8.16 Tracers of Past Ocean Circulation

J Lynch-Stieglitz, Georgia Institute of Technology, Atlanta, GA, USA
TM Marchitto, University of Colorado, Boulder, CO, USA

© 2014 Elsevier Ltd. All rights reserved.

This article is a revision of the previous edition article by J. Lynch-Stieglitz, volume 6, pp. 433–451, © 2003, Elsevier Ltd.

8.16.1 Introduction

Information about how the ocean circulated during the past is useful in understanding changes in ocean and atmospheric chemistry, changes in the fluxes of heat and freshwater between the ocean and the atmosphere, and changes in global wind patterns. The circulation of surface waters in the ocean leaves an imprint on sea surface temperature and is also inexplicably linked to the patterns of oceanic productivity. Much valuable information about past ocean circulation has been inferred from reconstructions of surface ocean temperature and productivity, which are covered in separate chapters. Here, the focus is on geochemical tracers that are used to infer the flow patterns and mixing of subsurface water masses.

Several decades ago, it was realized that the chemistry of the shells of benthic foraminifera (carbon isotope and Cd/Ca ratios) carries an imprint of the nutrient content of deep water masses (Boyle, 1981; Broecker, 1982; Shackleton, 1977). This led rapidly to the recognition that water masses in the Atlantic Ocean were arrayed differently during the Last Glacial Maximum (LGM) than they are today and the hypothesis that the glacial arrangement reflected a diminished contribution of low-nutrient North Atlantic Deep Water (NADW; Boyle and Keigwin, 1982; Curry and Lohmann, 1982). More detailed spatial reconstructions indicated a shallow nutrient-depleted water mass overlying a more nutrient-rich water mass in the glacial Atlantic. These findings spurred advances not only in geochemistry but also in oceanography and climatology, as workers in these fields attempted to simulate the inferred glacial circulation patterns and assess the vulnerability of the modern ocean circulation to changes observed for the last ice age.

While the nutrient distributions in the glacial Atlantic Ocean were consistent with a diminished flow of NADW, they also could have reflected an increase in inflow from the South Atlantic and/or a shallower yet undiminished deep water mass. Clearly, tracers capable of giving information on deep water flow rate, rather than nutrient content alone, were needed. Differences between surface water (measured on planktonic foraminifera) and deepwater (measured on coexisting benthic foraminifera) radiocarbon concentrations provided the first rate constraint (Broecker et al., 1988; Shackleton et al., 1988). Reduced amounts of Pa relative to the more particle-reactive Th in the glacial Atlantic suggested that deep water was exported from the Atlantic during glacial
times (Yu et al., 1996). Density gradients in upper waters reflect the vertical shear in oceanic transports, especially at intermediate depths where these gradients are largest (Lynch-Stieglitz et al., 1999b).

Many of these tracers of paleo-ocean flow have been applied to all of the ocean basins and have been extended in time throughout the Neogene. Despite this progress, a consistent picture of the circulation of the ocean during even the last ice age is yet to emerge. While circulation tracers suggest a rearrangement of water masses in the Atlantic, there is still considerable disagreement about the water masses and circulation in the rest of the world ocean. Some of this uncertainty arises from still insufficient data coverage but some is the result of conflicting information from the various deep circulation tracers. In this chapter, the methods used to reconstruct past ocean circulation, which will illuminate the source of some of this conflicting information, are examined in more detail.

### 8.16.2 Nutrient Water Mass Tracers

#### 8.16.2.1 Carbon Isotopes

Measuring the carbon isotope ratio in calcite tests of bottom-dwelling (benthic) foraminifera is perhaps the most widespread method for reconstructing the distribution and properties of deep-sea water masses. Carbon isotope ratios in foraminifera reflect that ratio in seawater. In turn, the carbon isotope ratio in the deep sea is primarily controlled by the regeneration of 13C-poor organic material and has a distribution much like a nutrient such as phosphate in the modern ocean. While a nutrient tracer reflects the increased contribution from the regeneration of organic material as the water mass ages, it also carries a signature of the initial nutrient content of the source regions. In today’s Atlantic, the contrast between high-nutrient Southern Ocean source water and low-nutrient NADW is strong, and the residence time of deep water in the Atlantic Ocean is short, allowing little additional accumulation of nutrients from sinking organic material. In this case, the nutrient tracers can be used to document the relative mixtures of northern and southern water masses.

#### 8.16.2.1.1 Controls on δ13C of oceanic carbon

During photosynthesis, organisms preferentially take up the lighter isotope of carbon (12C), increasing surface ocean δ13C. When the 13C-depleted organic matter is decomposed, the accompanying CO2 release decreases the δ13C of dissolved inorganic carbon at depth (Craig, 1970; Deuser and Hunt, 1969; Kroopnick, 1985). If this process were solely responsible for the distribution of δ13C in the ocean, δ13C of oceanic carbon would decrease by approximately 1.1‰ for every 1 μmol kg⁻¹ increase in oceanic PO4 (Broecker and Maier-Reimer, 1992). Reflecting this biological cycling, as a deep water mass with a homogeneous source ages (such as in the deep Indian and Pacific oceans), the δ13C and PO4 increase in this biologically expected ratio (Figure 1). However, the discrimination against 13C during photosynthesis increases from about 19‰ in the warm surface ocean to about 30‰ in the Antarctic, which means that the relative changes in PO4 and δ13C associated with the uptake and regeneration of organic material can vary regionally.

Carbon isotope fractionation during air–sea exchange is also an important factor in determining the isotopic composition of seawater. If the CO2 in the atmosphere were in isotopic equilibrium with the dissolved inorganic carbon in the ocean, the dissolved inorganic carbon would be enriched in 13C relative to atmospheric CO2 by about 8‰ at 20 °C (Inoue and Sugimura, 1985). This equilibrium fractionation depends on

![Figure 1](https://example.com/figure1.png)

**Figure 1** Deepwater (>2000 m) δ13C and PO4 data from the modern ocean. The lines indicate a ‘Redfield slope,’ and δ13Cair indicates the deviation from the mean ocean Redfield slope for δ13C and PO4 (Broecker and Maier-Reimer, 1992). While the deep Indian and Pacific values follow the slope expected for biologic processes, deep waters which form in the North Atlantic and Southern Ocean have lower and higher δ13C due to air–sea exchange. Reproduced from Lynch-Stieglitz J, Stocker TF, Broecker WS, and Fairbanks RG (1995) The influence of air–sea exchange on the isotopic composition of oceanic carbon: Observations and modeling. *Global Biogeochemical Cycles* 9: 653–665.
the temperature of equilibration, with the oceanic carbon more enriched relative to the atmospheric value by about 0.1‰ per degree of cooling (Mook et al., 1974). If the surface ocean were everywhere in isotopic equilibrium with atmospheric CO$_2$, the 30°C range in ocean temperatures would cause a 3‰ range in oceanic $\delta^{13}C$, with higher values where surface temperatures are cold and lower values in warm surface waters. This range is similar to the magnitude of $\delta^{13}C$ change induced by biological processes. Isotopic equilibrium is rarely reached, however, because the timescale for carbon isotope equilibration between ocean and atmosphere (about 10 years for a 50 m deep mixed layer) is about ten times longer than chemical equilibration between atmospheric CO$_2$ and dissolved inorganic carbon (Broecker and Peng, 1974; Tans, 1980). This isotopic equilibration time is significantly longer than the time that surface waters stay in one place in the ocean.

