CHAPTER EIGHTEEN

The Use of Oxygen and Carbon Isotopes of Foraminifera in Paleoceanography

Ana Christina Ravelo* *and* Claude Hillaire-Marcel

Contents

1. Introduction

Oxygen and carbon isotopes of foramininfera have been used in paleoceanography studies for decades. Urey (1947) laid the foundations for stable isotope geochemistry when he described and calculated the thermodynamic properties and fractionation of isotopes. Simultaneously, Alfred Nier (1947) developed mass spectrometry techniques allowing the measurement of minute differences in isotopic compositions between natural compounds. Urey's calculations and Nier's technological developments thus opened a large array of applications in stable isotopes geochemistry. Among these, and following McCrea's (1950) early work, Urey and his graduate students developed the use of oxygen isotope composition of calcite as a paleothermometer (Epstein, Buchsbaum, Lowenstam, & Urey, 1953; Urey, Epstein, Lowenstam, & McKinney, 1951). Cesare Emiliani, one of Urey's students, was the first to use oxygen isotope paleothermometry to reconstruct the glacial–interglacial swings in climate of the late Pleistocene using fossil foramininfera shells from deep-sea

* Corresponding author.

Developments in Marine Geology, Volume 1
ISSN 1572-5480, DOI 10.1016/S1572-5480(07)01023-8

sediments (Emiliani, 1955). Although he initially overestimated the glacial–interglacial temperature changes by not adequately taking into account the large changes in the oxygen isotopic composition of seawater, he was the first to use oxygen isotopic records in support of the Milankovitch theory (Emiliani & Geiss, 1959), and was responsible for the initial use of Marine Isotope Stages (MIS) (Emiliani, 1955).

In the early 1960s, major studies about isotope fractionation processes within the hydrological cycle were published by Craig (1961) and Dansgaard (1964). They led Shackleton (1967) to revise Emiliani's interpretation and to conclude that glacial/interglacial variations in foraminiferal oxygen isotope records were primarily influenced by changes in the oxygen isotopic composition of seawater, rather than temperature. In subsequent years, MIS finally emerged as a basic stratigraphic tool (Shackleton & Opdyke, 1973). Thus, the work of Urey, his students, Shackleton and others, developed fundamental concepts that launched the field of paleoceanography, and for the last 50 yr or so, measuring the oxygen and carbon isotopic composition of fossil foraminiferal calcite has been one of the most effective techniques for reconstructing ocean and climate conditions of past times.

Over the last few decades, oxygen and carbon isotopic records derived from measurements of fossil foraminiferal shells have been used to address a large range of questions regarding the evolution and history of the ocean and climate. However, these discoveries were not possible without parallel studies aimed at understanding biological factors, or 'vital effects', that cause some species of foraminifera to calcify out of equilibrium with seawater. In addition, the species-specific ecology of planktonic and benthic foraminifera has been studied to understand how isotopic records might be interpreted in light of, for example, the seasonality and depth of calcification in the water column (for planktonic species) and in the sediment (for benthic species). Overviews of oxygen isotope paleothermometry techniques and the 'vital effects' and ecological factors that impact the oxygen and carbon isotopes of biogenic carbonates have been recently published (Hoefs, 2004; Rohling & Cooke, 1999; Sharp, 2006). As such, this chapter is not intended to be a comprehensive review of foraminiferal oxygen and carbon stable isotope biogeochemistry, rather it is intended to be a practical introduction to the factors that must be taken into account when interpreting paleoceanographic records derived from measurements of the oxygen and carbon isotopic composition of foraminifera.

2. Notation and Standards

The stable isotopes of oxygen used in paleoceanographic studies are ^{16}O and ^{18}O, which comprise 99.63 and 0.1995% of the oxygen on Earth, respectively (Faure, 1986). The stable isotopes of carbon are ^{12}C and ^{13}C, which comprise 98.89 and 1.11% of the stable carbon on Earth, respectively (Faure, 1986). Accurate quantification of low abundances of the rare isotopes (^{18}O and ^{13}C) is possible only as ratios to the more common isotopes ($^{18}O/^{16}O$ and $^{13}C/^{12}C$) in the sample,

as expressed in comparison with the ratios of a known standard. The difference in the ratio of the sample compared with the standard is expressed as a delta (δ) value:

$$\delta^{18}O = \frac{^{18}O/^{16}O_{sample} - ^{18}O/^{16}O_{standard}}{^{18}O/^{16}O_{standard}} \times 1000$$

$$\delta^{13}C = \frac{^{13}C/^{12}C_{sample} - ^{13}C/^{12}C_{standard}}{^{13}C/^{12}C_{standard}} \times 1000$$

The $\delta^{18}O$ and $\delta^{13}C$ values have concentration units of per thousand, or 'per mil' (‰) relative to the standard. For example, a $\delta^{18}O$ value of 1.0‰ means that the sample has an $^{18}O/^{16}O$ ratio that is 0.1% greater than the standard, or a $\delta^{13}C$ value of −25‰ means that the sample has a $^{13}C/^{12}C$ ratio that is 2.5% lower than that of the standard.

The first step in analyzing the carbon and oxygen isotopic composition of most substrates is to produce carbon dioxide (CO_2) gas that has no offset or a known isotopic offset, relative to the sample; this is done by various methods depending on the substrate. To determine the $\delta^{18}O$ and $\delta^{13}C$ values of foraminifera shells, the shells are dissolved at a given temperature in orthophosphoric acid (see Bowen, 1966; Burman, Gustafsson, Segl, & Schmitz, 2005) to produce CO_2. To determine the $\delta^{18}O$ of seawater, CO_2 gas is isotopically equilibrated with seawater at a constant temperature following the original procedure of Epstein and Mayeda (1953). To determine the $\delta^{13}C$ value of dissolved inorganic carbon (DIC) of seawater, CO_2 is stripped from the seawater by acidification (e.g., St-Jean, 2003). Once CO_2 is isolated, a gas-source stable isotope mass spectrometer with three collectors is typically used to ionize the CO_2 gas and to quantify the isotopic ratios ($^{18}O/^{16}O$ and $^{13}C/^{12}C$) of the sample CO_2 and of an aliquot of CO_2 reference gas. Until recently, variations of natural isotope abundances were usually measured using dual inlet mass spectrometers derived from the original design of Alfred Nier, allowing the introduction and comparison of, alternatively, a reference gas and the sample gas, in the mass spectrometer ionization chamber (i.e., source). Recent improvements in mass spectrometers now allow similar measurements in continuous flow mode, using a carrier gas (helium) for CO_2 and introducing sequentially standard and sample gases. The $\delta^{18}O$ and $\delta^{13}C$ values can then be calculated.

Various standards are used in different laboratories, but all lab standards are calibrated to international reference standards. Originally, they were the "historical" PeeDee Belemnite (*Belemnitella americana*) shell from the Cretaceous PeeDee formation (PDB) and/or the Standard Mean Ocean Water (SMOW). The need for clarification arose in the 1990s, notably due to the exhaustion of the original PDB standard and because the definition of the "Standard Mean Ocean Water" was unclear. Coplen (1996) clarified guidelines to report isotopic compositions against standards of the *International Atomic Energy Agency* of Vienna, the VPDB and VSMOW (i.e., the "Vienna" PDB and SMOW). These guidelines are now largely adopted. Worthy of mention is the fact that most laboratories doing stable isotope studies on foraminifera also use the "Carrara Marble" standard as calibrated by

M. Hall (University of Cambridge) against VPDB ($\delta^{13}C = 2.25‰$; $\delta^{18}O = -1.27‰$). It should be noted that the reported carbon isotope composition of this "Carrara Marble" is slightly distinct from the value listed in IAEA documents for the Carrara Marble-C1 radiocarbon reference material ($\delta^{13}C = 2.42‰$).

All $\delta^{18}O$ and $\delta^{13}C$ values of carbonates, and all $\delta^{13}C$ values of dissolved inorganic carbon (DIC) of seawater are thus reported relative to VPDB, and all $\delta^{18}O$ values of water (snow, ice, rain, groundwater, seawater) are reported relative to VSMOW. Typically the analytical errors, or external precision, that are reported in the literature are based on the long term (month to year) reproducibility of a lab standard, and for calcite are approximately 0.05‰ for $\delta^{13}C$ and 0.08% for $\delta^{18}O$ (both $\pm 1\delta$), or slightly better.

3. Stratigraphic and Paleoecological Use of Foraminifera

The use of foraminiferal stable isotope data from deep-sea sediment studies requires minimum knowledge of both sediment-sample properties and analytical procedures. Due to benthic organism mobility, and given subsequent mixing of sediment, mixing of foraminiferal populations has differential impacts according to shell size (Bard, 2001) and sediment-sample thickness, for example. Mixing results in smoothed isotope records, adding to biases in peak-abundances for any given shell fluxes to the sea-floor (e.g., Guinasso & Shink, 1975), thus in the recording of isotopic "excursions" and shifts. The interpretation of foraminiferal isotopic data has thus intrinsic limitations in terms of temporal resolution, absolute timing, and sensitivity. Unfortunately, mixing is not a constant function, as briefly explained in Chapter 6, and foraminiferal fluxes also vary in time, thus making this caveat even more critical.

Any gradual change of isotopic composition observed in a given core where some "bioturbation" of the sediment has occurred can thus be interpreted either as the reflection of gradual changes in paleoenvironmental conditions, or as a smoothing effect through a sharp transition resulting from a rapid paleoenvironmental shift. In such situations, comparative measurements of single-shells from each sediment sample may provide a better insight into the modal distribution of isotopic compositions. Thomas, Zachos, Bralower, Thomas, and Bohaty (2002) used this approach to document a paleoclimate event in the Early Eocene. Improvements in analytical techniques notably with respect to sample size, means this approach can be used to examine critical isotopic transitions.

Another critical aspect when analyzing foraminiferal populations concerns the size dependence of isotopic compositions, notably in planktic foraminifers, a feature that was recognized long ago (see examples in Berger, Be, & Vincent, 1981 and Section 4.2, below). The usual procedure to obtain isotopic records thus consists of making isotopic measurements on specimens of a given size range (e.g., 150–250 μm for most planktic foraminifera). However, this size-selection may also result in paleoecologically biased reconstruction when large interannual and/or seasonal

variability in hydrographic conditions and primary productivity have been responsible for variable growth rates and variable size distributions of shells of a given species or morphotype. Size-selection may then results in records biased towards optimum environmental conditions and the smoothing out of departures from such conditions.

