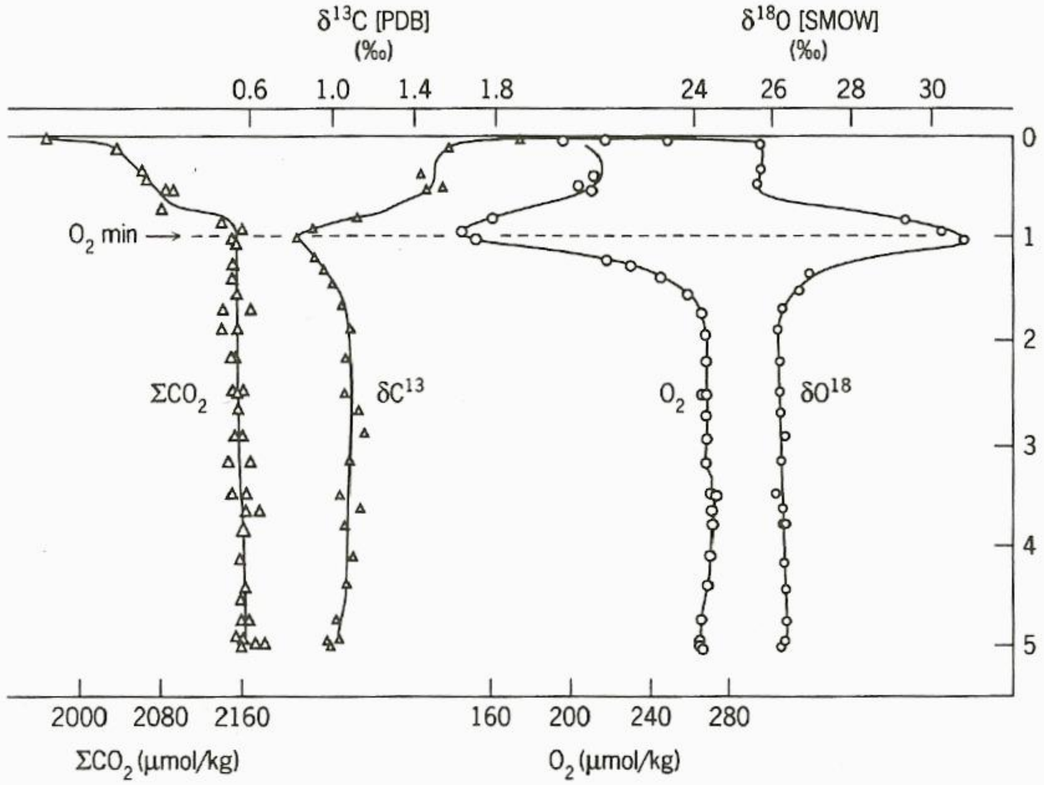

FIGURE 29.14. Vertical profiles of ΣCO_2, $\delta^{13}C$ [PDB] in DIC, dissolved O_2, and $\delta^{18}O$ (SMOW) in dissolved O_2 in the North Atlantic. *Source*: From P. Kroopnik, R. F. Weiss, and H. Craig, reprinted with permission from *Earth and Planetary Science Letters*, vol. 16, p. 106, copyright © 1972 by Elsevier Science Publishers, Amsterdam, The Netherlands.

TABLE 29.4

$\delta^{13}C$ [PDB] of DIC and a Carbonate Shell (The DIC values are for seawater at 15°C)

	$\delta^{13}C$(‰)
Total dissolved inorganic carbon	
At surface	+2.2
At 2.5 km (CO_2 maximum and O_2 minimum)	+0.27
In bottom water	+0.5
Foraminiferal tests	+2
Surface HCO_3^-	+2.5
Surface CO_3^{2-}	−0.5
Atmospheric CO_2	−6.5

Source: From H. Craig, reprinted with permission from the *Journal of Geophysical Research*, vol. 75, p. 693, copyright © 1970 by the American Geophysical Union, Washington, DC.