The exchange of atmospheric CO$_2$ with surface ocean aqueous CO$_2$ has the potential to leave oceanic carbon depleted in $^{13}C$ in areas of CO$_2$ invasion (e.g., high northern latitudes, low-pCO$_2$ surface waters) and enriched in $^{13}C$ in areas of CO$_2$ outgassing (e.g., equatorial upwelling regions, high-pCO$_2$ surface waters; Lynch-Stieglitz et al., 1995). This is because CO$_2$ gas that is dissolved in the ocean and exchanges between the ocean and atmosphere is isotopically lighter than the much larger pool of dissolved inorganic carbon that consists mainly of bicarbonate and carbonate ions. This effect is observed in the ocean because the timescale for carbon isotope equilibration between ocean and atmosphere (which drives the air-sea exchange of CO$_2$) is shorter than the timescale for isotopic equilibration, as noted above.

In general, surface ocean $\delta^{13}C$ lies somewhere between the value predicted if biological cycling alone controlled the distribution of $\delta^{13}C$ in the ocean and the value that would be at equilibrium with the atmosphere (Broecker and Maier-Reimer, 1992; Broecker and Peng, 1982; Gruber et al., 1999). The departure from the biologically expected value can be expressed as an air-sea exchange signature $\delta^{13}C_{\text{as}} = \delta^{13}C - (2.7 - 1.1 \times \text{PO}_4)$ (Broecker and Maier-Reimer, 1992; Lynch-Stieglitz et al., 1995). By definition, water with $\delta^{13}C_{\text{as}}$ of 0‰ has the same air-sea exchange signature as mean ocean deep water. A positive value of $\delta^{13}C_{\text{as}}$ means that the water has a higher $\delta^{13}C_{\text{as}}$ than mean ocean deep water (more of an influence of air-sea exchange at cold temperatures/less at warm temperatures), whereas a negative $\delta^{13}C_{\text{as}}$ value implies less $\delta^{13}C$ enrichment due to air-sea exchange than for mean ocean deep water.

$\delta^{13}C_{\text{as}}$ in surface waters is highest in the Antarctic and the North Pacific due to exchange with the atmosphere at low temperatures. The lowest values of $\delta^{13}C_{\text{as}}$ are found in the centers of the subtropical gyres. Surface waters circulate in these anticyclonic gyres long enough to allow the oceanic DIC time to equilibrate isotopically with the atmosphere at high temperatures, despite the relatively low rates of gas exchange. The situation in the North Atlantic seems slightly more complex. Air-sea exchange at cold temperatures will tend to raise the $\delta^{13}C_{\text{as}}$ of the northward moving upper waters but does not have time to overcome the effects of CO$_2$ invasion and the remnant low $\delta^{13}C_{\text{as}}$ of the northward flowing surface water. Deep waters leaving the surface in the North Atlantic and the Antarctic reflect the low and high $\delta^{13}C_{\text{as}}$, respectively.

### 8.16.2.1.2 Carbon isotope ratios in benthic foraminifera

Belanger et al. (1981) demonstrated that the $\delta^{13}C$ in the benthic foraminifera Planulina wuellerstorfi decreased from highest values in the Norwegian-Greenland Sea to lower values in the South Atlantic and lowest values on the East Pacific Rise. They argued that $P. wuellerstorfi$ is a reliable recorder of bottom water conditions and is not overly influenced by the incorporation of metabolic carbon. (While $wuellerstorfi$ is variously assigned to the genera Planulina, Cibicides, Cibicidoides, and Fontibotia by various workers, there is no disagreement on the assignment of the species.) They also found that $\delta^{13}C$ in the genera Oridorsalis and Pyrgo did not follow the expected deepwater progression in $\delta^{13}C$ and argued that the shell chemistry reflected the lower $\delta^{13}C$ of their pore water habitat. The same year, Graham et al. (1981) showed, with a larger set of core-top data, that $\delta^{13}C$ from the tests of $P. wuellerstorfi$ and Cibicidoides kullenbergi also follow the expected relationship with seawater chemistry. Graham et al. (1981) also found that these species show $\delta^{13}C$ values that are closest to what would be expected for precipitation in seawater. While they found that $\delta^{13}C$ values in $P. wuellerstorfi$ and C. kullenbergi reflect the $\delta^{13}C$ of the ambient water, these shells are a full 1‰ lower than expected for calcite formed in equilibrium with this water (Woodruff et al., 1980). However, carbon isotope equilibrium between calcite and dissolved carbon is not well known at the temperatures of the deep ocean (Grossman, 1984b; Romanek et al., 1992). These studies paved the way for the widespread reconstruction of deepwater $\delta^{13}C$, which followed soon afterward (Boyle and Keigwin, 1982; Curry and Lohmann, 1982; Curry et al., 1988; Duplessy et al., 1984, 1988).

Shown in Figure 2 is a comparison of Planulina and Cibicidoides $\delta^{13}C$ with estimated water column $\delta^{13}C$ from Duplessy et al. (1984). At the time of this study, there was little

high-quality water column $\delta^{13}C$ data with which to compare the core-top values. In subsequent years, however, more extensive and improved datasets have confirmed that, on average, Planulina and Cibicidoides $\delta^{13}C$ reflect water column $\delta^{13}C$ with little or no offset. Some of the scatter in Figure 2 may be attributed to errors in estimated oceanic $\delta^{13}C$ or core tops which are not Holocene in age. However, the more recent datasets also show that there can be significant offsets between the foraminifera and water column values at some locations, even when living foraminifera are compared to water column $\delta^{13}C$ collected at the same location.

Perhaps it is not unexpected that benthic foraminifera do not always cleanly record the isotopic composition of bottom water. The fact that all of the benthic foraminifera have $\delta^{13}C$ that is significantly lighter than what would be expected for equilibrium with bottom water provides the first clue that additional processes may be at work. As postulated by Belanger et al. (1981), some foraminifera may live in the pore waters of the sediment, where $\delta^{13}C$ of dissolved inorganic carbon is lower than in the overlying water column. Even so, the carbon isotopic composition of the calcite skeleton of most calcitic organisms does not reflect the composition of the ambient waters (Wefer and Berger, 1991) but is dominated by physiological or ‘vital’ effects which usually involve the incorporation of isotopically light metabolic carbon or kinetic fractionation during the transport of carbon to the calcification site or during calcification itself. The isotopic ratios of planktonic foraminifera are also dominated by these vital effects and are, in general, not in equilibrium with seawater (e.g., Spero and Lea, 1996; Spero et al., 1997).