Recent progress in the genetics of foraminiferal populations has shed new light on some of the aforementioned problems, but they have also shown that some genera could present morphological convergences between species or sub-species with drastically distinct ecological requirements, thus leading to potential biases in isotopic records if samples composed of a mixed assemblage of foraminifera are used for isotopic analyses. A morphotype commonly referred to as *Neogloboquadrina pachyderma* dextral (Npd) constitutes an example. Np is the most common species in sub-Arctic basins and the only planktic foraminifer present at very high latitudes. The left-coiled morphotype of this species (Npl) seems to represent a relatively homogeneous genetic population, whereas Npd may either correspond to a small percentage of specimens with true Np affinities, or to what Darling, Kucera, Kroon, and Wade (2006) identify now as a distinct species (*N. incompta*). This later taxon has ecological requirements and isotopic compositions not unlike those of the more temperate species *Globigerina bulloides* (e.g., de Vernal & Hillaire-Marcel, ~~in press~~). However, the dextral form of Np *stricto sensu* has isotopic compositions and likely ecological behaviors like those of Npl (e.g., Hillaire-Marcel, de Vernal, Polyak, & Darby, 2004).

Benthic foraminifers are less sensitive to most of the limitations discussed above, but they also require some analytical precautions. Most species show a well-developed ^{13}C-depleted organic lining. This requires an analytical pretreatment prior to CO_2 extraction with orthophosphoric acid to avoid contamination of the calcite-derived CO_2 by the isotopically light CO_2 from the lining. Pretreatment typically involves heating the sample for one to one and a half hours, in a furnace set at 250–300°C, under a flux of helium or under vacuum. As a matter of fact, the relative abundance of benthic foraminiferal linings vs. shells, in the sediment, can provide an index for quantifying carbonate dissolution (de Vernal, Bilodeau, Hillaire-Marcel, & Kassou, 1992) and thus for discarding isotopic records potentially biased by selective dissolution of lighter shells.

Within the above intrinsic limitations, the oxygen isotope composition of foraminiferal calcite is linked to environmental conditions through the so-called "paleotemperature equation" that represents a second order polynomial approximation of the thermodependent fractionation factor between calcite and water in the following (simplified) isotopic equilibrium:

$$1/3CaC^{16}O_3 + H_2^{18}O \rightarrow 1/3CaC^{18}O_3 + H_2^{16}O$$

Actually, isotopic exchanges between water and calcite occur through DIC species, and the final contribution of CO_3^{2-} or HCO_3^- ions to the calcite of the shell can be responsible of significant departures from the theoretical equilibrium, as discussed in Section 4.2 below. Many scientists working with foraminiferal calcite still use the 1953 equation of Epstein et al., slightly modified by Shackleton (1974), using notably experimental data from O'Neil that provide better constrains in the

low temperature domain ($<10^{\circ}$C) lacking in the original Epstein and others' dataset:

$$t = 16.9 - 4.38\,(\delta_c - A) + 0.10\,(\delta_c - A)^2$$
$$A = \delta_w - 0.27\%$$

where t represents the temperature (in $^{\circ}$C), δ_c and δ_w, the isotopic composition in δ-units (i.e., ‰ deviation of $^{18}O/^{16}O$ ratio vs. standard value) of, respectively, calcite (measured against VPDB), and ambient water (measured against VSMOW). The offset value of -0.27‰ allows for conversion to the VPDB scale after Coplen (1988). This equation is valid for calcite precipitation in seawater with near-normal salinity (as well as in freshwater), but may require adjustments in high salinity environments, where the oxygen-content of DIC species cannot be considered negligible with respect to that of ambient water. This somewhat complicated expression of the "classical" paleotemperature equation, linking oxygen compositions of biogenic calcite to that of its ambient water, is directly inherited from historical analytical procedures for $\delta^{18}O-CO_2$ and $\delta^{18}O-H_2O$ measurements developed in the 1950s by Urey and his students. Later on, several authors tried to better document the carbonate–water paleotemperature equation based on experimental growth of foraminifera shells (Erez & Luz, 1983; Bemis et al., 1988). These equations have small offsets but generally provide clustered slopes with $d\delta/dt$ relationships ranging from -0.21 to -0.23‰/$^{\circ}$C within the foraminiferal growth temperature domain.

Whatever its mathematical expression, the "paleotemperature equation" thus links the isotopic composition of calcite to temperature during calcite precipitation, and to the isotopic composition of ambient water. The latter depends in turn on a large array of variables, salinity being indirectly a primary one. In subsequent sections we will examine to what extent these environmental parameters can be quantitatively reconstructed from foraminiferal isotopic compositions.

4. Foraminiferal Oxygen Isotopes as Environmental Proxies

As discussed in the above section, the oxygen isotopic composition of a foraminifera shell reflects the oxygen isotopic composition of the seawater in which the shell calcifies, but the offset of the $\delta^{18}O$ of a foraminiferal shell from the $\delta^{18}O$ of seawater also depends on temperature assuming thermodynamic isotopic equilibrium between seawater and calcite (Figure 1). In the temperature range of biogenic calcite precipitation (i.e., $\sim$40 to -2°C), calcite is enriched in ^{18}O by 30–35‰, in comparison with ambient water, when both compositions are expressed against the same standard reference value. Within the same temperature range, the expression $(\delta_c - A)$ in the paleotemperature equation which is not much different from $(\delta_c - \delta_w)$ with δ_c and δ_w expressed against VPDB and VSMOW, respectively, varies between $\sim$0 and +5‰.

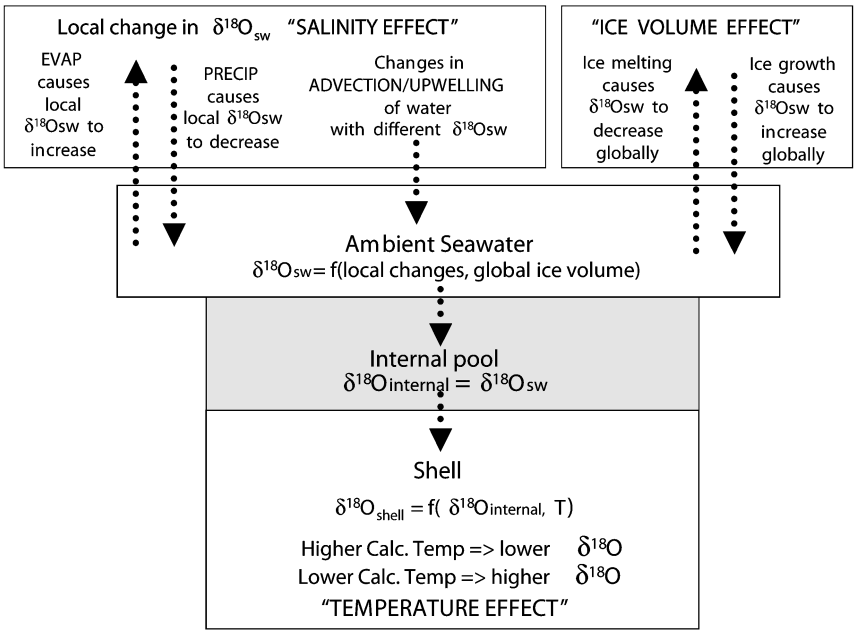

Figure 1 **Environmental factors that influence the δ^{18}O of foraminifera shells. This schematic assumes that thermodynamic equilibrium fractionation occurs, and does not depict potential vital effects.**

Many species produce shells that are in oxygen isotopic equilibrium with seawater, however some do not notably because of biological 'vital' effects. This section includes discussions of how downcore foraminiferal δ^{18}O records are used, in light of such effects, to record changes in the δ^{18}O of seawater and changes in the temperature of calcification.

4.1. Factors that Influence the δ^{18}O of Seawater

The δ^{18}O of seawater can vary with time due to several different processes, some which influence the δ^{18}O of the global ocean, and some which influence the local δ^{18}O of seawater. The δ^{18}O of the global ocean is primarily influenced by changes in the amount of water stored as ice on land which influences the δ^{18}O of the global ocean on the timescale of the mixing time of the ocean (millennium) (Shackleton, 1967), and by changes in temperature-dependent isotopic exchange with the oceanic crust (Gregory & Taylor, 1981; Muehlenbachs & Clayton, 1976) on the timescale that hydrothermal fluxes influence ocean chemistry (hundreds of millions of years). For the purposes of understanding late Cenozoic climate change, paleoceanographers typically focus on ice volume as the dominant factor influencing the δ^{18}O of the global ocean. Due to differences in vapor pressure, $H_2^{16}O$ evaporates more readily than $H_2^{18}O$, and therefore, the δ^{18}O value of water vapor, cloud droplets, and precipitation are low compared with that of seawater. Because

$H_2^{18}O$ condenses more readily than $H_2^{16}O$, as water is removed from clouds through precipitation, the remaining cloud water vapor becomes increasingly depleted in ^{18}O with increasing latitude and altitude, and decreasing temperature, in a Rayleigh distillation process. Thus, high latitude cloud water vapor and therefore snowfall derived from those clouds, is strongly depleted in ^{18}O, and therefore ice sheets are a reservoir of water with low $\delta^{18}O$ values, in the range of -30 to -50‰ (e.g., IAEA, 2000).

During glacial periods, when low $\delta^{18}O$ water is stored in ice sheets, the mean $\delta^{18}O$ value of the world's oceans was relatively high. For example, in the most recent glacial period ~21 ka ago, or the Last Glacial Maximum (LGM), the average $\delta^{18}O$ of the global ocean was ~1.1‰ higher than today (Adkins, McIntyre, & Schrag, 2002). Sea level during the LGM was at least 120 m below present day sea level (Fairbanks, 1989), and thus a rough estimate for the change in the average $\delta^{18}O$ of the global ocean due to glaciation is: 0.09‰/−10 m of sea level.

However, for any other time period, the precise relationship would depend on the average $\delta^{18}O$ of the ice sheets during that time period (which is dependent on their geographical location and the climatic conditions when they formed).

