framework that relates the presence of particular trace fossils, and the general extent of bioturbation, to the amount of oxygen available in sea-floor sediments (Figure 9.23a).

Sediments in which there was little or no oxygen are characterized by the preservation of fine-scale horizontal features of primary bedding, known as laminations. With increasing levels of oxygenation, a more complex bottom fauna burrows through the sea floor (see Figure 1.20), obliterating laminations and generating a diverse set of trace fossils. This framework has been shown to be applicable broadly to the geological record (e.g., Figure 9.23b) and has been useful for recognizing fine-scale transitions in oxygenation levels, both stratigraphically and geographically.

$\delta^{18}O$ and the Mg/Ca Ratio

Beyond the characterization of the ecological properties of the taxa preserved within a fossil assemblage, paleontologists are now making use of a sophisticated set of geochemical techniques that evaluate directly the isotopic properties of growth increments, or bands, preserved in the hard parts of many organisms. While these analyses are, of course, limited to the subset of preserved hard parts that have not been altered chemically after the death of the organism, the temporal resolution of the paleoenvironmental transitions diagnosed with these procedures is unmatched by any other paleontological method.

In many instances, it is possible to analyze samples collected with a microscopic coring device, within and across the annual growth increments of an organism. There can be environmental and geographic variation among the individuals of a species in the yearly emplacement of the "lighter" and "darker" bands that make up an annual increment in many organisms (Figure 9.24a). However, the geochemical transitions measured across these bands are often unmistakable.

We have already seen an illustration of the utility of oxygen isotopic techniques in Chapter 2, in the analysis of heterochrony in the Jurassic oyster *Gryphaea* [SEE SECTION 2.3]. This analysis depended on the ability of

