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# Nutrient Proxies

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## Introduction

The distribution of marine nutrients in the past is of interest to paleoceanographers for two main reasons. First, nutrients control oceanic primary productivity, which is believed to be an important control on atmospheric $CO_2$ on glacial–interglacial timescales. Second, nutrients are useful tracers of deep-water masses, and changes in the modes and locations of deep-water formation are believed to have fundamentally influenced Quaternary climates. Reconstruction of paleonutrients relies mainly on five proxies that are recorded in marine sediments: foraminiferal $\delta^{13}C$, Cd/Ca, Ba/Ca, and Zn/Ca; and organic matter $\delta^{15}N$.

## Carbon-13

### Systematics

Dissolved inorganic carbon (DIC), also known as $\Sigma CO_2$, is composed of three dominant species in seawater: dissolved carbon dioxide ($CO_2(aq)$), bicarbonate ($HCO_3^-$), and carbonate ($CO_3^{2-}$), having relative concentrations on the order of 1%, 90%, and 10%, respectively. Furthermore, carbon has two stable isotopes: $^{12}C$ (98.9%) and $^{13}C$ (1.1%). Fractionation between these two isotopes is expressed in delta notation:

$$\delta^{13}C = \left[ \left( ^{13}C/^{12}C \right)_{sample} / \left( ^{13}C/^{12}C \right)_{standard} - 1 \right] \times 1000 \quad [1]$$

where the standard is a calcium carbonate, usually referenced to the PeeDee Belemnite standard. On this scale, the $\delta^{13}C$ of DIC ranges between about $-1‰$ and $2.5‰$ in the world's oceans (Kroopnick, 1985). Photosynthetic fixation of carbon preferentially utilizes $^{12}C$ such that primary marine organic matter $\delta^{13}C$ is typically between $-20‰$ and $-30‰$. This leaves the remaining surface ocean DIC pool slightly enriched in $\delta^{13}C$. As organic matter sinks through the water column and decays, its $^{12}C$-rich carbon is regenerated along with other nutrients such as phosphate and nitrate, resulting in a water column $\delta^{13}C$ profile that is inversely correlated with these nutrients (Figure 1). If biogeochemical cycling were the only process acting on the DIC pool, $\delta^{13}C$ would decrease by about 1.1‰ for each 1 $\mu mol\ kg^{-1}$ increase in dissolved phosphate, and an oceanic range of about 3.3‰ would be possible (Lynch-Stieglitz et al., 1995). Regional differences in the $\delta^{13}C$ of marine organic matter may alter the slope of this relationship.

In addition to biogeochemical cycling, the $\delta^{13}C$ of surface ocean DIC is significantly affected by air–sea exchange of $CO_2$. If DIC were at isotopic equilibrium with atmospheric $CO_2$, it would be enriched by about 8‰ relative to the atmosphere at 20 °C. This value results from the dominance of $HCO_3^-$, which is enriched by 8.5‰ relative to the atmosphere, with smaller contributions from $CO_3^{2-}$ (6‰) and $CO_2(aq)$ ($-1‰$) (Lynch-Stieglitz et al., 1995). The enrichment for $HCO_3^-$ (and

therefore DIC) increases by about 0.1‰ per degree of cooling. However, isotopic equilibration between the surface ocean mixed layer and the atmosphere is never reached because the time required (on the order of a decade) is longer than surface ocean mixing times. The extent of equilibration may be increased through longer air–sea contact time or high winds, which would increase DIC $\delta^{13}C$. A final air–sea effect occurs in areas where there is net movement of $CO_2$ into or out of the surface ocean. Both $CO_2(aq)$ and atmospheric $CO_2$ are isotopically light compared to DIC. Regions that absorb $CO_2$ from the atmosphere, such as the low-$pCO_2$ North Atlantic, therefore experience $\delta^{13}C$ depletion. Areas that emit $CO_2$ to the atmosphere, such as the high-$pCO_2$ eastern equatorial Pacific, experience $\delta^{13}C$ enrichment. The net effect of the various air–sea exchange processes spans a surface ocean range of about 2‰ (Lynch-Stieglitz et al., 1995). In addition, the anthropogenic evolution of atmospheric $CO_2$ toward lower $\delta^{13}C$ values, known as the Suess effect, results in a progressive lowering of surface water $\delta^{13}C$ that has already propagated into the deep North Atlantic (Olsen and Ninnemann, 2010).