Foraminiferal $\delta^{18}O$ records do not only reflect changes in global ice volume, but they also reflect changes in the $\delta^{18}O$ of seawater due to local processes. As discussed above, $H_2^{16}O$ evaporates more readily than $H_2^{18}O$, and $\delta^{18}O$ values of precipitation are low compared with that of seawater. Consequently, evaporation causes surface water salinity and $\delta^{18}O$ values to increase, and precipitation causes surface water salinity and $\delta^{18}O$ values to decrease. Because salinity and $\delta^{18}O$ are both influenced by the balance of evaporation relative to precipitation, they are highly correlated in the surface ocean with higher values at low latitudes and lower values at high latitudes. Building on a dataset from the GEOSECS expedition, analyzed by Harmon Craig, LeGrande, and Schmidt (2006) and Schmidt, Bigg, and Rohling (1999) provided a larger $\delta^{18}O$ database with which to assess the distribution of $\delta^{18}O$ throughout the modern ocean (Figure 2). Taking into account the global distribution of surface water salinity and $\delta^{18}O$, the relationship between geographical variations in $\delta^{18}O$ and salinity is roughly: 0.5‰/1.0 psu. This relationship is approximately what is expected due to Rayleigh distillation processes, with high-latitude surface water being influenced by excess precipitation that has low values, and low-latitudes being dominated by excess evaporation which causes relatively high $\delta^{18}O$ values of surface water. However, regional relationships of $\delta^{18}O$ to salinity are dominated by the effects of mixing between regional precipitation (fresh water) and seawater, and as such, the slope of regional mixing lines deviate significantly from the global relationship given above. As a consequence, in tropical regions, where the $\delta^{18}O$ of rainfall is relatively high (0 to −10‰) the slope of the mixing line is less steep and the relationship between surface water $\delta^{18}O$ and salinity is less than the global average of 0.5‰/psu. For example in the eastern equatorial Atlantic, the western equatorial Atlantic, and the eastern equatorial Pacific, the relationship between $\delta^{18}O$ and salinity of surface water is only 0.08, 0.18, and 0.26‰/psu, respectively (Fairbanks, Charles, & Wright, 1992). As a result, the $\delta^{18}O$ values of tropical and sub-tropical surface water, away from coastal regions where rivers enter the ocean, are fairly uniform, ranging from ~0.9 to 1.2‰ in the tropical Atlantic, and ~0.2–0.5‰ in the tropical Pacific.

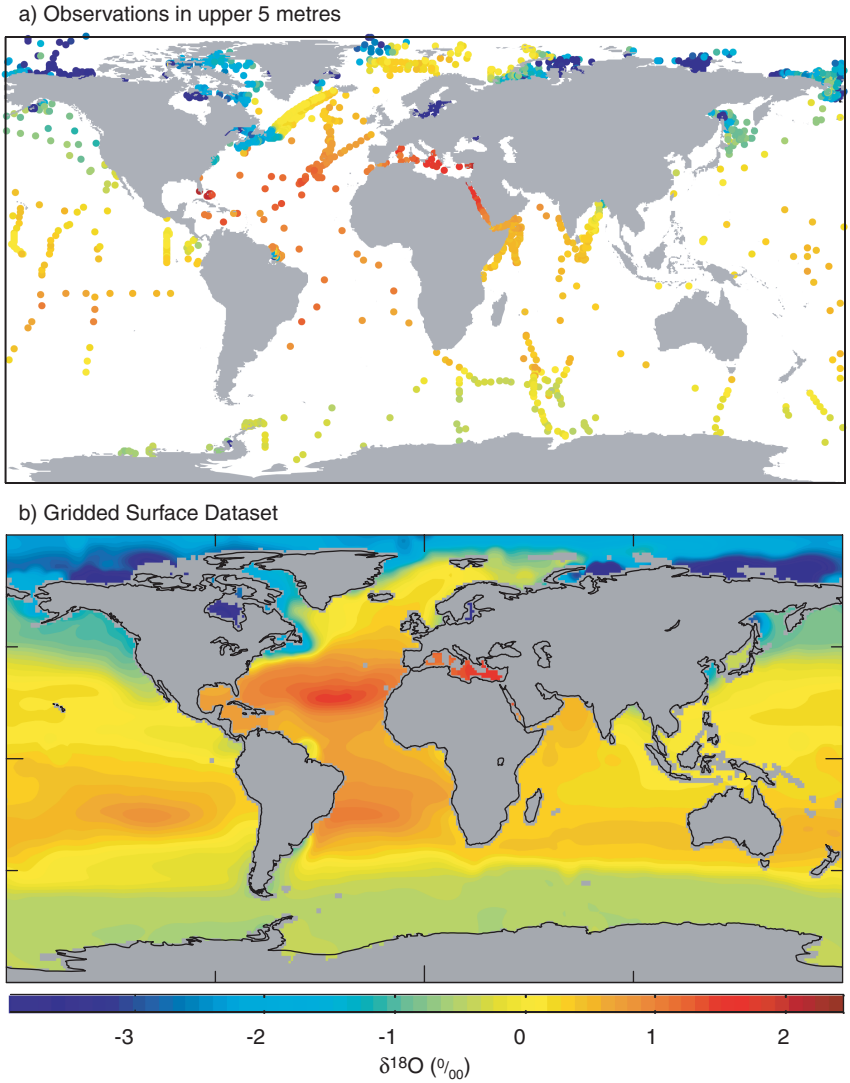

Figure 2 (a) All $\delta^{18}O$ measurements from the upper 5 meters of the water column (Schmidt et al., 1999) illustrates good data coverage in the Arctic and Atlantic Oceans, but very sparse data in areas such as the Pacific and Southern Oceans; (b) the 1 X 1 gridded data set of surface $\delta^{18}O$. Figure is from LeGrande and Schmidt (2006). Reproduced by permission of American Geophysical Union.

At high latitudes, where precipitation has relatively low values and falls directly on to the ocean surface or where large amounts of freshwater from Arctic rivers and snow and ice melt enters the ocean, the relationship between $\delta^{18}O$ and salinity of surface water is greater than 0.5‰/psu. The situation is slightly more complicated in the North Atlantic where water mass advection linked to the Atlantic Meridional Overturning component of the general thermohaline circulation tightly controls

the salinity relationships in the surface water layer. A strong longitudinal regionalism superimposes the latitudinal gradients (Figure 3) with $\delta^{18}O$ vs. salinity gradients that vary from 0.4‰/psu northeastward, under the influence of the evaporated waters of the North Atlantic Drift, to 0.6‰/psu, northwestward, where Arctic rivers constrain the freshwater end-member of the relationship ($\delta^{18}O$ ranging from ~−19 to −22‰ for most Arctic rivers, except the Ob that is slightly less ^{18}O-depleted; Cooper et al., 2005). As a matter of fact, Arctic surface waters significantly depart from simple mixing patterns between two end-members (Bédard, Hillaire-Marcel, & Pagé, 1981) (Figure 3). There, sea-ice growth from low salinity surface waters is responsible for the production of isotopically light brines that sink and mixes with the subsurface more saline North Atlantic Water mass. When sea-ice melts, it releases high $\delta^{18}O$-low salinity waters that mix with the surface layer resulting in a large scatter in $\delta^{18}O$ vs. salinity data (Figure 3).

Thus, in addition to the precipitation/evaporation balance, processes linked to sea-ice growth and melting as well as advection or upwelling of seawater can impact local $\delta^{18}O$ of surface water significantly. The influence of advection is clear for high latitude regions (Rohling & Bigg, 1998), but it is likely to be a less significant factor at low latitude in localities away from rivers and upwelling regions.

In sum, variations in the $\delta^{18}O$ of surface water at any one location reflects changes in the $\delta^{18}O$ of the global ocean due to changes in ice volume, changes in the local precipitation/evaporation balance, changes in the input of freshwater (if close to continental margins) through rivers or snow/ice melt which may reflect regional continental climate change, changes in contribution of advected or upwelled water with a different $\delta^{18}O$ value to that location and, at high latitudes, disturbances due to sea-ice growth and melting processes.

The $\delta^{18}O$ of seawater in the deep ocean reflects primarily the distribution of subsurface water masses. Like salinity, the $\delta^{18}O$ of subsurface water is basically conservative, and therefore the distribution of $\delta^{18}O$ in the deep ocean reflects water mass flow and mixing. The relationship between $\delta^{18}O$ and salinity in the deep ocean is different than that in the surface ocean mainly because the $\delta^{18}O$ values of deep Southern Ocean water are low relative to the $\delta^{18}O$ values of surface water of the same salinity (Figure 4). Around Antarctica, sea-ice formation also causes brine rejection increasing the salinity and density of the deep Southern Ocean Water. However, sea-ice formation only very slightly fractionates oxygen isotopes (Tan & Fraser, 1976; Tan & Strain, 1999), although on purely thermodynamics ground, ice should be ~3‰ enriched in ^{18}O vs. liquid water (O'Neil, 1968). Thus, brine rejection causes increased salinity, but practically no increase in $\delta^{18}O$ of surface water. As a result, deep Southern Ocean water has relatively low $\delta^{18}O$ values (–0.3‰) given its relatively high salinity (~34.7 psu). In regions where deep water forms, such as the North Atlantic, the $\delta^{18}O$ of deep water is relatively high (+0.3‰), as expected for water with relatively high salinity (~35.0 psu). In past times, changes in the circulation of deep water masses and/or in the contribution of brines to deep water masses, could have had an impact on the $\delta^{18}O$ values of deep water recorded at a single location (Adkins et al., 2002) (Figure 4). The implications are that the relationship between salinity and $\delta^{18}O$ of seawater is different in the deep ocean compared with the surface ocean, and that temporal variations in the