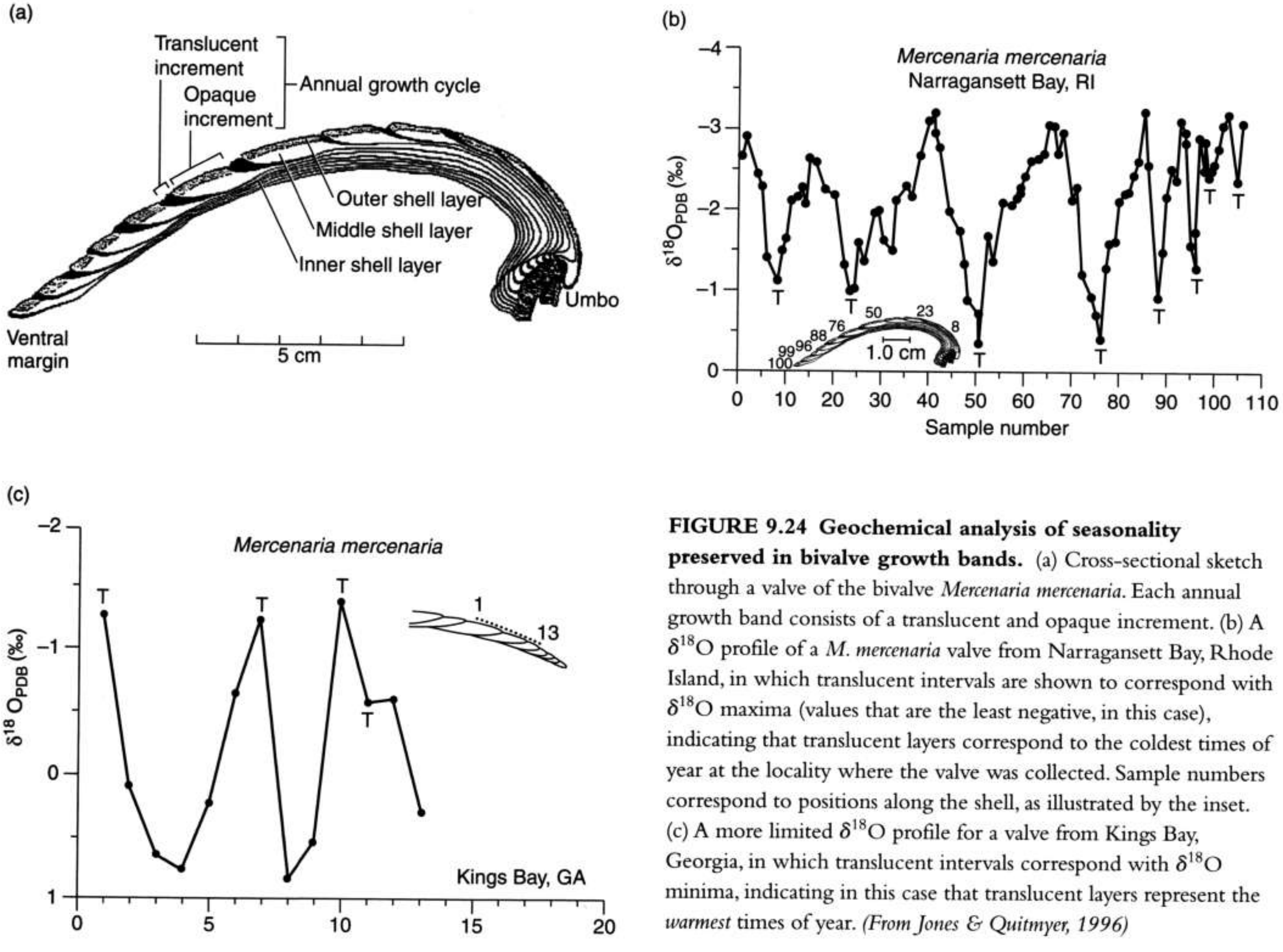

FIGURE 9.24 Geochemical analysis of seasonality preserved in bivalve growth bands. (a) Cross-sectional sketch through a valve of the bivalve *Mercenaria mercenaria*. Each annual growth band consists of a translucent and opaque increment. (b) A $\delta^{18}O$ profile of a *M. mercenaria* valve from Narragansett Bay, Rhode Island, in which translucent intervals are shown to correspond with $\delta^{18}O$ maxima (values that are the least negative, in this case), indicating that translucent layers correspond to the coldest times of year at the locality where the valve was collected. Sample numbers correspond to positions along the shell, as illustrated by the inset. (c) A more limited $\delta^{18}O$ profile for a valve from Kings Bay, Georgia, in which translucent intervals correspond with $\delta^{18}O$ minima, indicating in this case that translucent layers represent the *warmest* times of year. *(From Jones & Quitmyer, 1996)*

paleontologists to recognize seasonal and annual growth increments based on variations in the relative concentrations of two naturally occurring isotopes of oxygen, ^{16}O and ^{18}O, which can be measured with an instrument known as a mass spectrometer. Although the concentrations of these two isotopes in skeletal material may be affected by several factors, there is a measurable association of the ratio of these two isotopes with the temperature in surrounding waters at the time of skeletal accretion.

Isotopic ratios are generally reported in terms of their deviations from standard substances, in parts per thousand (‰), as defined in the following equation:

$$\delta X = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 10^3$$

where δX is the enrichment (if positive) or depletion (if negative) of any high-mass isotope X (e.g., ^{18}O, in comparisons of ^{18}O and ^{16}O), and R is the high-mass to low-mass isotopic concentration ratio. Standard substances with which samples are compared in oxygen isotopic assessments include a belemnite cephalopod collected from the Upper Cretaceous Peedee Formation of the eastern United States (PDB) and present-day standard mean ocean water (SMOW).

Equations have been developed empirically for calcitic and aragonitic material that enable a researcher to estimate changes in the ambient temperature of a marine setting based on the δ^{18}O value determined for the sample. In a relative sense, a higher value for δ^{18}O (i.e., enrichment in ^{18}O relative to ^{16}O) corresponds to a lower temperature at the time of skeletal accretion. As an example, the annual record of oxygen isotopic variation can be observed in a specimen of a Recent bivalve, *Mercenaria mercenaria*, collected from Narragansett Bay, Rhode Island, as illustrated in Figure 9.24b. Here, translucent (dark) increments correspond dependably to colder portions of the year, as evidenced by the enrichment in ^{18}O associated with these increments. Elsewhere, however, translucent increments have been shown to correspond to the warmest portions of the year (see Figure 9.24c), suggesting that paleontologists should be cautious in assessing the significance of light and dark banding. Nevertheless, the oxygen isotopic pattern appears to record faithfully the temperature profile on an annual basis, regardless of timing during the year of light and dark increments.

The utility of oxygen isotope profiles for assessing seasonality can be seen further in the example illustrated in Figure 9.25, which records δ^{18}O and temperature profiles based on the microsampling of successive growth bands of fish otoliths (ear stones) collected at localities spanning the Eocene–Oligocene boundary in the Gulf Coast region of the United States. A comparison by Linda Ivany and colleagues (2000) of otolith profiles for Eocene versus Oligocene specimens suggests that, while there was little change in summer temperatures across the boundary, there appears to have been a significant decrease in winter temperatures, indicating an overall increase in seasonality. It remains to be determined whether this apparent paleoclimatic change was associated with a major extinction that took place at that time, but the coincidence is intriguing.

Geologists are now making routine use of isotopic analyses in the study of ancient environments. Among the other isotopic suites that are of particular importance to paleontologists are the ^{13}C/^{12}C suite, which is useful for diagnosing the presence of photosynthetic activity [SEE SECTION 10.5], and the ^{34}S/^{32}S suite, which provides an indication of the degree of oxygenation.

The use of δ^{18}O as a paleo-thermometer is not limited to assessment of temperature variations recorded in the growth bands of individual skeletons or skeletal elements. It can also be used to diagnose an extended record of temperature change in a region based on intraspecific stratigraphic variations in the average isotopic compositions of samples of skeletal elements. Researchers typically assess δ^{18}O trends for more than one species because different species sometimes exhibit different stratigraphic δ^{18}O trends through the same interval. As we will see in Chapter 10 [SECTION 10.4], the demonstration of a similar stratigraphic pattern among several species provides compelling evidence that the pattern transcends taxonomic bias.