The $\delta^{13}C$ of sedimentary marine carbonates has not varied as much over time as has its $\delta^{18}O$, as illustrated in Figure 29.15. Since the deep waters are isolated from the atmosphere, changes in the carbon isotope composition of benthic plankton are thought to record shifts in the $\delta^{13}C$ of deep-water DIC. Such isotopic shifts have likely been caused by changes in the oceanic cycling of organic matter. Since the isotopic composition of biogenic calcite is close to that of DIC, changes in its rates of production and dissolution are unlikely to have affected the oceanic distributions of ^{12}C and ^{13}C.

On the other hand, an increase in the rate of POM remineralization in the deep sea should have caused the $\delta^{13}C$ of deep-water DIC to decline. This decline would then have been recorded in the biogenic calcite. As shown in Figure 29.15, this appears to have occurred during periods of glaciation. An increase in remineralization should also have caused deep-water phosphate concentrations to rise. Assuming that the remineralized POM had a C to P ratio of 106 to 16, the increase in deep-water phosphate concentrations can be estimated from the degree of ^{13}C depletion recorded by the forams. With this

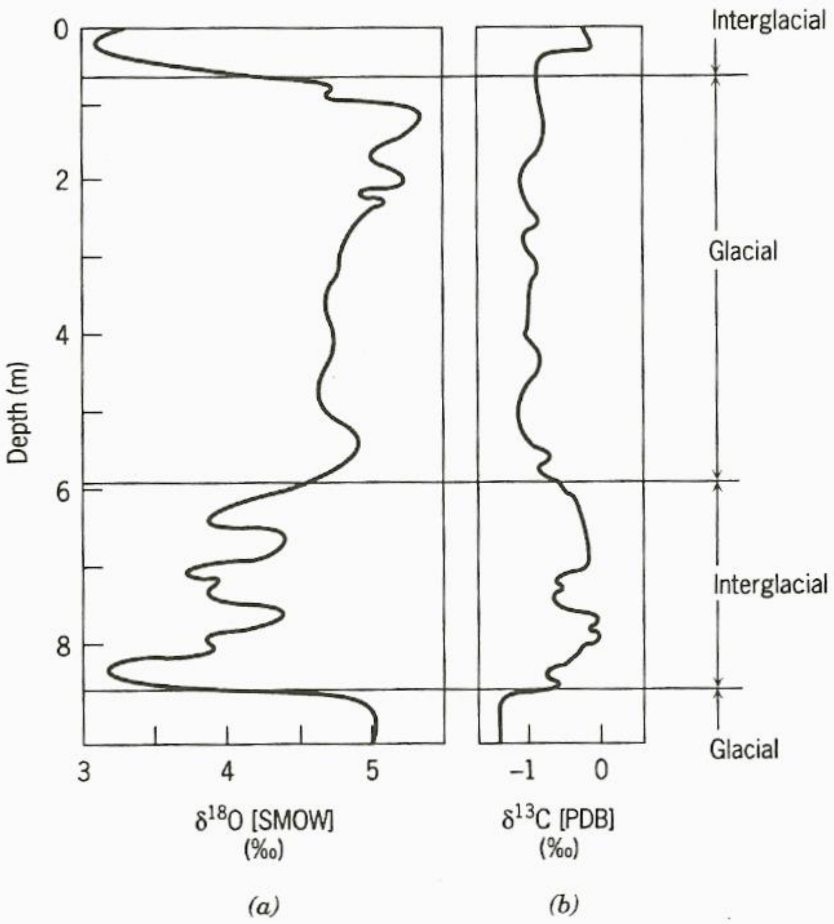

FIGURE 29.15. (*a*) $\delta^{18}O$ [PDB] and (*b*) $\delta^{13}C$ [PDB] for benthic forams as a function of depth in a core from the eastern margin of the north Atlantic Ocean (25°N 17°W). *Source*: From *Tracers in the Sea*, W. S. Broecker and T.-H. Peng, copyright © 1982 by the Lamont-Doherty Geological Observatory, Palisades, NY, p. 305. Reprinted by permission. Data from *The Fate of Fossil Fuel CO_2 in the Oceans*, N. J. Shackleton (eds.: N. R. Anderson and A. Malahoff), copyright © 1977 by Plenum Press, New York, p. 418. Reprinted by permission.

approach, the $\delta^{13}C$ of sedimentary calcite has provided information on how deep-water nutrient concentrations have changed over time.