A more detailed look at how benthic foraminifera record bottom water $\delta^{13}C$ has been made through careful analysis of stained (live or recently living) benthic foraminifera collected from surface sediment, combined with measurements of both water column and pore water $\delta^{13}C$ (Grossman, 1984a,b; Mackensen and Douglas, 1989; Mackensen et al., 1993; McCorkle et al., 1990, 1997; Rathburn et al., 1996; Tachikawa and Elderfield, 2002). These studies confirm earlier notions that different species show different microhabitat preferences, with some species (including most Cibicidoides and Planulina) living on or near the sediment surface and others (including Uvigerina) living within the sediment. The deeper-dwelling species show depleted $\delta^{13}C$ values relative to bottom waters that, in general, reflect the magnitude of the pore water depletions. These studies suggest that this microhabitat effect is the dominant control on benthic foraminiferal $\delta^{13}C$ and that variations in the vital effects between species are small. While the number of Cibicidoides analyzed has been small, the Cibicidoides species tend to have the smallest isotopic depletion relative to bottom waters.

However, the isotopic depletion even for Cibicidoides can be significant, especially in areas where productivity, and thus the supply of organic material to the sediment, is high. Mackensen et al. (1993) showed that living and dead specimens of P. wuellerstorfi showed substantial depletions relative to bottom waters, particularly beneath high-productivity fronts in the Southern Ocean. While P. wuellerstorfi has been reported to live above the sediment surface (Lutze and Thiel, 1989), Mackensen et al. (1993) postulate that the foraminifera are calcifying within the organic fluff layer that can be found in high-productivity environments, with their low $\delta^{13}C$ value reflecting either the low-$\delta^{13}C$ environment within the fluff layer or high growth rates of the foraminifera within these environments. Subsequent studies, however, have shown that the relationship between $\delta^{13}C$ and overlying productivity can be complex (Corliss et al., 2006; Eberwein and Mackensen, 2006; Zarriess and Mackensen, 2011).

These relationships have been generally confirmed with downcore $\delta^{13}C$ studies. These studies show that the $\delta^{13}C$ from Uvigerina (infaunal) is always more negative than for Cibicidoides and that this offset is variable in space and time, consistent with the microhabitat model. While many early isotopic studies were performed using Uvigerina because it was thought to best reflect oxygen isotope equilibrium, most deepwater $\delta^{13}C$ reconstructions now use Cibicidoides or Planulina species. It is broadly acknowledged that these records, particularly in high-productivity areas, might be influenced by a microhabitat effect. However, by avoiding high-productivity areas and using supplemental information about changes in bottom water characteristics and overlying productivity, this method has continued to yield regionally coherent and sensible patterns of deepwater $\delta^{13}C$.

8.16.2.2 Cadmium in Benthic Foraminifera

The use of Cd/Ca measurements in the tests of benthic foraminifera for deepwater nutrient reconstructions was developed in parallel with the carbon isotope method. Dissolved Cd concentrations in seawater follow a nutrient-like distribution, while Ca concentrations mainly reflect variations in salinity. Benthic foraminifera incorporate Cd and Ca into their shells in proportion to the ratio of these elements in seawater, which allows for the reconstruction of deepwater Cd (and thus macronutrient) distributions.

8.16.2.2.1 Cd in seawater

Cd in seawater has a nutrient-like profile, with depleted values in warm surface waters and the most enriched concentrations in intermediate and deep waters (Boyle et al., 1976). Many high-quality Cd measurements in seawater over the last 20 years have confirmed this nutrient-like behavior, with Cd showing a tight correlation with phosphorus in seawater. While it is still not clear whether most Cd is taken up as an essential micronutrient or inadvertently, the cycling within the ocean is dominated by incorporation into organic tissue in the surface ocean and regeneration of elemental Cd as this material is respired below the surface. The relationship with phosphorus is not linear, with a lower slope at lower phosphorus concentrations (Figure 3). This curvature may be due to preferential uptake of Cd over P by phytoplankton, though not at a fixed (‘Redfield’) ratio (Elderfield and Rickaby, 2000). As dissolved phosphorus is drawn down in the sunlit surface ocean, the Cd/P ratio of seawater decreases. When high-Cd/P organic matter is remineralized below the surface, the Cd/P of seawater climbs again, and the net result is a curve whose shape depends on the effective fractionation factor between organic matter Cd/P and seawater Cd/P. Since different deep waters have undergone different extents of remineralization, and may be mixtures of water masses with different preformed Cd/P ratios, there are real differences in the Cd/P relationships in different
of ocean regions (Elderfield and Rickaby, 2000), which may of course change through time. Because Cd is also removed from seawater via CdS precipitation in suboxic sediments, the global seawater Cd inventory, and thus the global Cd/P relationship, can change as the extent of suboxic sediments changes (Rosenthal et al., 1995a,b; van Geen et al., 1995). However, the residence time for Cd in seawater is sufficiently long, and the expansion of deep-sea suboxia sufficiently small, that the Cd concentration during the last glacial period is unlikely to have been lower than today by more than 5% (Boyle and Rosenthal, 1996). This allows us to make meaningful inferences about the cycling of major nutrients via reconstructions of the past Cd concentration in seawater.

8.16.2.2 Cd/Ca in foraminifera

Boyle (1981) showed that with careful attention to cleaning, benthic foraminiferal shells reflect the concentration of some trace metals (including Cd) in seawater, with a preferential incorporation of Cd over Ca into foraminifera. The empirical distribution coefficient ($D$, ratio of Cd/Ca in foraminifera to Cd/Ca in seawater) was shown to be 2.9, based primarily on deep-sea core tops (Boyle, 1988). More core-top measurements at all water depths have subsequently shown that this distribution coefficient increases with depth, starting at ~1.3 above 1 km and increasing to a maximum of ~2.9 below 3 km (Boyle, 1992). Recent measurements suggest that the shallow water value may be as high as 1.7 and is not discernibly temperature dependent (Bryan and Marchitto, 2010; Marchitto, 2004). Once the depth-dependent distribution coefficient is applied, the reconstructed Cd from foraminiferal tests shows a linear relationship to Cd estimated for the overlying water (Figure 4). Boyle et al. (1995) showed that the aragonitic foraminifer Hoeglundina elegans has a $D$ of 1 that shows no depth dependence. McCorkle et al. (1995) observed an unexpected decrease in the apparent distribution coefficient of Cd and other trace metals with depth between 2.5 and 4 km in the deep Pacific, which suggested dissolution-driven loss of Cd from the foraminiferal calcite after burial. Elderfield et al. (1996) favored the idea that the lower $D$ in deep Pacific waters is a calcification response to the low carbonate saturation state, rather than representing postdepositional dissolution, a possibility acknowledged by McCorkle et al. (1995) and supported by laboratory dissolution experiments (Marchitto et al., 2000). There has been no systematic attempt to correct paleoceanographic Cd reconstructions for this apparent low carbonate saturation state effect, though Zn/Ca (Marchitto et al., 2000) and B/Ca (Yu and Elderfield, 2007) hold some promise in this regard.