Complications in the interpretation of δ^{18}O trends can arise for other reasons, including variations through time in the volume of ice occurring on the earth. Because ^{16}O is lighter than ^{18}O, water molecules containing ^{16}O evaporate more readily than those containing ^{18}O, and it follows that ^{16}O will occur preferentially in the precipitation derived from evaporated water. Given that the growth of glaciers depends on the water supplied by this ^{16}O-enriched precipitation, it stands to reason that ^{16}O will be sequestered preferentially in glacial ice, thereby causing a global enrichment in ^{18}O in sea water (i.e., increased δ^{18}O) during intervals of increased glaciation. Of course, we would expect the earth to be cooler globally during an interval of glacial advance, and this cooling might be reflected in a positive excursion in δ^{18}O at a given locality. However, it is possi-

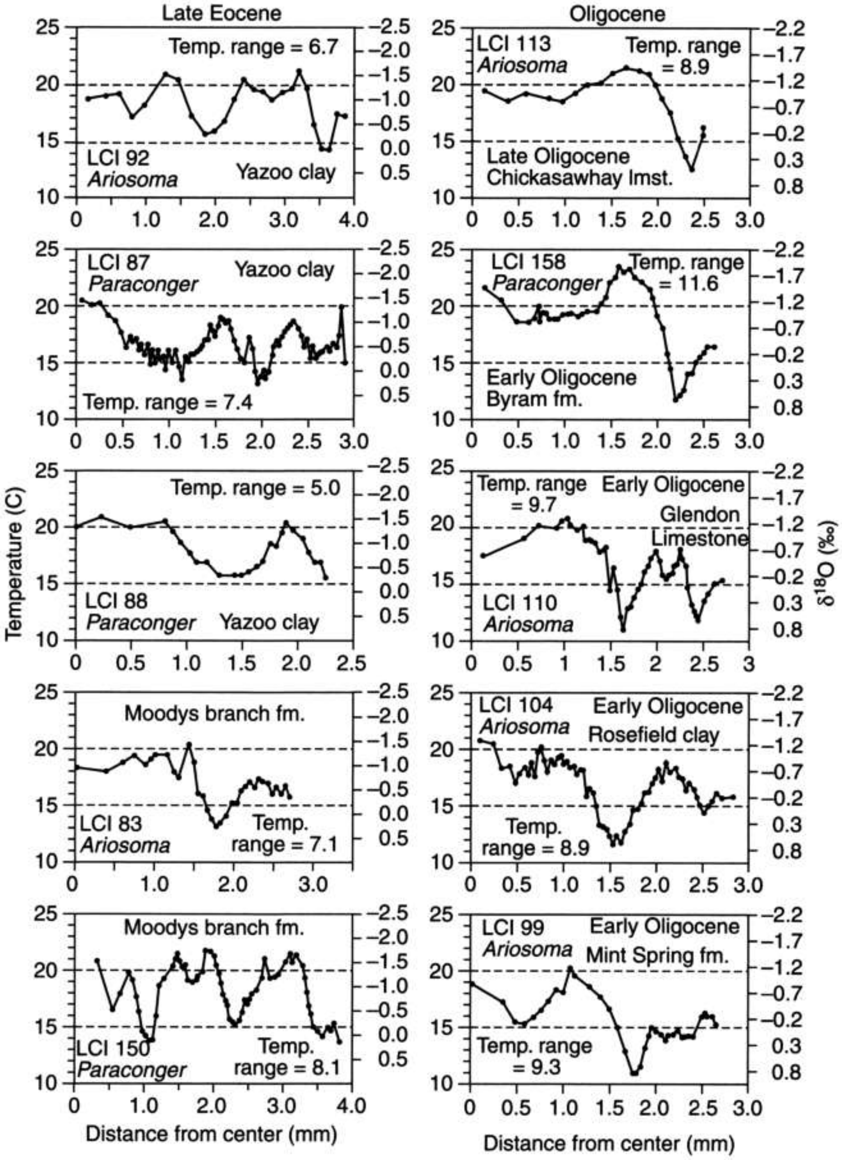

FIGURE 9.25 Temperature records, based on $\delta^{18}O$ profiles from microsampling of several Late Eocene and Oligocene fish otoliths. Note the tendency of Oligocene profiles to exhibit greater amplitudes, primarily because of colder temperatures during the winter. Summer temperatures remained fairly constant from the Late Eocene into the Oligocene. *(From Ivany et al., 2000)*

ble that excursions related to changes in ice volume will overwhelm patterns that would otherwise reflect local or regional temperature variations that did not parallel the advance or retreat of glaciers.

With this in mind, additional methods for estimating ancient temperatures have been developed that use other elements preserved in fossil skeletons. These should be viewed as supplements to assessments based on $\delta^{18}O$. One of the more promising of these approaches uses the ratio of magnesium to calcium (Mg/Ca) preserved in the skeletons of foraminifera. While not entirely free of its own complications, a strong empirical association with temperature has been recognized in the Mg/Ca ratios of several present-day benthic foraminiferal species. In general, the Mg/Ca ratio preserved in benthic foraminifera increases exponentially with increased temperature (Figure 9.26); temperature changes through time can therefore be diagnosed by this alternative means.