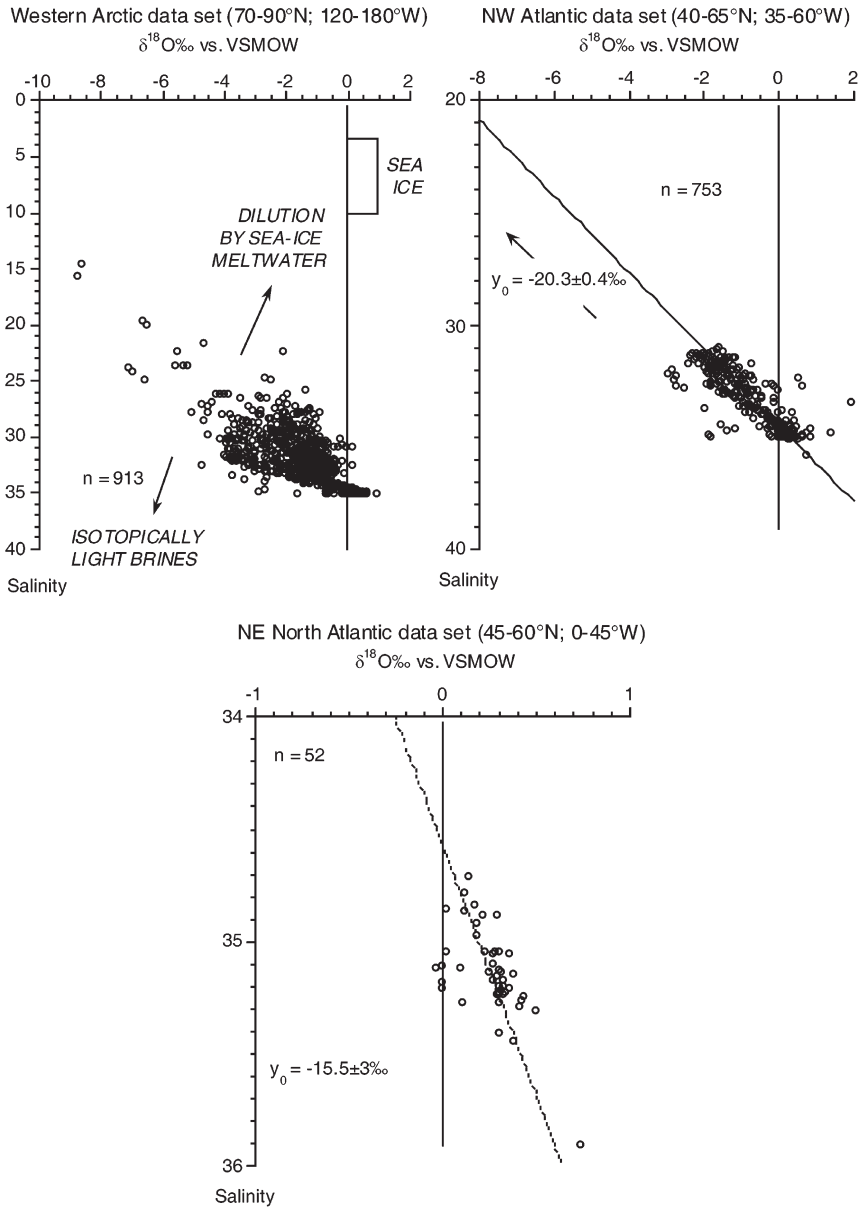

Figure 3 Salinity vs. $\delta^{18}O$–H_2O relationship in the Arctic vs. North Atlantic Oceans (surface layer: 0–500 m). The scatter of values, in the Arctic, illustrate processes linked to sea-ice growth and melting. In the North Atlantic, a strong contrast exists between the NW sector, where Arctic rivers constrain the $\delta^{18}O$ value of the freshwater end-member of the mixing system, and the NE sector, where the influence of mixing with evaporated waters dominates. Data from Schmidt et al. (1999).

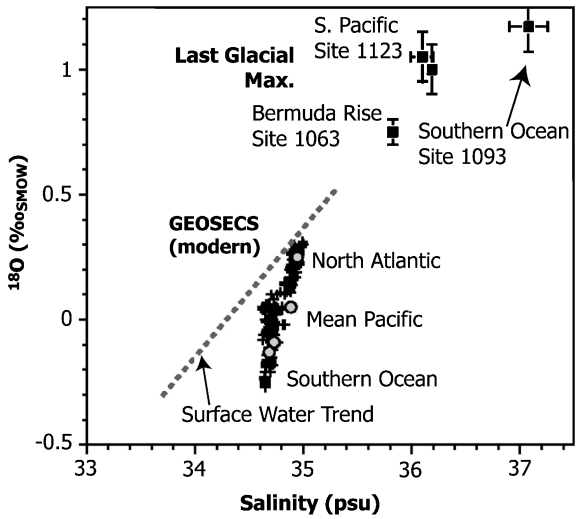

Figure 4 The $\delta^{18}O$ and salinity of deep-water masses from Adkins et al. (2002) deviates from the surface water relationship between $\delta^{18}O$ and salinity. The North Atlantic end-member has values close to the surface water line because it is derived from surface water in the North Atlantic. However, the Southern Ocean end-member has relatively high salinity because it is derived partially from sea-ice formation and brine rejection which enriches the salinity but not the ^{18}O. In the last glacial maximum, $\delta^{18}O$ and salinity of all water masses are enriched because fresh low $\delta^{18}O$ water was stored in ice sheets, however, the relationship between the deep-water masses was different, indicating that the signature of deep-water sources was different.

$\delta^{18}O$ of deep water in any one location reflect several indicators of climate change: global ice volume and changes in the $\delta^{18}O$ signatures and mixing of deep water masses.

A final caveat about $\delta^{18}O$-salinity relationships mostly concerns the North Atlantic and the Arctic. It relates to meltwater pulses and has been relatively well documented for the deglacial period (e.g., Flower, Hastings, Hill, & Quinn, 2004). Inland storage of water in the glacier and surrounding glacial lakes may result in the delayed release of ^{18}O-depleted freshwaters into the ocean at the occasion of major drainage events. This pattern may slightly bias the coupling of the $\delta^{18}O$ of the ocean to salinity and sea level changes.

4.2. Factors that Influence the $\delta^{18}O$ of Foraminifera

The interpretation of a foraminiferal $\delta^{18}O$ record must take into account all processes described above which alter the $\delta^{18}O$ value of seawater where the foraminifera calcifies its shell. In addition, the $\delta^{18}O$ of the shell is offset from the seawater $\delta^{18}O$ values because of the thermodynamic isotopic fractionation that occurs during calcite precipitation (Figure 1). In many species of foraminifera, the shell calcite is in oxygen isotopic equilibrium with seawater, and thus the isotopic separation factor between calcite and seawater ($\varepsilon \sim \delta^{18}O_{CaCO_3} - \delta^{18}O_{H_2O}$) is inversely related to calcification temperature (for equilibrium fractionation, the $\delta^{18}O$ of calcite

decreases by ~0.21–0.23‰ for a 1°C increase in temperature for a given $\delta^{18}OH_2O$). As such, if the $\delta^{18}O$ of seawater is known, foraminiferal calcite can be used as a paleothermometer to reconstruct past ocean temperature. Whatever the paleotemperature equation used (see Section 3 above), given the uncertainty in the $\delta^{18}O$ of seawater in the past and the lack of absolute precision on the temperature dependence of the $CaCO_3$–H_2O isotopic equilibrium in the low temperature range, it is most common to use the slopes of these equations to quantify relative changes in temperature after the potential influences of ice volume and local to regional impacts on the $\delta^{18}O$ of seawater are constrained.

While it is common to apply oxygen isotope paleotemperature equations, there is strong indication that foraminifera sometimes do not calcify in oxygen isotopic thermodynamic equilibrium with seawater notably because of biological 'vital' effects. Such effects were identified very early, notably by Duplessy, Lalou, and Vinot (1970). Some of these 'vital effects' seem to be related to the photosynthetic activity of algal symbionts. In contradiction to the explanation proposed by Duplessy et al. (1970), there is no firm evidence for the incorporation of low $\delta^{18}O$ metabolic CO_2 during calcite precipitation. Species that contain algal symbionts probably have higher calcification rates (through CO_2 consumption by algae), which induce a kinetic fractionation resulting in a 0.35–0.5‰ depletion in $\delta^{18}O$ of large (adult) shells relative to equilibrium values [see Ravelo & Fairbanks, 1992; Spero, 1992; Spero, Bijma, Lea, & Bemis, 1997; Spero & Lea, 1993, and references therein].

The fact that the $\delta^{18}O$ of a foraminifera shell changes with size in some species indicates that there are ontogenetic effects probably related to changes in the intensity of photosynthesis and/or changes in depth habitat as a foraminifera matures from juvenile to adult (Williams, Bé, & Fairbanks, 1979; Spero & Lea, 1996). The absence of size-dependent changes in $\delta^{18}O$ of calcite for many non-symbiont bearing species confirms the idea that changes in photosynthetic rates can drive some ontogenic effects (Ravelo & Fairbanks, 1995). However, in some cases, the $\delta^{18}O$ of calcite increases with shell size, even in non-symbiont bearing species, due to the addition of gametogenic calcite as the foraminifera sinks at the end of its lifecycle, as has been clearly documented for *Globorotalia truncatulinoides* (Lohmann, 1990).

The other factor that may influence the $\delta^{18}O$ of foramininfera is carbonate ion concentrations ($[CO_3^{2-}]$), which causes decreasing $\delta^{18}O$ of calcite with increasing $[CO_3^{2-}]$ (Spero et al., 1997). The $[CO_3^{2-}]$ may influence calcification rates and induce kinetic fractionation effects, with competitive incorporation of bicarbonate and dissolved carbonate ions in calcite. This could explain why even non-symbiont bearing planktonic and benthic foraminifera sometimes do not calcify in oxygen isotopic equilibrium with seawater (Bemis, Spero, Bjima, & Lea, 1998; Spero et al., 1997). However, the potential role of dissolved carbonate ions and pH on the isotopic composition of foraminiferal calcite is still controversial (Deines, 2005; Zeebe, 2005) and will require further examination.

Overall, there are documented effects of photosynthesis, $[CO_3^{2-}]$, and gametogenic calcification which influence the $\delta^{18}O$ of planktonic foramininfera causing slight $\delta^{18}O$ depletion in symbiont-bearing species, and $\delta^{18}O$ enrichment in species

that add a lot of gametogenic calcite in the subsurface. For benthic foraminifera, interspecies differences in $\delta^{18}O$ are probably due to the $[CO_3^{2-}]$ of the microenvironment, with the lower pH and $[CO_3^{2-}]$ of porewaters causing slight $\delta^{18}O$ enrichment in infaunal species (e.g., *Uvigerina* spp.) compared with epifaunal species (*Cibicidoides* spp.) which calcify in oxygen isotopic equilibrium with ambient water (Bemis et al., 1988). Once the potential biological and $[CO_3^{2-}]$ effects are accounted for, the paleotemperature estimates must be put into proper oceanographic context. For example, many planktonic foraminifera species have strong seasonal or depth habitat preferences (Figure 5), and the interpretation of $\delta^{18}O$ records must take into account these preferences (see Section 6).