To the extent that the $\delta^{13}C_{\text{DIC}}$ of infaunal benthic foraminifera reflects the low $\delta^{13}C$ of pore waters, it would be expected that infaunal Cd/Ca also reflects the interstitial rather than the bottom water concentrations. However, while interstitial $\delta^{13}C$ values decrease with increasing depth in the sediment due to the regeneration of isotopically light organic matter, the distribution of Cd in pore water is more complex. In shallow pore waters, Cd increases due to regeneration of organic material but in suboxic sediments Cd decreases due to precipitation of CdS (McCorkle and Klinkhammer, 1991; Rosenthal et al., 1995a,b). As a consequence, we would not necessarily expect a systematic relationship between the Cd/Ca of epifaunal versus infaunal foraminifera as there is for $\delta^{13}C$. Tachikawa and Elderfield (2002) showed that for three sites in the North Atlantic, pore waters were 2–4 times enriched in Cd relative to bottom waters. They found that P. wuellerstorfi, whose $\delta^{13}C$ values suggested that they calcified in bottom waters at the sediment surface, had a $D$ of 3–4, consistent with culture studies (Havach et al., 2001). The infaunal species showed
a lower D of about 1 with respect to the pore water Cd concentrations. The net effect is that the Cd/Ca in *P. wuellerstorfi* and the infaunal species is quite similar, consistent with previous observations across a range of conditions (e.g., Boyle, 1992). Further, Tachikawa and Elderfield argue that the depth-dependent D for the infaunal *Uvigerina* may actually reflect a trend in the enrichment of pore water Cd relative to bottom water Cd, though this cannot explain the depth dependence of D in the epifaunal *P. wuellerstorfi* (Boyle, 1992). Regardless of the details surrounding infaunal D values, it is expected that Cd/Ca in *P. wuellerstorfi* or other surface dwelling foraminifera should give a more direct measure of bottom water Cd. As with δ13C, careful interpretation aided by consideration of supplemental information about changes in bottom water characteristics has yielded regionally coherent and sensible patterns of deepwater Cd (e.g., Boyle, 1992; Marchitto and Broecker, 2006).

### 8.16.2.3 Ba/Ca

Like Cd, dissolved Ba in a broad sense cycles like a nutrient, depleted in surface waters and higher in deep waters, but the surface depletion is moderate, and the regeneration of Ba occurs deeper than for labile nutrients like phosphorus. This pattern is due to the removal of Ba by barite precipitation in decaying organic matter and subsequent barite dissolution in the deep sea. This process coincidently results in a close correlation between Ba and alkalinity in today’s ocean (Lea, 1993). Lea and Boyle (1989) showed that the barium content in benthic foraminiferal shells is controlled by the barium concentration in bottom waters, with a D of ~0.4. Ba/Ca in foraminifera has been used, like Cd/Ca, as a paleotracer of water masses (e.g., Lea and Boyle, 1990) and appears to suffer from the same carbonate saturation state-linked effect as Cd/Ca (McCorkle et al., 1995).

### 8.16.2.4 Zn/Ca

Zn is a necessary micronutrient for phytoplankton and especially diatom growth. This requirement results in a very strong correlation between oceanic dissolved Zn and Si concentrations (Bruland et al., 1978). Benthic foraminiferal Zn/Ca is controlled by bottom water dissolved Zn concentration, with a maximum D in *P. wuellerstorfi* and *Uvigerina* of ~9 (Marchitto et al., 2000) and a value closer to 22 in *C. pachyderma* (Bryan and Marchitto, 2010). Because of the close relationship between Si and Zn, Zn/Ca in foraminifera is particularly useful for tracing the Si-rich bottom water that originates in the Southern Ocean (Marchitto et al., 2002). Like Cd/Ca and Ba/Ca, the apparent distribution coefficient for Zn decreases in waters which are more undersaturated with respect to calcium carbonate. Because they respond to saturation state differently, Cd/Ca and Zn/Ca can theoretically be used together to assess both the nutrient content and carbonate ion concentrations in deep water masses (Marchitto et al., 2000, 2002).

### 8.16.2.5 Silicon Isotopes

A promising new proxy for the reconstruction of deepwater silicic acid concentrations is the isotopic composition of Si in sponge spicules. Hendry et al. (2010) have shown that the fractionation of Si isotopes increases with ambient Si(OH)₄ concentration. This effect is thought to be related to the growth rate of the sponge spicules, which should respond to the Si(OH)₄ concentration.

### 8.16.3 Conservative Water Mass Tracers

In general, nutrient-type tracers have been used to infer the sources and mixing of deep water masses in the past, despite the complication that the nutrient content of deep water depends both on the nutrient content at its source and the addition of nutrients via regeneration of organic matter as the water mass ages. The utility of this method is primarily due to the large and readily measured contrasts in the nutrient-related tracers. Headway is now being made in the use of conservative tracers that reflect the mixing of source waters alone (such as temperature and salinity in the modern ocean).

#### 8.16.3.1 Mg/Ca in Benthic Foraminifera

Mg/Ca ratios in benthic foraminifera reflect the calcification temperature (e.g., Martin et al., 2002; Rathburn and deDeckker, 1997; Rosenthal et al., 1997b). In principle, temperature can be used as a conservative tracer for subsurface water masses, but at present, the uncertainties in converting Mg/Ca to temperature overwhelm the deep water temperature gradients that distinguish water masses of different origins. In particular, the saturation state of bottom water appears to exert a strong secondary influence on Mg/Ca, as it does for the other trace metal ratios (Elderfield et al., 2006). Emerging research is targeting additional ratios like Mg/Li (Bryan and Marchitto, 2008; Lear et al., 2010) and infaunal taxa like *Uvigerina* (Elderfield et al., 2010) in the hope of isolating or minimizing the carbonate ion effect so that Mg/Ca could be used to assess the contributions to intermediate water masses, where the temperature signals are more easily distinguished.