The $\delta^{13}C$ of sedimentary organic matter also varies down core, but the causes of these variations are not well understood. Most sedimentary organic matter is derived from surface-water POM synthesized by phytoplankton. Thus the $\delta^{13}C$ of this POM is largely determined by the isotopic composition of the phytoplankton. The $\delta^{13}C$ of phytoplankton is determined by temperature, metabolic pathway, and the isotopic composition of the DIC pool. As shown in Figure 29.16, phytoplankton that grow at lower temperatures have larger ^{13}C depletions. This is primarily the result of an increase in the magnitude of the fractionation factor.

The magnitude of this kinetic fractionation is also dependent on the pathway of carbon metabolism in the plant. C_3 plants fractionate the carbon isotopes to a greater degree than do the C_4 (grasses) and CAM (succulents) plants. The $\delta^{13}C$ of plants is also determined by the isotopic composition of their carbon source. For land plants, this is atmospheric CO_2 ($\delta^{13}C$ [PDB] = −7‰) and for marine plants, carbon is assimilated as HCO_3^- ($\delta^{13}C$ [PDB] = ~0‰). As shown in Figure 29.17, this causes most terrestrial C_3 plants to have a lower

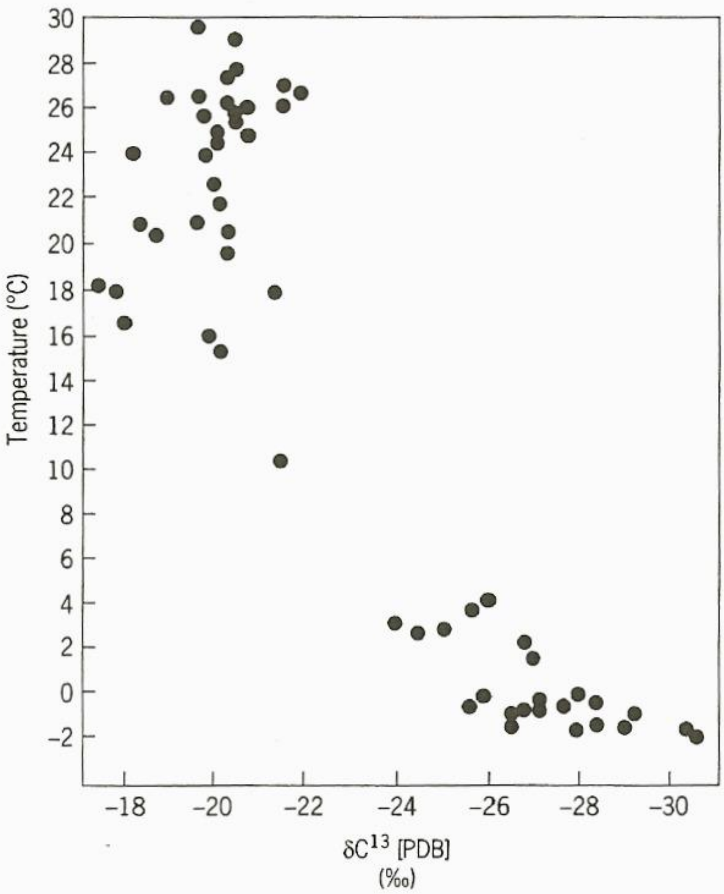

FIGURE 29.16. $\delta^{13}C$ [PDB] of total organic carbon in phytoplankton versus surface temperatures. *Source*: From *Advances in Organic Geochemistry, 1973*, W. M. Sackett, B. J. Eadie, and M. E. Exner (eds.: B. Tissot and F. Bienner), copyright © 1974 by Editions Technip, Paris, France, p. 668. Reprinted by permission.