In the above context, one specific feature of Arctic specimens of the planktic foraminifera *N. pachyderma* (*stricto sensu*), left as well as right-coiled (Npl and Npd), must be examined. As early as the sixties, Van Donk and Matthieu (1969) had noticed large departure from isotopic equilibrium with ambient Arctic waters in such shells. Later on, several authors further documented this offset (Kohfeld et al., 1996; Bauch et al., 1997; Hillaire-Marcel et al., 2004) which varies from –1 to –3‰ relative to equilibrium conditions for a calcite precipitated at mid-thermocline depth (Figure 6). Interestingly, despite this offset, the shells still present a size-dependence in their $\delta^{18}O$ values, but with a reverse trend, in comparison with their North Atlantic counterpart (Figure 7). Hillaire-Marcel et al. (2004) have interpreted this feature as a response to the reverse temperature gradient of the Arctic

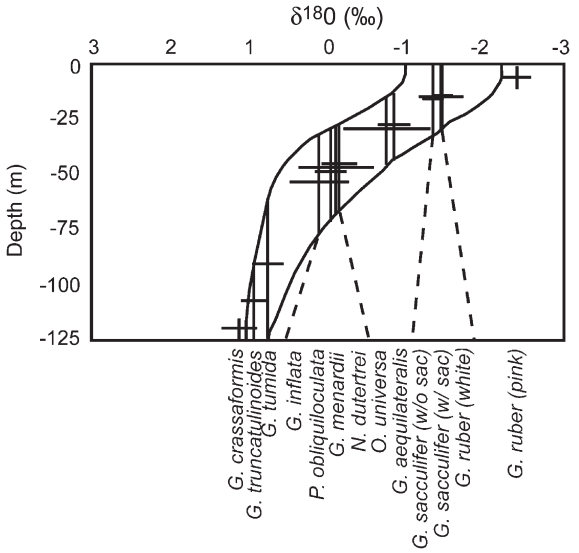

Figure 5 The $\delta^{18}O$ of tropical Atlantic species of foraminifera from a core top (V29-144) from Ravelo and Fairbanks (1992). The profiles are the envelope around the monthly predicted $\delta^{18}O$ of calcite profile predicted for the upper 125 m of the water column overlying the core top. Core top foraminifera values are plotted to overlap with the predicted profiles in order to infer calcification depth in the water column. The vertical lines are the average $\delta^{18}O$ values for each species, and the horizontal lines crossing each vertical line are the standard deviation of the measurements which are made on different size fractions.

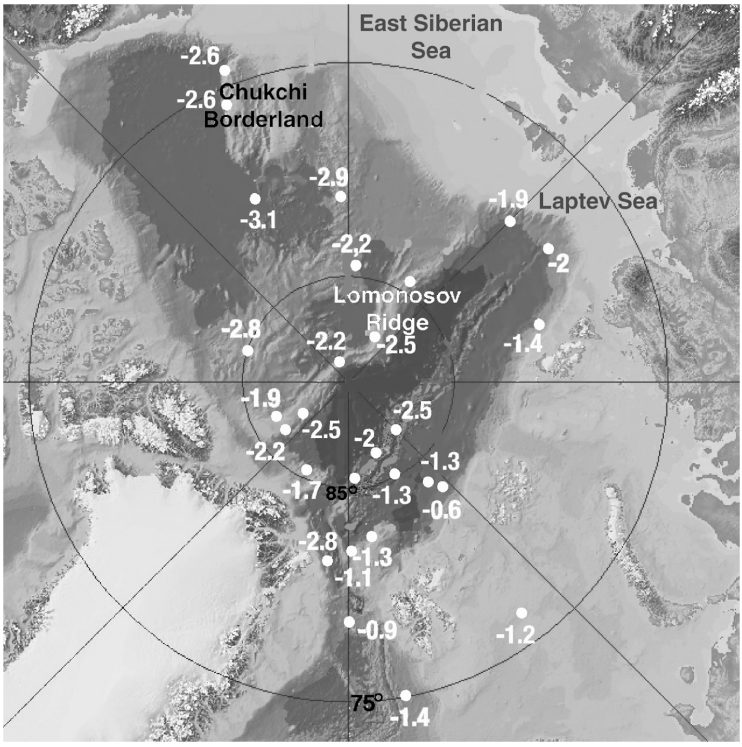

Figure 6 Compilation of isotopic offsets between foraminiferal (*N. pachyderma* left coiled – Npl) calcite δ^{18}O-values and equilibrium conditions for a calcite precipitated at mid-depth along the pycnocline between the surface cold and dilute water layer and the underlying North Atlantic Water (from literature; see refs. in Hillaire-Marcel et al., 2004). Npl populations are from surface sediment samples. These offsets are tentatively linked to the rate of production and accumulation of isotopically light brines along this pycnocline, due to sea-ice formation. Arctic topography from the GEBCO (1979) and IBCAO (2000) maps.

Ocean thermocline, where cold low salinity waters overly an intermediate more saline and warmer water mass originating from the North Atlantic. Due to the low salinity prevailing in the surface water layer, Npl cannot occupy this layer. It has been shown to occupy essentially the 35–36 psu domain with few questionable excursions below this minimum threshold (e.g., Hilbrecht, 1996). Thus Arctic Npl populations are restricted to the more saline (and slightly warmer) interface with the underlying North Atlantic subducted water that makes a large gyre into the Arctic Ocean, as an intermediate water mass. As a matter of fact, experiments by Spero and Lea (1996) on the more temperate species *G. bulloides*, have also shown that despite an overall offset with equilibrium conditions, isotopic shifts between shells were still preserving temperature differences.

With respect to the overall −1 to −3‰ isotopic offset in Arctic Npl shells, the temperature along the thermocline cannot be the cause. The only correlation that has been put forth by several authors is an apparent increase of this offset with the

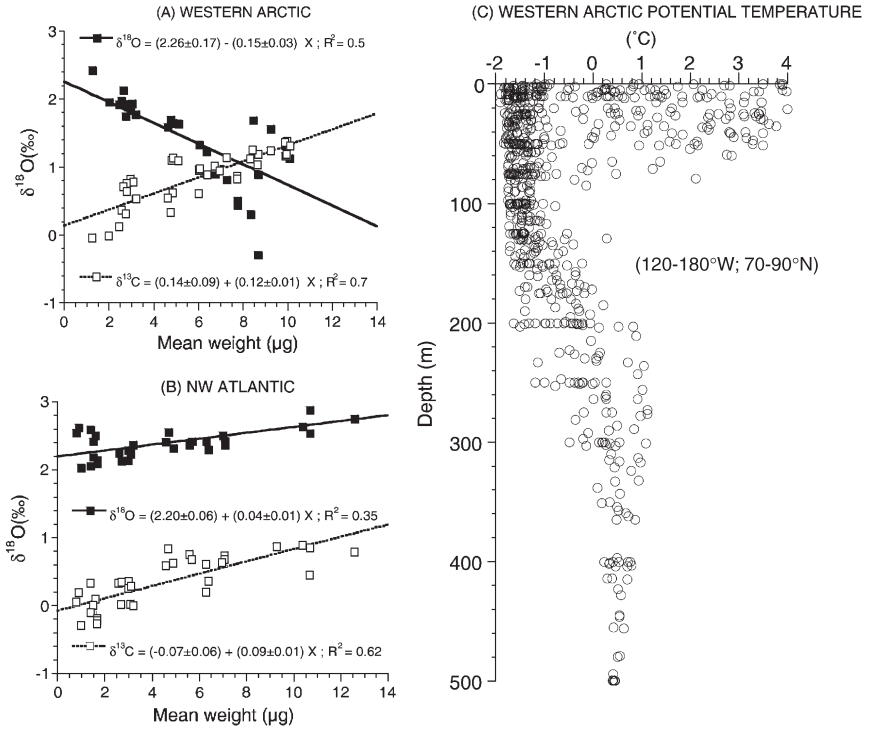

Figure 7 Example of size dependence of isotopic compositions in the deep-dwelling *N. pachyderma* left coiled (Npl) assemblages from Arctic (A) and North Atlantic (B) surface sediments interpreted as a consequence of Npl-calcite precipitation along the thermocline with either negative (North Atlantic) or positive (western Arctic) gradients within the underlying water mass (from Hillaire-Marcel et al., 2004). Note that in the Arctic Npl cannot develop in the very shallow dilute layer due to its low salinity (C). Data from Candon (2000).

duration/intensity of the sea-ice cover. From this viewpoint, Npl presents another peculiarity as well: its tolerance to very high salinity conditions. In brines linked to Antarctic sea-ice formation Spindler (1996) identified live specimens in water of up to 82 psu, and Npl growth in water with up to 58 psu. Given their tolerance to high salinity conditions and their growth at the top of the pycnocline above the underlying North Atlantic Water mass, Npl are likely to grow in high-salinity, low-$\delta^{18}O$ droplets (or thin layers) in regions where sinking isotopically depleted brines form in the Arctic (see Section 4.1 above). As such, the isotopic offset of Npl relative to equilibrium would indeed show some proportionality with the intensity of sea-ice (and brine) formation.

Whatever the cause for the modern behavior of Npl in Arctic environments, its abundance in the glacial North Atlantic Ocean, where it often represented most of planktic foraminifers, has led to intensive investigations. The interpretation of its isotopic composition changes, often linked to salinity changes in surface waters (e.g., Duplessy et al., 1992), is a challenge in view of all parameters that may account for its $\delta^{18}O$ values. In principle, salinity and temperature changes should be

the most important factors. Independent estimates of temperature, such as Mg/Ca ratios in Npl shells (see Chapter 19), could help to constrain surface salinity. Unfortunately, the fact that Npl lives in the low-temperature range of the Mg/Ca calibration curve results in equivocal interpretations as demonstrated by Meland et al. (2006).

Attempts at directly linking $\delta^{18}O$ values to potential density values (σ_θ), which also depends on salinity and temperature, have been made (e.g., Hillaire-Marcel, de Vernal, Bilodeau, & Stoner, 2001). Indeed, both δ and σ_θ expressions show analogies and are directly proportional to salinity and inversely proportional to temperature:

$$\delta = \left(\frac{R_i}{R_s} - 1\right) \times 10^3 \text{ and } \sigma_\theta = \left(\frac{\rho_i}{\rho_m} - 1\right) \times 10^3$$

where R_i and R_s stand for $^{18}O/^{16}O$ ratios in the shell and reference materiel, ρ_i and ρ_m, for the density of the ambient water and that of pure water (at the same temperature). The rationale is to obtain information on the density structure of the upper water column, at sites of the North Atlantic where deep convection may or may not occur. Unfortunately, this approach requires an independent calibration of the σ_θ vs. δ relationship. This relationship is nearly linear, at sites where salinity is the prominent parameter, and polynomial, where temperature also plays an important role. Thus, solving the basic "paleotemperature" equation remains largely an issue dependent on the site, on the time and the foraminiferal species considered. Some hopes are seen ahead, in the development of new isotopic measurement techniques. Recently, it has been shown that in addition to the measurements of CO_2 masses 44, 45, 46, representing various combinations of O and C isotopes, it is possible to measure mass 47 (proportional to ^{13}C–^{18}O bonds in carbonate minerals, a direct function of the temperature during crystal growth), thus providing an access to the equilibrium temperature, independent of changes in the $^{18}O/^{16}O$ of environmental water (Ghosh et al., 2006). The analytical precision achieved is still insufficient to consider immediate applications in paleoceanography, but there may be hope to improve it in near future.