#### 8.16.3.2 Pore Water Chemistry

The δ18O of seawater is set in the short term by processes which occur at the ocean surface (evaporation, precipitation, sea ice formation and melt; Craig and Gordon, 1965), so it can be used as a conservative tracer in the subsurface ocean. The δ18O of glacial-age water has been reconstructed by measuring the δ18O of pore water in deep-sea sediment (e.g., Schrag and dePaolo, 1993; Schrag et al., 2002). The maximum contribution of high δ18O from the LGM appears at a depth of 20–60 m within the sediments. The actual δ18O of the glacial-age deep water must be reconstructed by modeling the diffusion of water within the sediments. Estimates for the bottom water temperature (also a conservative tracer) at the LGM can then be made by using the benthic foraminiferal δ18O along with information from pore waters about the δ18O of the water in which it calcified. Similarly, salinity can be reconstructed using pore water [Cl] (Adkins and Schrag, 2001). While the number of locations with such data is limited, Adkins et al. (2002) show the promise of using pore water δ18O and [Cl] to
reconstruct the properties of deep water masses. As more data are collected, these tracers will also be useful for reconstructing the sources and mixing of deep water masses.

### 8.16.3.3 Oxygen Isotopes in Benthic Foraminifera

The $\delta^{18}O$ of foraminiferal calcite reflects the $\delta^{18}O$ of the water in which it calcified and the temperature of calcification. Since both temperature and $\delta^{18}O$ of seawater are imprinted on a water mass at the surface, the $\delta^{18}O$ of foraminifera is a conservative tracer that can be used to determine the sources and mixing of water masses in the deep ocean. The use of $\delta^{18}O$ as a conservative tracer does not require the separation of the temperature and $\delta^{18}O$/salinity components of the foraminiferal $\delta^{18}O$ signal. Despite the fact that oxygen isotope measurements are routinely gathered simultaneously with carbon isotopes, the use of $\delta^{18}O$ as a tracer for ocean circulation has lagged behind the use of $\delta^{13}C$. Zahn and Mix (1991) showed that gradients in deep water foraminiferal $\delta^{18}O$ are small due to the fact that NADW is warmer than Antarctic Bottom Water (which would lead to lower foraminiferal $\delta^{18}O$), while $\delta^{18}O$ of NADW is higher (counteracting the temperature effect). They also demonstrated that there are significant issues with interlaboratory and interspecies calibration that interfere with the effective use of this tracer. However, recent studies have shown that *Cibicidoides* and *Planulina* do a good job of tracking calcification temperature (Figure 5: Duplessy et al., 2002; Lynch-Stieglitz et al., 1999a). While early studies showed that *Cibicidoides* $\delta^{18}O$ did not reflect equilibrium calcification (O’Neil et al., 1969), later determinations of equilibrium calcification are consistent with the observed values for core-top *Cibicidoides* (Kim and O’Neil, 1997; Lynch-Stieglitz et al., 1999a). Some of the interlaboratory calibration problems arise because most mass spectrometry labs routinely calibrate using a carbonate standard (NBS-19) that can be up to 6% lower in $\delta^{18}O$ than benthic foraminifera from the deep ocean during glacial periods. Care must be taken to calibrate regularly with standards spanning a large range of isotopic ratios and appropriate corrections must be made for many mass spectrometers (e.g., Ostermann and Curry, 2000). While the range of foraminiferal $\delta^{18}O$ in the deep ocean is small, the foraminifera seem to be able to record these differences well. Mackensen et al. (2001) and Matsumoto et al. (2001) also showed regionally coherent patterns of benthic foraminiferal $\delta^{18}O$ in the Southern Ocean. Lund et al. (2011) used vertical profiles of benthic foraminiferal $\delta^{18}O$ to constrain the relative strength of transport and mixing in the deep glacial Atlantic. With careful attention to laboratory calibration, deep and intermediate water foraminiferal $\delta^{18}O$ reconstructions show great promise as a conservative tracer for ocean circulation.

### 8.16.3.4 Clumped Isotopes

There has been much recent progress in developing clumped-isotope thermometry in carbonates. The enrichment of $^{13}C$–$^{18}O$ bonds in carbonates relative to that expected from a random distribution of these isotopes of carbon and oxygen ($\Delta_{c2}$) appears to be strongly temperature dependent (Ghosh et al., 2006). This relationship appears to hold for both the calcite in foraminifera (Tripati et al., 2010) and the aragonite in deep-sea corals (Thiagarajan et al., 2011). A thermodynamically based paleothermometer from oceanic carbonates which would allow for both temperature reconstructions and, when combined with $\delta^{18}O$ of the calcite, water column $\delta^{18}O$ reconstruction constitutes a major development. However, the precision of this method is insufficient at present to distinguish the temperatures of deep water masses, and more work is needed.

### 8.16.3.5 Carbon Isotope Air–Sea Exchange Signature

Because the $\delta^{13}C$ in seawater is influenced by both biological cycling and air–sea exchange, one can use data on co-occurring

![Figure 5](image-url)  

**Figure 5** The isotopic fractionation, expressed as the difference between the $\delta^{18}O$ of foraminiferal calcite and the $\delta^{18}O$ of seawater (converted from SMOW to a PDB-like (Peedee Belemnite) scale by subtracting 0.27, in accordance with paleoceanographic convention) versus temperature of calcification. *Cibicidoides* and *Planulina* from Lynch-Stieglitz et al. (1999a) (small pluses, dashed line is a linear regression through these data) and Duplessy et al. (2002) (circles, solid line is a linear regression through these data) are shown along with results from the inorganic precipitation experiments of Kim and O’Neil (1997) (triangles).
nutrients (which are influenced only by biological cycling) to isolate δ13C differences that arise from air–sea exchange (Lynch-Stieglitz and Fairbanks, 1994; Oppo and Horowitz, 2000; Rickaby and Elderfield, 2005; Zahn and Stuber, 2002). Because the air–sea exchange signature is reset only at the surface, it is a conservative tracer for ocean circulation. Today, newly formed NADW and Weddell Sea Bottom Water have δ13C air–sea exchange signatures that differ by 0.8‰ (Lynch-Stieglitz et al., 1995). However, the patterns in the air–sea exchange signature are only as good as the contributing δ13C and Cd/Ca data, and areas where either dissolution or productivity overprints may be a problem must be avoided, limiting the use of this tracer.