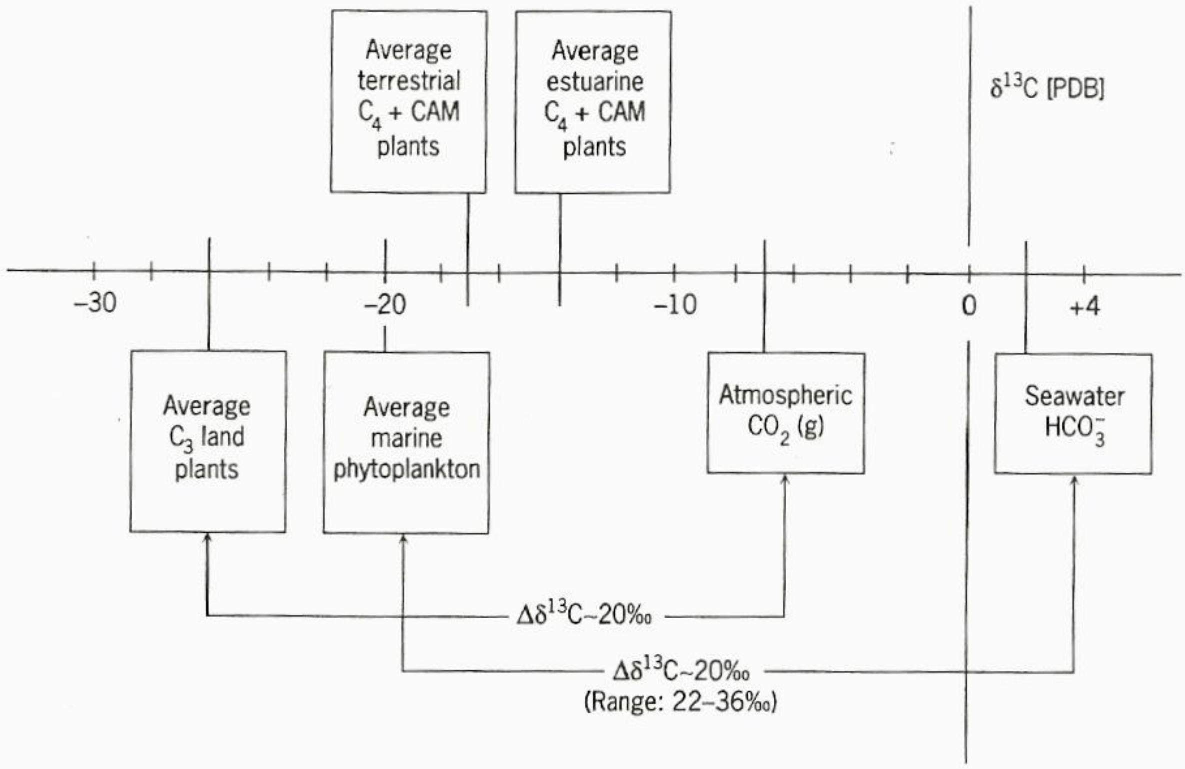

FIGURE 29.17. The influence of carbon source and kinetic fractionation on the average isotopic composition of marine and terrestrial plants. The isotopic composition of HCO_3^- represents that which would be present if isotopic equilibrium is achieved at 15°C.

$\delta^{13}C$ (−26‰) than most marine (−20‰) phytoplankton, which also use C_3 metabolism. Likewise, the average $\delta^{13}C$ of terrestrial C_4 and CAM plants (−17‰) is lower than that of their estuarine analogs (−12‰), which are primarily marsh grasses. It is important to note that variations in environmental conditions and biochemical behavior cause the isotopic composition of these plants to be quite variable. For example, the reported range in the $\delta^{13}C$ of marine plankton is −18 to −30‰.

Animals do not significantly fractionate the carbon isotopes as they pass organic matter up the food chain. As a result, the isotopic composition of an animal's tissues is similar to its source of dietary carbon. Thus the isotopic composition of the animal's tissues can be used to assess the source of their dietary carbon. This approach requires that all possible dietary sources be known. They must also be isotopically distinguishable from each other. If this is the case, the relative contribution of each carbon source can be assessed, as shown in Figures 29.18 and 29.19.