5. Foraminiferal Carbon Isotopes as Environmental Proxies

The $\delta^{13}C$ of a foraminifera shell reflects the carbon isotopic composition of the DIC in seawater in which the shell calcified, but it is not in isotopic equilibrium with seawater. The main reason that it is not equilibrium is because biogenic calcification is relatively rapid, resulting in kinetic isotope fractionation, and because of strong biological 'vital' effects. Kinetic fractionation for C-isotopes does not imply similar effects for O-isotopes, since the "equilibrating" pools of oxygen from seawater is considerably larger than that of carbon. In addition, the $\delta^{13}C$ of DIC in seawater ($\delta^{13}C_{DIC}$) is not uniform throughout the world's ocean, nor is the average $\delta^{13}C_{DIC}$ of the ocean constant with time. Thus, paleoceanographic records

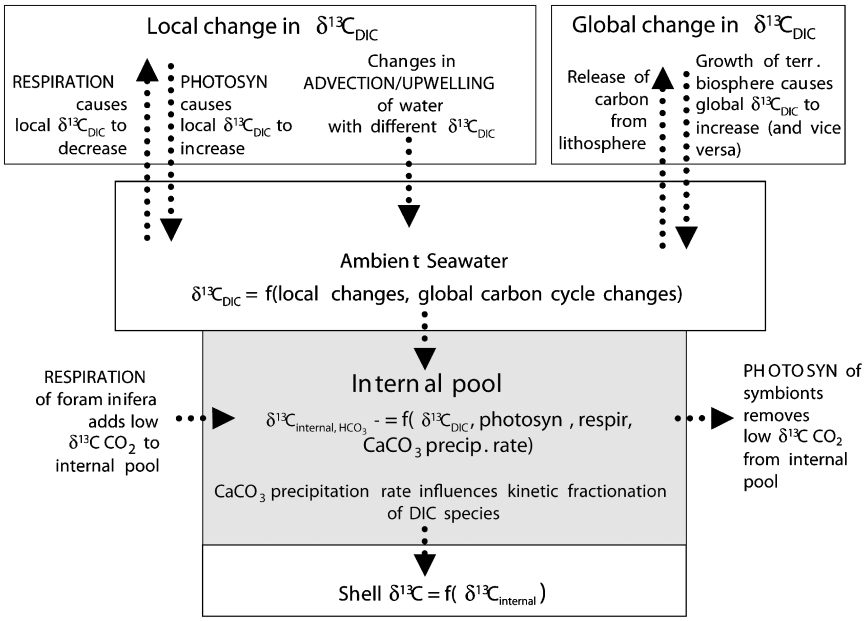

Figure 8 Factors that influence the $\delta^{13}C$ of foraminifera shells.

of foraminaferal $\delta^{13}C$ reflect multiple parameters (Figure 8). This section includes discussions of how downcore ~~foraminaferal~~ $\delta^{13}C$ records are used, in light of vital effects, to monitor changes in $\delta^{13}C_{DIC}$.

5.1. Factors that Influence the $\delta^{13}C$ of DIC of seawater

The average $\delta^{13}C_{DIC}$ of the whole ocean is influenced by the global carbon cycle, specifically the partitioning of carbon between the ocean, atmosphere, and terrestrial biosphere reservoirs. Because photosynthesis discriminates against ^{13}C and in favor of ^{12}C, the terrestrial biosphere (living vegetation and soil organic matter) is a reservoir of ^{13}C-depleted carbon (with a major mode of $\delta^{13}C$ values of around −25‰ due to the photosynthetic cycle of C3-plants; Park & Epstein, 1960; Bender, 1971). If the size of the terrestrial biosphere increases, carbon with low $\delta^{13}C$ values is sequestered, and the ocean and atmosphere become enriched in ^{13}C. The average ocean and atmosphere $\delta^{13}C$ value can also be influenced by changes in geological sources and sinks of carbon (e.g., gas hydrates, volcanic outgassing, organic matter accumulation and sedimentation, alteration of ophiolites, etc.).

Thermodynamic (temperature-dependent) equilibration between the surface ocean DIC and the atmospheric CO_2 influences their isotopic separation factor $\varepsilon \cong \delta^{13}C_{CO_2} - \delta^{13}C_{DIC}$, which increases by 0.1‰ with a 1° decrease in surface ocean temperature (Mook, Bommerson, & Staverman, 1974; Zhang, Quay, & Wilbur, 1995; Szaran, 1997; see also Siegenthaler & Münnich, 1981). However, because the ocean contains more than 50 times more inorganic carbon than the atmosphere, changes in surface temperature have a large influence on the $\delta^{13}C$

value of the atmospheric CO_2 and a significant but reduced influence on the $\delta^{13}C$ of the surface ocean, but a negligible effect on the $\delta^{13}C_{DIC}$ of the ocean as a whole. Therefore, changes in the $\delta^{13}C_{DIC}$ of the mean ocean primarily respond to changes in the size of the terrestrial biosphere and/or to a perturbation in the carbon cycle due to a geological sink/source. Because the carbon in the biosphere and in organic carbon sinks is usually characterized by very low $\delta^{13}C$ values compared with those of the ocean DIC, the transfer of carbon between these reservoirs and the ocean DIC can be quantified (e.g., Emerson & Hedges, 1988; Buchmann, Brooks, Flanagan, & Ehleringer, 1998).

As in the case of foraminiferal $\delta^{18}O$ paleoceanographic records, foraminiferal $\delta^{13}C$-records can be influenced by other factors besides changes in the isotopic composition of the mean ocean. Specifically, as outlined below, the $\delta^{13}C_{DIC}$ of seawater at any one location can be influenced by local changes in the balance between photosynthesis and respiration, changes in the relative mixture of water masses, and changes in the original $\delta^{13}C_{DIC}$ signature of water masses reaching the site location. In the surface ocean, where photosynthesis dominates over respiration, [DIC] is relatively low and $\delta^{13}C_{DIC}$ is relatively high reflecting the net export of low $\delta^{13}C$ carbon (in the form of organic particulate matter with values around –19 to –23‰; Deines, 1980; Macko, Engle, & Quian, 1994; see also Burdige, 2006) out of the surface water. In the deep ocean, where respiration of organic particulate matter dominates, [DIC] is relatively high and $\delta^{13}C_{DIC}$ is relatively low (Figure 9). Thus, changes in photosynthesis or respiration will readily impact the $\delta^{13}C_{DIC}$ of seawater. For example, increases in photosynthesis that lead to greater export of carbon from the surface to the deep ocean, thus a stronger 'biological pump', would result in a larger surface to deep water $\delta^{13}C_{DIC}$ difference. Because photosynthesis and respiration also influence major nutrient distributions in the ocean, the concentrations of, for example, dissolved phosphate or nitrate in the ocean are inversely related to the $\delta^{13}C_{DIC}$ (e.g., Ortiz, Wheeler, Mix, & Key, 2000), and thus changes in the foraminiferal $\delta^{13}C$ are often interpreted as changes in the $\delta^{13}C_{DIC}$ once the impact of global carbon cycle changes on the mean ocean $\delta^{13}C_{DIC}$ values is taken into account. This relationship between foraminifera $\delta^{13}C$ values and photosynthetic activity in the surface ocean has been used for quite some time as a proxy for quantifying paleoproductivity changes between glacial and interglacial periods (e.g., Zahn, Winn, & Sarnthein, 1986; Sarnthein, Winn, Duplessy, & Fontugne, 1988).

Although changes in photosynthesis/respiration strongly influence major nutrient concentrations and $\delta^{13}C_{DIC}$, there are other possible causes of local changes in the $\delta^{13}C_{DIC}$ of seawater at a given location linked to water mass formation and circulation. As deep water forms in high latitude regions where surface-water cools and sinks, it obtains its $\delta^{13}C_{DIC}$ signature from its surface water sources. North Atlantic Deep Water (NADW) has relatively high $\delta^{13}C_{DIC}$ values owing to its North Atlantic surface water source, and Antarctic Bottom Water (AABW) has relatively low $\delta^{13}C_{DIC}$ values because it is comprised of Southern Ocean surface water and deep water from all basins, all of which are sources with relatively low $\delta^{13}C_{DIC}$ values (Figure 9). Today, in the Atlantic Ocean, mixing between nutrient-depleted, high $\delta^{13}C_{DIC}$ NADW flowing from north to south and denser

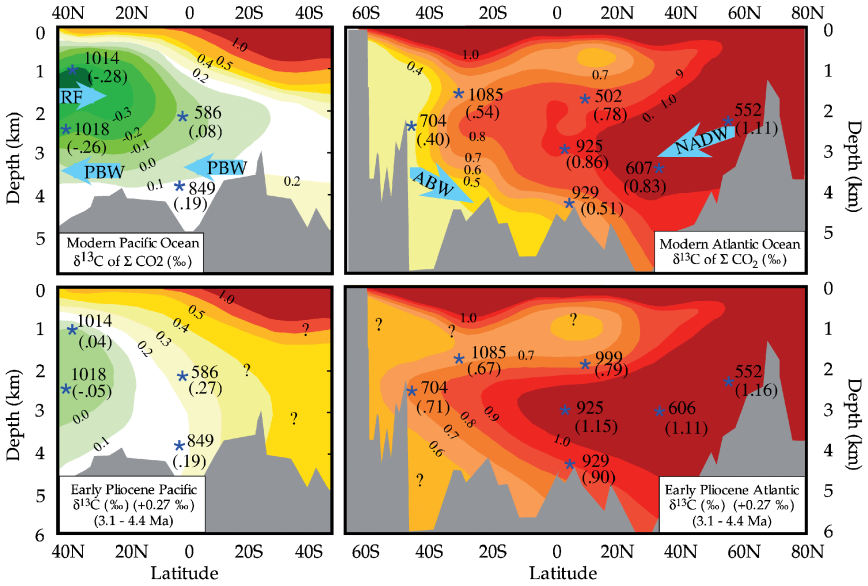

Figure 9 Upper panel: The $\delta^{13}C_{DIC}$ distribution throughout the western Atlantic and Pacific oceans, redrawn from Kroopnick (1985). The $\delta^{13}C_{DIC}$ is relatively high in the surface ocean where photosynthesis dominates, and is relatively low in the deep ocean where respiration dominates. The $\delta^{13}C_{DIC}$ of the North Atlantic Deep Water (NADW) is relatively high, reflecting the North Atlantic surface water source of NADW. The $\delta^{13}C_{DIC}$ distribution in the Atlantic mainly reflects mixing between different water masses with different $\delta^{13}C_{DIC}$ signatures. In the Pacific, the $\delta^{13}C_{DIC}$ distribution reflects the 'aging' of Pacific Bottom Water (PBW) and the mid-depth return flow (RF). The asterisks are plotted at the depth and latitude of some Ocean Drilling Program (ODP) sites. ODP site numbers are given next to the average values (in parentheses) of benthic foraminifera (*Cibicidoides* spp.) $\delta^{13}C$ from the interglacial periods of the last 400,000 yr reproduce the modern distribution of $\delta^{13}C_{DIC}$ fairly well (Ravelo & Andreasen, 2000). Lower panel: The distribution of $\delta^{13}C$ values of water masses during an interval of time within the warm Pliocene period reconstructed using the average $\delta^{13}C_{cal}$ values of benthic foraminifera (*Cibicidoides* spp.) at each site; 0.27 is added to all values to account for the global $\delta^{13}C$ offset between the Pliocene and late Pleistocene (Ravelo & Andreasen, 2000).