8.16.4 Neodymium Isotope Ratios

Deep water masses of the ocean have distinctive neodymium isotope ratios that are recorded in manganese nodules (Albarede and Goldstein, 1992; Albarede et al., 1997), dispersed manganese–iron oxides in deep-sea sediment (e.g., Gutjahr et al., 2007; Rutberg et al., 2000), and iron oxides on fish teeth (Martin and Haley, 2000) and in foraminifera (e.g., Klevenz et al., 2008; Vance et al., 2004). Seawater is thought to acquire its Nd isotope signal at the ocean boundaries, via surface inputs (dust and riverine) and exchange with sediment (Frank, 2002; Goldstein and Hemming, 2003; Lacan and Jeandel, 2005). Away from the boundaries, especially in the deep Atlantic where the residence time of water is short compared to the residence time of Nd, the isotopes of this element can serve as a quasiconservative tracer (Piepgras and Wasserburg, 1980). Nd isotope ratios in NADW are low, reflecting the addition of Nd from continentally derived detrital material, which is predominantly old, whereas Nd isotope ratios in the North Pacific are high, reflecting input from recent volcanic activity. In regions where there is active mixing between these water masses (the Atlantic Ocean and the Southern Ocean), both seawater and the Fe–Mn oxyhydroxides that precipitate from it have intermediate values, as is the case for the nutrient and conservative water mass tracers.

8.16.5 Circulation Rate Tracers

The water mass tracers discussed above can be used to assess the sources of subsurface water masses and the mixture of waters from different sources. However, this information can be used only to assess the relative rates of renewal of these deep water masses from the various source regions (e.g., Legrand and Wunsch, 1995). There are several geochemical techniques that can be used to assess the rates of ocean circulation.

8.16.5.1 Radiocarbon

Carbon-14 (radiocarbon) is produced in the atmosphere by cosmic rays and decays with a half-life of 5730 years. Natural radiocarbon levels in the ocean are highest at the surface where they partially equilibrate with atmosphere. Deepwater concentrations are highest in newly formed NADW and decrease to the lowest values in the deep Pacific where the deep waters have been out of contact with the atmosphere for longest (Stuiver et al., 1983). Benthic foraminifera record the radiocarbon concentrations of the deep water in which they grew, but the 14C in the foraminifera decays over time, with >99% gone after 40,000 years. In order to reconstruct the seawater radiocarbon content at the time the foraminifera were living, radiocarbon measurements can be made on benthic and planktonic foraminifera from the same interval in the core (Broecker et al., 1988, 1990; Shackleton et al., 1988) in order to determine the age of the benthic foraminifera. However, the radiocarbon content of the planktonic foraminifera will reflect not only their age but also the initial radiocarbon content of the near-surface water in which they grew. The initial radiocarbon in surface and near-surface waters can be significantly less than expected for equilibrium with the atmosphere due to the relatively long time required for carbon isotopic equilibrium between the surface ocean and atmosphere. One must also account for the fact that the radiocarbon content in the atmosphere changes with time, a change which impacts the initial radiocarbon content of surface waters as well. This means that deep waters at a given location may have initially formed under a different atmospheric radiocarbon burden than that recorded by codeposited planktonic foraminifera (Adkins and Boyle, 1997).

Also complicating the use of concurrent benthic and planktonic radiocarbon concentrations to assess water mass radiocarbon is the necessary assumption that benthic and planktonic foraminifera from the same depth interval are actually the same age. If the peak abundances of planktonic and benthic foraminifera occur at different depths in a core, bioturbation can introduce a spread in the planktonic–benthic ages in cores with low accumulation rates, which is unrelated to changes in bottom water age (Broecker et al., 1999; Peng et al., 1977). While these problems can be overcome by using high-sedimentation-rate cores (e.g., Keigwin and Schlegel, 2002), the widespread use of this technique has been limited primarily by the identification of suitable cores with high enough foraminiferal abundances for accurate radiocarbon determinations. Sediments with high accumulation rates tend either to have low foraminiferal abundances (due to dilution by terrigenous material) or to be in high-productivity regions of the ocean where surface waters are expected to be far from equilibrium with the atmosphere and variable through time.

Another approach to constraining the age required to extract seawater 14C content from benthic foraminifera is to use stratigraphic correlation. Numerous cores with high accumulation rates record seawater characteristics such as surface temperature or oxygen content that vary in concert with either Greenland or Antarctic air temperatures, as recorded by ice cores. Assuming the oceanic changes are nearly synchronous with the polar records, the ice core chronologies (which are independent of 14C) can be applied to the sediments and therefore to the benthic foraminifera (Skinner and Shackleton, 2004). This approach is mainly limited by the quality of the correlation and the assumption of synchronicity.

A third way to measure the deepwater radiocarbon ventilation age in the past is by using deep-dwelling benthic corals (Adkins et al., 1998; Goldstein et al., 2001; Mangini et al., 1998). Here, the age of the coral can be independently determined using uranium series dating, allowing the radiocarbon
content of the coral to be used to determine the radiocarbon content of deep water at the time the coral grew. This method is unaffected by bioturbation but is currently limited by the availability of deep-sea benthic corals.

Changes in the ventilation of the ocean can also be assessed by looking at how the 14C content of the atmosphere has changed through time (e.g., Hughen et al., 1998). The atmospheric 14C content is controlled both by the rate of 14C production in the atmosphere from cosmic ray bombardment and the rate at which 14C is transferred into the ocean. While a decrease in the ventilation of the ocean causes a buildup of radiocarbon in the atmosphere, one must also account for changes in production (believed to be dominated by changes in geomagnetic field strength) before interpreting the atmospheric radiocarbon changes in terms of ocean circulation (Hughen et al., 1998; Lal and Charles, 2007).

### 8.16.5.2 231Pa/230Th Ratio

Both protactinium and thorium are produced in the water column and scavenged by particles onto the seafloor. Because protactinium is scavenged less efficiently by marine particles (Anderson et al., 1983), much of the protactinium produced in the Atlantic Ocean is transported to the Southern Ocean by deep waters before it is scavenged onto the seafloor. This produces a low (below production) 231Pa/230Th ratio in Atlantic Ocean sediments and a high 231Pa/230Th ratio in Southern Ocean sediments (Yu et al., 1996). Reconstruction of the 231Pa/230Th ratio suggests that this pattern of Pa export persisted in glacial times, and a low deepwater residence time for the LGM Atlantic has been inferred (Yu et al., 1996). Time series of Pa/Th from the North Atlantic have been used to infer changes in circulation over the deglaciation (Gherardi et al., 2009; McManus et al., 2004).

However, the 231Pa/230Th ratio in sediments depends on the complex interplay between deep water movement and the differential scavenging of the two elements throughout the ocean basin (Marchal et al., 2001; Siddall et al., 2007). The scavenging of Pa and Th depends both on the composition of the particles and the particle flux. Biogenic opal fractions Th from Pa much less effectively than other particle types; as a consequence, ratios in Southern Ocean sediments will be very sensitive to particle composition (Luo and Ku, 1999; Yu et al., 2001). While the Atlantic 231Pa/230Th fluxes are low and today predominantly reflect the short residence time of deep waters in this basin, the Pacific ocean, 231Pa/230Th ratios are most sensitive to particle flux, with higher ratios where the scavenging is most intense at the boundaries (Yu et al., 2001). Robust paleocirculation reconstructions from 231Pa/230Th ratios will, in general, require detailed knowledge of particle fluxes and composition (Gil et al., 2009; Lippold et al., 2009) as well as good spatial coverage from a number of sediment cores (Burke et al., 2011; Siddall et al., 2007).