Diagenesis appears to cause a small ^{13}C depletion in sedimentary organic matter. This is thought to be the result of the preferential decomposition of compounds that happen to be enriched in ^{13}C. As shown in Figure 29.20, plant metabolites, such as proteins and carbohydrates, are enriched in ^{13}C relative to cellulose, lipids, and lignin. Since proteins and carbohydrates are more reactive, these compounds should degrade first. Since ^{13}C-enriched carbon is removed, the residual POM becomes depleted in ^{13}C.

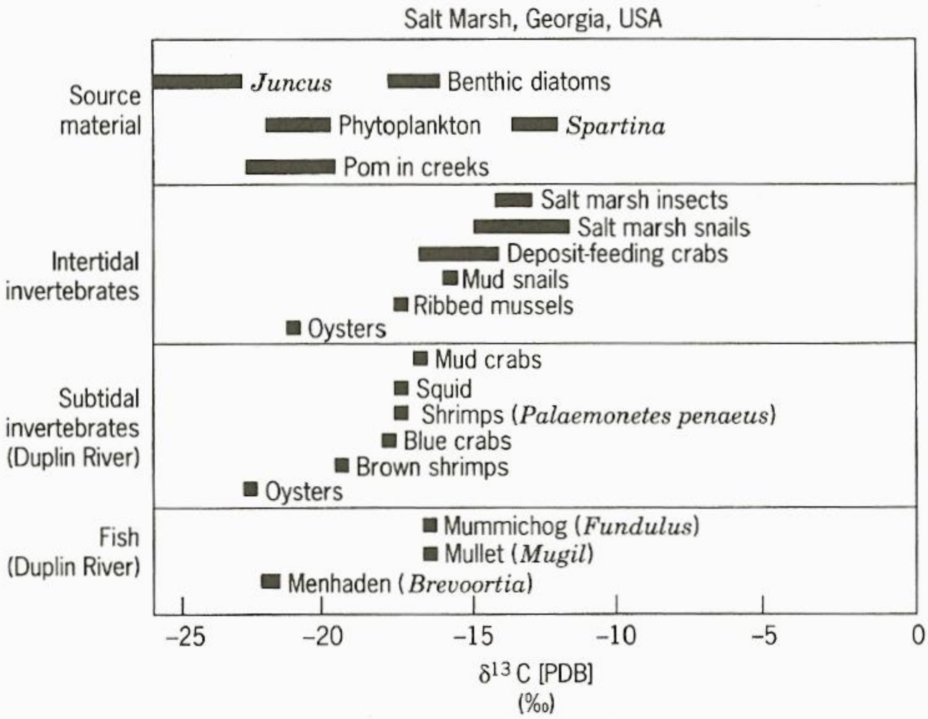

FIGURE 29.18. $\delta^{13}C$ [PBD] of organisms and POM in a salt-marsh estuary (Sapelo Island, GA). *Source*: From *Biogeochemical Processes at the Land-Sea Boundary*, K. H. Mann (eds.: P. Laserre and J. M. Martin), copyright © 1986 by Elsevier Science Publishers, Amsterdam, The Netherlands, p. 130. Reprinted by permission. Data from E. B. Haines and C. L. Montague, reprinted with permission from *Ecology*, vol. 60, p. 52, copyright © 1979 by the Ecological Society of America, Tempe, AZ; and E. B. Haines, reprinted with permission from *Estuarine and Coastal Marine Science*, vol. 4, p. 611, copyright © 1976 by Kluwer Academic Publishers, Dordrecht, The Netherlands.

The phenolic acid moieties (Figure 23.14*b*) are unique degradation products of woody plant detritus and so can be used as an unequivocal indicator of the presence of terrestrial organic matter. As shown in Figure 29.21, the $\delta^{13}C$ of coastal sediments is inversely related to its phenolic acid content. This relationship reflects the relative ^{13}C depletion of terrestrial organic matter as compared to marine POM, the latter being composed primarily of detrital plankton tissues. This relationship also indicates that even after early diagenetic alteration, terrestrial organic matter is still isotopically distinguishable from marine organic matter.