nutrient-enriched, low $\delta^{13}C_{DIC}$ AABW flowing south to north results in a strong horizontal nutrient gradient in the deep Atlantic basin (Figure 9). The $\delta^{13}C_{DIC}$ values in epibenthic foraminifera provide a way to reconstruct past deep-water mass distribution and changes in the relative strength of deep-water masses (i.e., the North Atlantic component of the thermohaline circulation). For example, the distribution of water masses has been reconstructed for the Early Pliocene warm period indicating that the mixing zone between NADW and AABW was shifted south due to enhanced flux of NADW relative to AABW (Figure 9) (Ravelo & Andreasen, 2000). In contrast, the mixing zone shifted northward and to shallower depths during cold periods [Pleistocene glaciations and Heinrich events (Zahn et al., 1997)] in response to a strong reduction in the production rate of NADW relative to AABW (Figure 10) (e.g., Duplessy et al., 1984, 1988; Zahn et al., 1986;

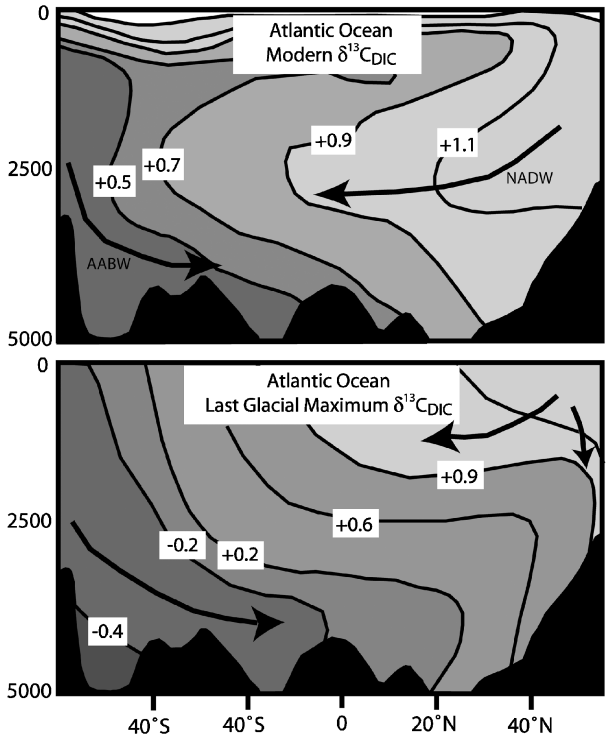

Figure 10 LGM vs. modern conditions in the Atlantic Ocean, based on $\delta^{13}C$ values in benthic foraminifera from variable depths (Duplessy et al., 1988; Labeyrie et al., 1992). A much shallower distribution of the LGM NADW is apparent.

Sarnthein et al., 1988, 1994; Curry, Duplessy, Labeyrie, & Shackleton, 1988; Boyle, 1997).

In the Pacific Ocean, AABW enters the south Pacific and flows northward, becoming more nutrient-enriched and ^{13}C-depleted as it returns at mid-depth (~2 km). This mid-depth water, found throughout the North Pacific, is the most nutrient-enriched and oldest (radiocarbon depleted) water in the global ocean. Reconstruction of Pacific $\delta^{13}C$ distributions using benthic foraminifera can be used to monitor the aging of mid-depth water in the North Pacific. For example, in the Pliocene warm period, the mid-depth water of the Pacific had higher $\delta^{13}C$ values probably indicating enhanced ventilation (less aging) of the interior of the Pacific Ocean (Figure 9). In sum, deep-water nutrient distributions and gradients are reflected in the distribution of $\delta^{13}C_{DIC}$ (Kroopnick, 1985). In past times, either a change in the circulation pattern or the relative strength of deep-water masses can impact the $\delta^{13}C_{DIC}$ of deep water at a sediment core location.

Surface water $\delta^{13}C_{DIC}$ at a given location can also be influenced by changes in the mixing of water masses, especially the vertical upwelling of deeper (low $\delta^{13}C_{DIC}$) water into the surface. As described above, changes in the $\delta^{13}C_{DIC}$ at any one location is likely to reflect both global average $\delta^{13}C_{DIC}$ changes due to

perturbations in the global carbon cycle and changes in the local $\delta^{13}C_{DIC}$ due to processes that also influence the nutrient distribution in the ocean: photosynthesis, respiration, and variations in the advected or upwelled relative contributions of water masses with different $\delta^{13}C_{DIC}$ signatures to the region. An additional mechanism that impacts $\delta^{13}C_{DIC}$, and that is unrelated to processes that influence the nutrient distributions in the ocean, is isotopic thermodynamic equilibration between the atmospheric CO_2 and oceanic DIC. Although the average $\delta^{13}C_{DIC}$ of the surface ocean reflects isotopic equilibrium with the atmosphere globally, many regions are not locally in isotopic equilibrium. The locations where the surface ocean $\delta^{13}C_{DIC}$ does approaches equilibrium are in regions with high air–sea CO_2 fluxes (e.g., the Southern Ocean) and regions with long surface water residence times (e.g., sub-tropical gyres). In past times, the $\delta^{13}C_{DIC}$ of the surface ocean could ~~vary~~ if there ~~was~~ locally more or less isotopic equilibration with the atmosphere (due to changes in residence time or changes in air–sea CO_2 fluxes). Alternatively, in regions where equilibration tends to have a large impact on the $\delta^{13}C_{DIC}$ of surface water, then $\delta^{13}C_{DIC}$ could vary with a change in temperature (since air–sea carbon isotopic fractionation is temperature dependent). Since the source of deep water is high latitude surface water, then changes in the thermodynamic equilibration of surface waters can have an impact on the $\delta^{13}C_{DIC}$ of deep-water masses (Charles, Wright, & Fairbanks, 1993). The thermodynamic isotopic fractionation between the atmosphere and the ocean is a potential mechanism by which changes in the $\delta^{13}C_{DIC}$ of the ocean and the concentration of nutrients can be decoupled in past times. Thus, to reconstruct nutrient distributions accurately requires other proxies that are not influenced by air–sea exchange. However, regardless of the causes of changes in the $\delta^{13}C_{DIC}$ signature of water masses, the mixing zone between water masses can be reconstructed and can provide tremendous insight into circulation patterns of past times as illustrated by Duplessy et al. (1988) and Labeyrie et al. (1992) in the case of the relative strength of NADW.

In sum, $\delta^{13}C_{DIC}$ is influenced by many processes: The average $\delta^{13}C_{DIC}$ of the global oceans is influenced by changes in the amount of carbon stored on land, and by changes in the sink/source of carbon from geological reservoirs. The $\delta^{13}C_{DIC}$ at any one location can be related to the balance of photosynthesis vs. respiration, the relative mixture of water masses with different $\delta^{13}C_{DIC}$ signatures, and changes in the $\delta^{13}C_{DIC}$ of source waters from which those water masses are derived. The $\delta^{13}C$ analyses of plantkonic and benthic foraminifera are used to reconstruct changes in $\delta^{13}C_{DIC}$, but foraminiferal calcite is not in isotopic equilibrium with DIC and is readily affected by microhabitat conditions.

5.2. Factors that Influence the $\delta^{13}C$ of Foraminifera

Differences of isotopic composition between small (possibly juvenile) and large (possibly mature) specimens may depend on (i) distinct "vital effects", (ii) changes of habitat during the life cycle and/or seasonal shifts in environmental conditions, (iii) the deposition of secondary calcite in large sinking shells, and (iv) differential dissolution of shells depending on the thickness of their walls during early diagenetic processes (e.g., Lohmann, 2006).

The $\delta^{13}C$ of foraminiferal calcite is not what would be expected if calcite were in isotopic thermodyamic isotopic equilibrium with the DIC of seawater due to both abiotic kinetic fractionation and biological vital effects. Abiotic kinetic fractionation results in a $1.0 \pm 0.2‰$ (Romanek, Grossman, & Morse, 1992) enrichment of $\delta^{13}C$ in calcite relative to bicarbonate (HCO_3^-), which comprises ~95% of the DIC at the pH of the modern ocean. Over the range of expected foraminiferal calcification rates and temperatures, this enrichment is nearly constant (Romanek et al., 1992; Turner, 1982); this abiotic kinetic fractionation effect causes foraminiferal calcite $\delta^{13}C$ to be $1.0 \pm 0.2‰$ enriched relative to $\delta^{13}C_{DIC}$. However, the observed $\delta^{13}C$ offset between foraminiferal calciate and $\delta^{13}C_{DIC}$ varies widely depending on species and ontogenetic stage because of biological vital effects in planktonic (Ravelo & Fairbanks, 1995) and benthic (Grossman, 1987) species.

Like $\delta^{18}O$, the $\delta^{13}C$ of calcite is influenced by photosynthesis of algal symbionts and respiration, however the impact of these biological processes on the $\delta^{13}C$ of foraminiferal shells is much more severe. Both photosynthesis and respiration have an impact on the microenvironment (Figure 8), or 'internal carbon pool' of the foraminifera which can have a different pH, DIC concentration, and $\delta^{13}C_{DIC}$ than the surrounding ambient seawater (Zeebe, Bijma, & Wolf-Gladrow, 1999). The $\delta^{13}C_{DIC}$ of the internal carbon pool can be enriched in ^{13}C when CO_2 with low $\delta^{13}C$ values is sequestered by algae during photosynthesis, and can be depleted in ^{13}C when contaminated by low $\delta^{13}C$ metabolic CO_2 during respiration. Since the foraminifera draws on this internal pool, the $\delta^{13}C$ of the foraminiferal test can be influenced by the rate of photosynthesis, respiration, and calcite precipitation relative to the turnover rate of DIC in the internal pool. In addition, the rate of isotopic equilibration during CO_2 hydroxylation and hydration within the internal pool is slow relative to calcite precipitation, and thus the chemistry of the internal pool (its pH and CO_3^{2-}concentration) and the rate of precipitation which influences the degree of isotopic equilibration between species of carbon, can influence the $\delta^{13}C$ of the test (McConnaughey, 1989a, 1989b). The chemistry of the internal pool, and therefore the degree of kinetic fractionation as described by McConnaughey (1989a, 1989b), can be influenced both by biological processes as well as by the ambient seawater chemistry, specifically the pH and concentration CO_3^{2-} of seawater (Spero et al., 1997).