### 8.16.5.3 Geostrophic Shear Estimates from δ18O in Benthic Foraminifera

Physical oceanographers routinely use the distribution of density in the ocean to help quantify ocean circulation. A balance between the pressure gradient force and Coriolis term (geostrophic balance) is assumed. Velocity can then be calculated from density information using either a measured or assumed velocity at a reference level or by combining the geostrophic balance with other constraints, such as conservation of tracer flow across a section. This approach has also been applied to paleoceanography by using vertical density profiles reconstructed from the oxygen isotopic composition of foraminiferal calcite (Lynch-Stieglitz et al., 1999a).

The δ18O from calcite tests of benthic foraminifera preserved in ocean sediments can be used to estimate upper ocean density because both the δ18O of calcite (δ18Ocalcite) and seawater density increase with increasing salinity or decreasing temperature (Lynch-Stieglitz et al., 1999a). For times in the geologic past, the ability to reconstruct density from δ18Ocalcite is most limited by knowledge of the relationships between δ18Owater and salinity as well as the relationships between temperature and salinity. However, it is the gradients in density that are used for geostrophic calculations, and the reconstructed density gradients are less affected by these limitations than the density itself.

This technique has been used to reconstruct the flow of the Gulf Stream in the Florida Straits by reconstructing vertical density profiles on either side of this current (Lund et al., 2006; Lynch-Stieglitz et al., 1999b, 2009, 2011). Perhaps more useful for reconstruction of the large-scale ocean circulation is the fact that the density difference between the eastern and western margins of the ocean basins reflects the strength of the geostrophic overturning circulation (Lynch-Stieglitz, 2001; Lynch-Stieglitz et al., 2006).

At present, the vertical density structure for the past ocean can be reconstructed using benthic foraminifera only where the seafloor intersects the upper water column, at ocean margins, islands, and shallow seamounts. Although planktonic foraminifera calcify at various depths within the upper water column, we have no way to reconstruct quantitatively the depth at which they calcified. However, the oxygen isotopic composition of deep-dwelling planktonic foraminifera can be used to reconstruct the spatial pattern and direction of upper ocean flows (Bostock et al., 2006; LeGrande and Lynch-Stieglitz, 2007; Matsumoto and Lynch-Stieglitz, 2003; Ortiz et al., 1997).

### 8.16.6 Nongeochemical Tracers of Past Ocean Circulation

While this is a geochemistry volume, any review of tracers of past ocean circulation would be incomplete without mention of some of the sedimentological and paleontological approaches to reconstructing past ocean flow. Sediment grain size has been used to reconstruct current intensity since the 1970s (Ledbetter and Johnson, 1976). More recent grain size studies emphasize the mean size of the ‘sortable silt’ fraction (>10 μm), which is least likely to display cohesive behavior (McCave et al., 1995). Stronger currents show larger sortable silt size due to changes in both deposition and winnowing with current speed. The magnetic properties of sediments (concentration of magnetic particles) have been used to infer flow paths and strength of the overflows in the North Atlantic (Ballini et al., 2006; Kissel et al., 1999).

Benthic foraminiferal assemblages have been related to distinct deep water masses and have been used for tracking these
water masses during the past (Schnitker, 1974; Streeter, 1973). In more recent years, it has been determined that the deep-sea benthic assemblage responds strongly to the flux of organic material from overlying surface productivity (e.g., Loubere, 1991; Miller and Lohmann, 1982), limiting its use as a water mass tracer to low-productivity regions (Schnitker, 1994).

8.16.7 Ocean Circulation during the LGM

Some of these methods have been applied to examine ocean circulation throughout the Cenozoic era, and others to examine century-scale changes during the very recent past. However, all of the methods have been used to look at ocean circulation...

Figure 6 (a) Modern distribution of the major nutrient PO₄ in the western Atlantic (Conkright et al., 2002) and LGM distributions of (b) δ¹³C (Bickert and Mackensen, 2004; Curry and Oppo, 2005), and (c) Cd (Marchitto and Broecker, 2006) inferred from benthic foraminifera. Reproduced from Lynch-Stieglitz J, Adkins JF, Curry WB, et al. (2007) Atlantic meridional overturning circulation during the Last Glacial Maximum. Science 316: 66–69, with permission from the American Association for the Advancement of Science.
during the LGM (about 19,000–23,000 years ago) and thus have their maximum geographic coverage during this time. Here, the picture of ocean circulation that these techniques have produced for the LGM is briefly examined. The various paleoceanographic methods outlined above each have their advantages and pitfalls, times and places where they should work well, and environments where variables other than ocean circulation complicate the interpretations. There is no single ocean circulation scenario for the LGM that is consistent with all of the available data from all of the tracers. In the following description, regionally coherent signals are weighted more heavily than data from isolated sediment cores. Data in regions where the complications may overwhelm the signal (e.g., high-productivity regions for $\delta^{13}$C data, the low-carbonate very deep ocean for Cd data) are weighted less heavily. A quantitative description of past ocean circulation will require many more data and better understanding of the tracers, combined with better techniques for dealing with the kinds of uncertainties and multiple processes that affect the paleoceanographic proxies.

Past circulation in the Atlantic Ocean basin has been reviewed by Lynch-Stieglitz et al. (2007). The most prominent feature of the glacial Atlantic is a water mass divide at about 2-km water depth. Both Cd/Ca and $\delta^{13}$C distributions suggest a strong stratification in the North Atlantic Ocean, with a low nutrient, high-$\delta^{13}$C water mass (often called Glacial North Atlantic Intermediate Water, GNAIW) occupying depths down to about 2000 m and a high nutrient, low-$\delta^{13}$C water mass of southern origin underneath (Figure 6; e.g., Boyle and Keigwin, 1987; Curry and Oppo, 2005; Duplessy et al., 1988; Marchitto and Broecker, 2006; Oppo and Lehman, 1993). An expansion of southern-source waters into the deep Atlantic is supported by higher Nd isotope ratios (Roberts et al., 2010) and lower radiocarbon concentrations (Keigwin, 2004; Robinson et al., 2005). The existence of these two distinct water masses despite the mixing processes that would tend to blend them suggests that one or both were renewed relatively rapidly (Curry and Oppo, 2005), although reduced mixing might have played a role as well (Lund et al., 2011).