As with the carbonates, down-core variations in the $\delta^{13}C$ of sedimentary organic matter are thought to reflect long-term changes in the oceanic cycling of organic matter. The relationship is more complicated for organic matter because its isotopic composition is strongly influenced by short-term variability in environmental conditions and biological speciation, as well as by diagenesis. Nevertheless, the evolution of life must have caused a large readjustment in the sizes and isotopic composition of the global carbon reservoirs. Isotopic evidence suggesting the presence of life has been observed in rocks as old as 3.5 billion years. Though the isotopic record is somewhat compromised by the effects of metamorphosis, these rocks also contain structures that appear to

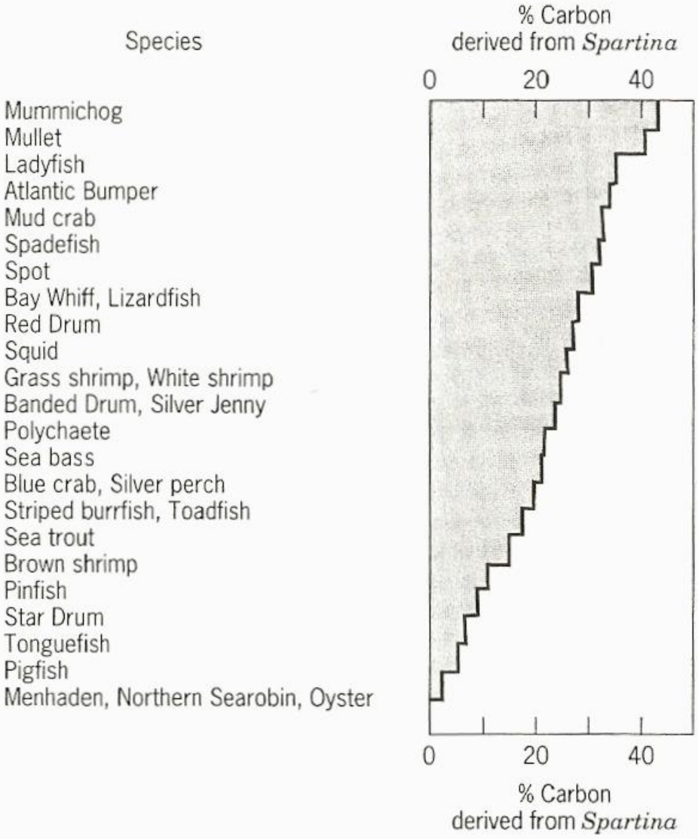

FIGURE 29.19. Percentage of carbon in several invertebrates and fish derived from *Spartina* as estimated from their $\delta^{13}C$. *Source*: From *Biogeochemical Processes at the Land–Sea Boundary*, K. H. Mann (eds.: P. Laserre and J. M. Martin), copyright © 1986 by Elsevier Science Publishers, Amsterdam, The Netherlands. Reprinted by permission. Data from E. H. Hughes and E. B. Scherr, reprinted with permission from the *Journal of Experimental Marine Biology and Ecology*, vol. 67, p. 239, copyright © 1983 by Elsevier Science Publishers, Amsterdam, The Netherlands.

be fossilized remains of stromatolites. Thus life appears to have evolved very early in this planet's history.

The Nitrogen Isotopes

The ranges in $\delta^{15}N$ of some naturally occurring substances are given in Figure 29.22. As with carbon, the marine chemistry of nitrogen is largely controlled by biological processes, many of which are accompanied by kinetic fractionations. The most notable exception to this is nitrogen fixation. As a result, the biomass of nitrogen fixers has a $\delta^{15}N$ value close to that of its metabolic substrate, atmospheric N_2 (0‰). As shown in Figure 29.23, nitrogen-fixing plankton are readily identifiable by their unique isotopic composition (Group III). Their metabolism is favored only under conditions of extreme nitrogen limitation, which accounts for their presence only in waters with low DIN concentrations.