Given the multiple potential factors that determine the offset between the $\delta^{13}C$ of foraminiferal calcite and $\delta^{13}C_{DIC}$, there are significant species-specific differences in this offset. In general, foraminiferal $\delta^{13}C$ values tend to be lower than what would be expected by abiotic kinetic fractionation (calcite $\delta^{13}C$ enrichment of 1.0+0.2‰ relative to $\delta^{13}C_{DIC}$) alone, probably due to the contamination of the internal pool with CO_2 from respiration possibly combined with the kinetic fractionation effects described by McConnaughey (1989a, 1989b). This is true for benthic foraminiferal species (Grossman, 1987; Mackensen, Schumacher, Radke, & Schmidt, 2000; McCorkle, Corliss, & Farnham, 1997) and many planktonic species, particularly those without algal symbionts (Ravelo & Fairbanks, 1995). In addition, algal-bearing planktonic species typically have strong size-dependent $\delta^{13}C$ values, with increasing $\delta^{13}C$ values with size, probably due to increases in the rate of photosynthesis (Ravelo & Fairbanks, 1995; Spero & Deniro, 1987) (Figure 11),

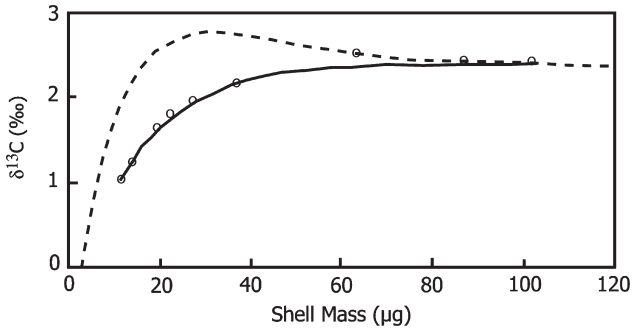

Figure 11 The $\delta^{13}C$ of *Globigernoides sacculifer* (a symbiont-bearing planktonic foraminifera) from the core top of V28-122 from Ravelo and Fairbanks (1995). Each circle is the average $\delta^{13}C$ values of 10–15 shells vs. the average mass of an individual shell. The increase in $\delta^{13}C$ values with size reflects the increasing effect of photosynthesis on the $\delta^{13}C$ of the shell as the foraminifera grows. The dashed curve is the calculated $\delta^{13}C$ of calcite being added at a given shell mass. See Ravelo and Fairbanks (1995) for a full explanation.

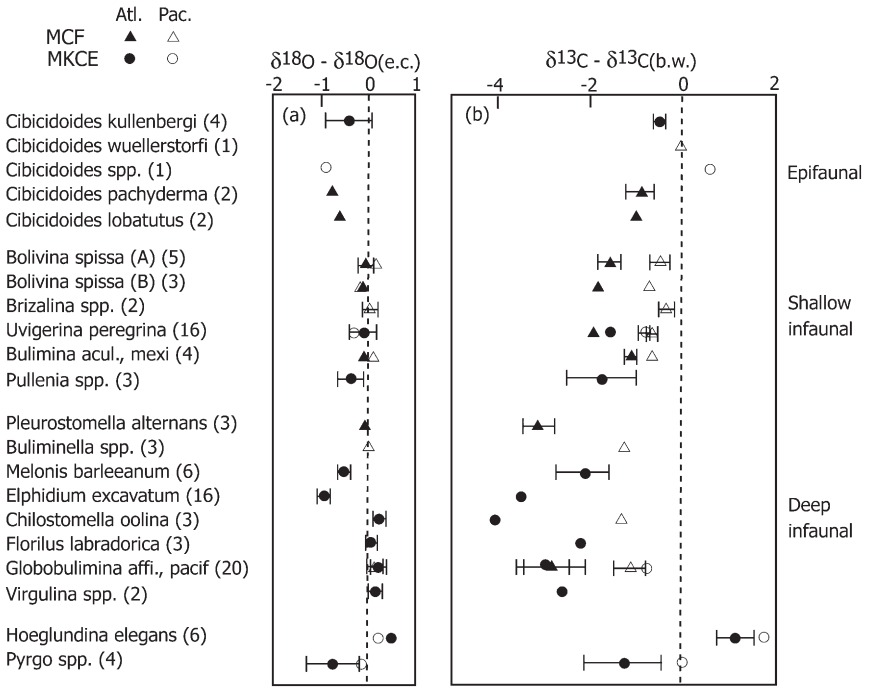

Figure 12 Average $\delta^{18}O$ offsets from calcite in equilibrium with bottom water ($\delta^{18}O$ e.c.) (a) and average $\delta^{13}C$ (b) offsets from bottom water DIC ($\delta^{13}C$b.w.) (b) were calculated for each species in each core. The averages and standard deviations of single-core values are shown here. The values in parentheses give the number of cores in which each species was analyzed. Triangles denote data from McCorkle et al. (1997) ("MCF") and circles show data from McCorkle et al. (1990) ("MKCE"); solid symbols show the averages of Atlantic Ocean cores and open symbols show Pacific Ocean averages. The species are grouped according to their stained abundance patterns with epibenthic and epifaunal species at the top (five *Cibicidoides* spp.), shallow infaunal species in the second group (*B. spissa* to *Pulknia* spp.), and intermediate and deep infaunal species in the third group (*P. alternans* to *Virgulina* spp.). Figure is redrawn from McCorkle et al. (1997).

however the $\delta^{13}C$ enrichment relative to $\delta^{13}C_{DIC}$ often remains below $1.0 \pm 0.2‰$ indicating that other factors (e.g., respiration) continue to influence the $\delta^{13}C$ of the test throughout the foraminifera lifecycle. In large adult shells, the $\delta^{13}C$ size-dependence decreases, and paleoceanographic studies that utilize symbiont-bearing planktonic foraminifera almost always rely on records produced from shells from the largest size fraction in which abundant shells are found.

As described above, species-specific $\delta^{13}C$ offsets from the $\delta^{13}C_{DIC}$ are attributed to the combination of abiotic kinetic fractionation, biological vital effects of photosynthesis and respiration on the internal carbon pool, and kinetic fractionation due to the slow isotopic equilibration of carbon species within the internal pool. However, it is also important to account for the fact that there can be large species-specific differences in the habitat and ecological preferences, and therefore in the $\delta^{13}C_{DIC}$ of the ambient seawater in which the foraminifera live. For example, different species of planktonic foraminifera have different temperature, nutrient, and light requirements and therefore can live and calcify at different vertical depths and seasons. As such their shells will reflect the vertical and seasonal variations in $\delta^{13}C_{DIC}$ within the upper ocean. Benthic foraminifera have different oxygen and food requirements and therefore can live and calcify at different depths in the sediments. Since the $\delta^{13}C_{DIC}$ of porewaters can be quite depleted in sediment with high rates of respiration of sedimentary organic matter, infaunal species tend to have lower $\delta^{13}C$ values than epifaunal species growing at the same time at the same location (Mackensen et al., 2000; McCorkle et al., 1997) (Figure 12).

6. Conclusion and Summary

Paleoceanographic records derived by analyzing the $\delta^{13}O$ and $\delta^{13}C$ of foraminiferal shells must obviously be generated and interpreted with caution and with close consideration of a wide array of factors. The common strategies are to generate records using only one species in order to minimize the variability due to specific biological effects. Furthermore, it is common to select species that have well-known ecological preferences that are fairly predictable across regions with different oceanographic conditions in the modern ocean. Otherwise, it is difficult to interpret records accurately with respect to understanding how isotopic records might be biased by the potential effects of changes in seasonality, nutrient levels, and depth habitat, not to mention interannual variability (with exceptional blooms) and early diagenetic effects (mixing, selective dissolution). It is also common to use shells from one size fraction of the sediment; usually the largest abundant size fraction in which shells are abundant is chosen since the ontogenetic isotope fractionation effects are more severe during early stages of growth, although this may result in a bias toward optimal conditions for the given species, and not necessarily the mean conditions of the time interval considered.

These practices are thought to minimize variability due to biological factors, and the resulting $\delta^{18}O$ downcore record can then be interpreted as primarily a reflection of changes in the $\delta^{18}O$ of seawater, the temperature of calcification, and possibly ocean carbon chemistry ($[CO_3^{2-}]$). The resulting $\delta^{13}C$ downcore record will reflect changes in the $\delta^{13}C_{DIC}$ and $[CO_3^{2-}]$. The isotopic composition ($\delta^{18}O$

and $\delta^{13}C_{DIC}$) of seawater, the temperature of calcification, and the seawater carbon chemistry can each vary as a function of multiple processes as discussed above. For example, changes in $\delta^{13}C_{DIC}$ could be related to changes in the global carbon cycle, regional changes in water mass mixing and sources, photosynthesis/respiration processes, and changes in $[CO_3^{2-}]$. However, in some cases, isotopic records are predominantly influenced by single oceanographic/climate process. Perhaps the best example of this is the dominance of ice volume changes, relative to changes in calcification temperature and $[CO_3^{2-}]$, on most foraminiferal $\delta^{18}O$ records. For this reason, $\delta^{13}O$ records remain one of the best stratigraphic tools available for correlating records across the globe.

In many cases, because records from around the globe all have some shared variance due to whole ocean changes in $\delta^{18}O$ and $\delta^{13}C_{DIC}$, then comparisons between records (differences) can be used to isolate changes in local conditions in one location relative to another. If the $\delta^{13}O$ and $\delta^{13}C_{DIC}$ characteristics of water masses can be reconstructed, then changes in relative flux of each water mass can be quantified using cores in the mixing zone between end-members. However, in most cases, to isolate absolute changes in local oceanographic conditions and to separate the influence of multiple effects, other paleoceanographic proxies in the same core must be analyzed, and to understand the context (e.g., the geographic extent) of a single record, comparisons with records from other regions must be made.

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