It also seems clear at this point that the LGM $^{231}$Pa/$^{230}$Th ratio in Atlantic sediments was comparable to those we find today (Gherardi et al., 2009; McManus et al., 2004; Yu et al., 1996). This too would argue against a much slower circulation of deep waters in the Atlantic Ocean during glacial times. The cross basin contrast in $\delta^{18}$O of benthic foraminifera, however, was much smaller (Figure 7; Lynch-Stieglitz et al., 2006). This would suggest that the glacial circulation was not simply a shallower version of today’s meridional overturning circulation, whereby surface and intermediate waters travel into the North Atlantic to compensate the export of NADW.

Less is known about the state of the LGM Pacific Ocean, largely because poor carbonate preservation in the Pacific Ocean limits the availability of cores with benthic foraminifera. Under saturation with respect to calcium carbonate in the Pacific also complicates the interpretation of the trace metal-based methods that suffer from carbonate ion effects. However, as in the Atlantic, the carbon and oxygen isotope data suggest a deep hydrographic boundary at about 2000-m water depth (Herguera et al., 1992, 2010; Keigwin, 1998; Matsumoto et al., 2002; Mix et al., 1991), with a low-$\delta^{13}$C, high-$\delta^{18}$O water mass below this divide and a high-$\delta^{13}$C, low-$\delta^{18}$O water mass above this divide. Like today, the lowest $\delta^{13}$C waters in the Pacific are in the far north but at deeper depths (>2000 m water depth) than today (Figure 8; Herguera et al., 2010; Matsumoto et al., 2002). There is now considerable evidence that intermediate waters in the North Pacific were

![Figure 7](image-url)
more oxygen-rich during the LGM (van Geen et al., 2003), consistent with the δ¹³C-based scenario of waters more depleted in nutrients at intermediate depths. The LGM Indian Ocean is also characterized by a benthic divide at about 2000 m, with higher δ¹³C and lower Cd reconstructed for the upper water mass (Boyle et al., 1995; Kallel et al., 1988; McCorkle et al., 1998). This deep hydrographic boundary is also seen off southern Australia (Lynch-Stieglitz et al., 1996).

For both the upper and lower water masses, there is a general progression from highest δ¹³C in the North Atlantic to intermediate values in the South Atlantic and South Australia to progressively lower δ¹³C values in the North Pacific (excluding the deepest Southern Ocean). Goldstein et al. (2001) also argue, based on limited glacial-age radiocarbon data, that the modern progression of youngest deep waters in the North Atlantic, intermediate values in the Southern Ocean, and oldest values in the deep Pacific was preserved during glacial times. The δ¹⁸O values in the upper water mass are similar from North Atlantic to North Pacific, within the considerable scatter in the data. Whether or not the GNAIW reached the Pacific or there was another source of nutrient-poor upper deep water forming in the North Pacific remains a source of debate (Keigwin, 1998; Lynch-Stieglitz et al., 1996; Matsumoto et al., 2002; Oppo and Horowitz, 2000), although box model results do argue for GNAIW export out of the Atlantic (Sigman et al., 2003).

Finally, there appears to be an even denser water mass that occupies the deepest portion of the Southern Ocean. This deep water has high δ¹⁸O values and very low δ¹³C, with lowest δ¹³C values (about −1‰) observed in the Atlantic sector of the Southern Ocean (Figure 6). While there was some thought that the low δ¹³C values may reflect a productivity-related overprint (Mackensen et al., 1993), a convincing case has been made that the δ¹³C values are regionally coherent and unrelated to other measures of overlying productivity (Mackensen et al., 2001; Ninnemann and Charles, 2002). Nd isotope values within this water mass have less of a North Atlantic signature than today (Rutberg et al., 2000). Unfortunately, there is not enough spatial coverage at present to document convincingly the extent of this deep water mass in the Indian and Pacific sectors of the Southern Ocean. The Cd/Ca data are even more limited than the δ¹³C data in the Southern Ocean, due largely to low foraminiferal abundance and potential overprints from saturation state; these data nonetheless suggest that the low δ¹³C values are not accompanied by a significant increase in nutrients (Rosenthal et al., 1997a). This suggests that reduced air–sea exchange may have been responsible, at least in part, for the lower δ¹³C in the deep Southern Ocean relative to the rest of the deep LGM ocean (Marchitto and Broecker, 2006; Toggweiler, 1999).

Reconstructions of salinity from pore water [Cl] (Adkins et al., 2002) suggest that this deep Southern Ocean water mass was considerably saltier than deep waters in the Atlantic and Pacific basins (Figure 9). Adkins et al. (2002) also argue that pore water δ¹⁸O suggests that this dense, salty water is produced as a by-product of sea ice formation. Furthermore, there is limited evidence that this water mass had very low radiocarbon levels, indicating isolation from the atmosphere and very sluggish ventilation rates (Skinner et al., 2010). It is therefore thought that this deep southern water mass was able to store significant amounts of carbon and thus contribute to lower glacial atmospheric CO₂ levels (e.g., Sigman and Boyle, 2000; Toggweiler, 1999). While this capacity would have been greatly enhanced if the water mass filled all ocean basins up to the ~2-km LGM nutricline, the most extreme characteristics (lowest δ¹³C, highest salinity) appear limited to the Southern Ocean, suggesting other deep water sources in the world ocean.

![Figure 9](image-url) Estimates of LGM potential temperature (theta) and salinity from pore water profiles (Adkins et al., 2002). The modern and LGM mean salinities (assuming 125 m of eustatic seawater change) are indicated with the thin and bold arrows, respectively. All deepwater temperature estimates for the LGM are close to the freezing point of seawater (−1.98 °C). The data thus indicate a cold, high-salinity water mass in the deep Southern Ocean. Reproduced from Adkins JF, McIntyre K, and Schrag DP (2002) The salinity, temperature, and δ¹⁸O of the glacial deep ocean. Science 298: 1769–1773, with permission from the American Association for the Advancement of Science.)
8.16.8 Conclusions

Considerable strides have been made in the last twenty-five years in developing methods to reconstruct past ocean circulation. There are now a number of different geochemical methods that can yield information on paleo-ocean flow. However, as the use of each method develops, it becomes clear that there are multiple processes affecting both the tracers themselves and their imprint into the sediments. We are still just beginning to understand most of these methods and there are limited amounts of data available. A full understanding of these factors and how to separate out their effects, combined with multiple measurements using methods affected by different processes, can ultimately lead to well-constrained reconstructions of past ocean circulation. However, even now, these methods are capable of giving us a tantalizing glimpse of the ocean during the LGM, when the water masses were arranged in a distinctly different pattern than they are today.

References


Curry WB and Oppo DW (2005) Glacial water mass geometry and the distribution of $\delta^{14}$C of $\Sigma$CO$_2$ in the western Atlantic Ocean, Paleoceanography 20: PA1017.