Phytoplankton living in waters with higher DIN concentrations are able to achieve some kinetic fractionation during nutrient assimilation. As a result

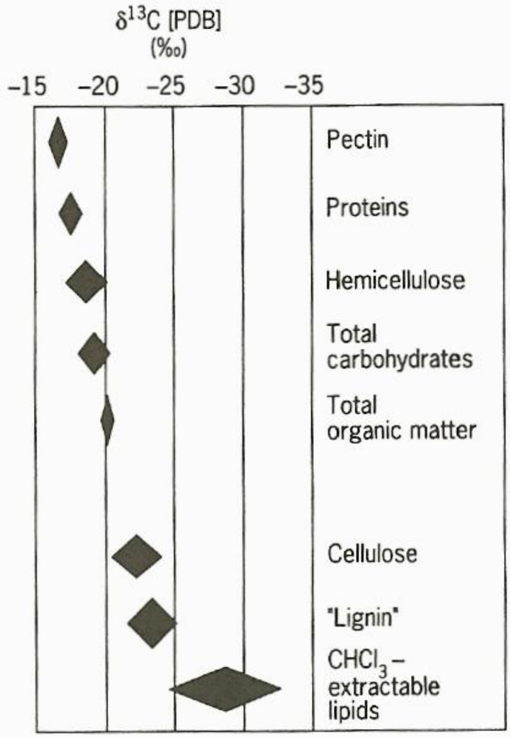

FIGURE 29.20. $\delta^{13}C$ [PDB] in various biochemical constituents isolated from marine phytoplankton. *Source*: From *Stable Isotope Geochemistry*, J. Hoefs, copyright © 1980 by Springer-Verlag, Heidelberg, Germany, p. 129. Reprinted by permission. Data from E. T. Degens, M. Behrendt, G. Gotthardt, and E. Reppmann, reprinted with permission from *Deep-Sea Research*, vol. 15, p. 14, copyright © 1968 by Pergamon Press, Elmsford, NY.

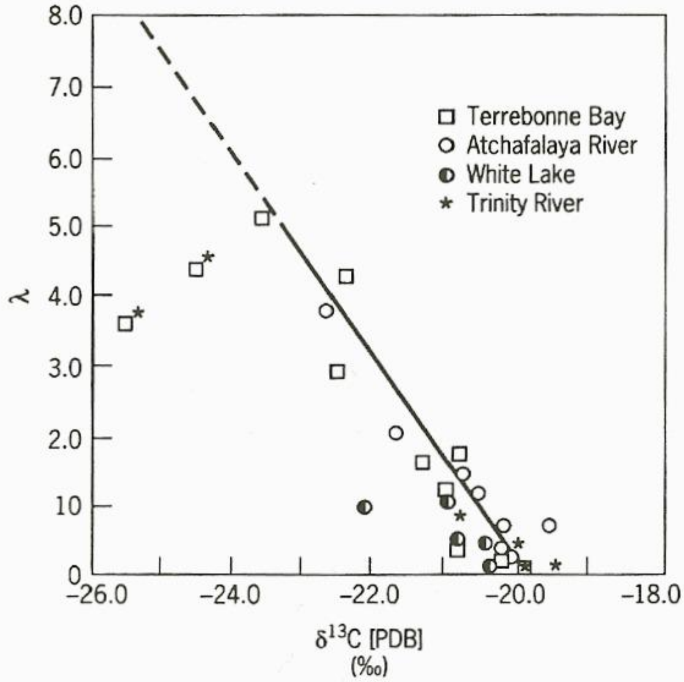

FIGURE 29.21. $\delta^{13}C$ [PDB] versus λ in coastal sediments. λ is the total weight in milligrams of two acidic phenols (vanillyl and syringyl) that are produced from the oxidation of 100 mg of sedimentary organic carbon. Since these phenols (Figure 23.14*b*) are ubiquitous and unique constituents of lignin, they are source tracers for the presence of terrestrial organic matter in marine sediments. *Source*: From J. I. Hedges and P. L. Parker, reprinted with permission from *Geochimica et Cosmochimica Acta*, vol. 40, p. 1026, copyright © 1976 by Pergamon Press, Elmsford, NY.