### Paleoceanographic Reconstruction

Reconstruction of past ocean $\delta^{13}C$ relies mainly on the calcitic ($CaCO_3$) tests of protozoa called Foraminifera. Foraminiferal calcite carbon is presumed to be derived from dissolved $HCO_3^-$, and may therefore be expected to record the $\delta^{13}C$ of DIC, in the absence of complicating biological effects. Core-top calibrations show that various taxa of benthic Foraminifera faithfully reflect the $\delta^{13}C$ of bottom water DIC (Duplessy et al., 1984). Epifaunal species are preferred for reconstructions because infaunal taxa record pore water values, which are typically lower than those of bottom waters due to organic matter remineralization (Zahn et al., 1986). However, the $\delta^{13}C$ of even epifaunal species may be lower than that of bottom waters in regions where organic matter rain rates are very high (Mackensen et al., 1993).

Benthic foraminiferal $\delta^{13}C$ provides a picture of the past distribution of deep-water masses. Biogeochemical cycling and air–sea exchange cause most surface waters, particularly those stripped of nutrients, to be more enriched in $\delta^{13}C$ compared to the deep ocean. North Atlantic Deep Water (NADW) is today formed from such low-nutrient waters, and therefore carries a high-$\delta^{13}C$ signature (Figure 2). In contrast, Antarctic Bottom Water (AABW) and Antarctic Intermediate Water (AAIW) are formed from poorly ventilated surface waters and therefore carry low-$\delta^{13}C$ signatures. Lowest $\delta^{13}C$ values are found today in the deep North Pacific, far from the well-ventilated NADW source.

Today NADW transports a large amount of heat into the North Atlantic, and past changes in its formation are believed to have strongly impacted regional climates. The most extensively studied period in this regard is the Last Glacial Maximum
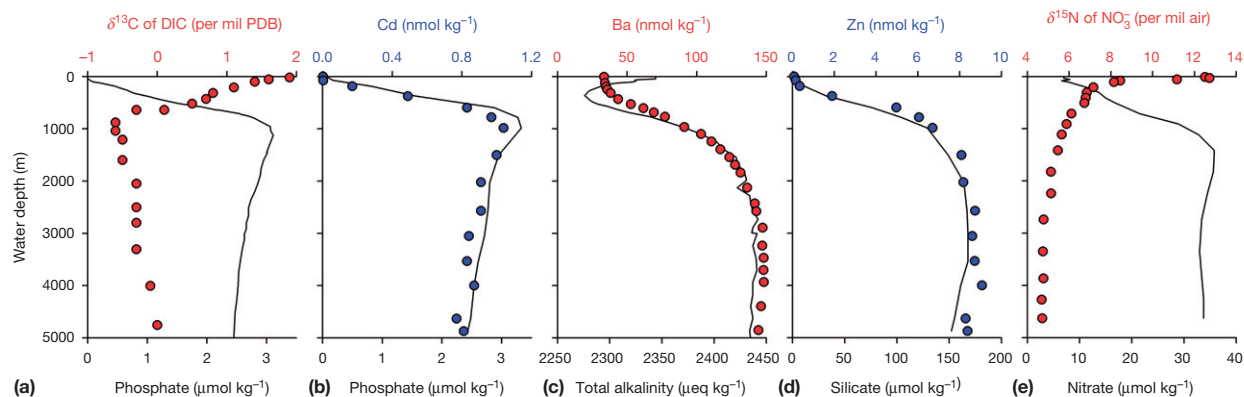
**Figure 1**  Modern seawater profiles of the main nutrient proxies. (a) $\delta^{13}C$ of DIC (Kroopnick, 1985) compared to dissolved phosphate (Broecker et al., 1982) in the central North Pacific; (b) Dissolved Cd compared to dissolved phosphate in the eastern North Pacific (Bruland, 1980); (c) Dissolved Ba (Ostlund et al., 1987) compared to total alkalinity (Broecker et al., 1982) in the central North Pacific; (d) Dissolved Zn compared to dissolved silica in the eastern North Pacific (Bruland, 1980); (e) $\delta^{15}N$ of dissolved nitrate compared to dissolved nitrate in the Indian sector of the Southern Ocean (Sigman et al., 1999).



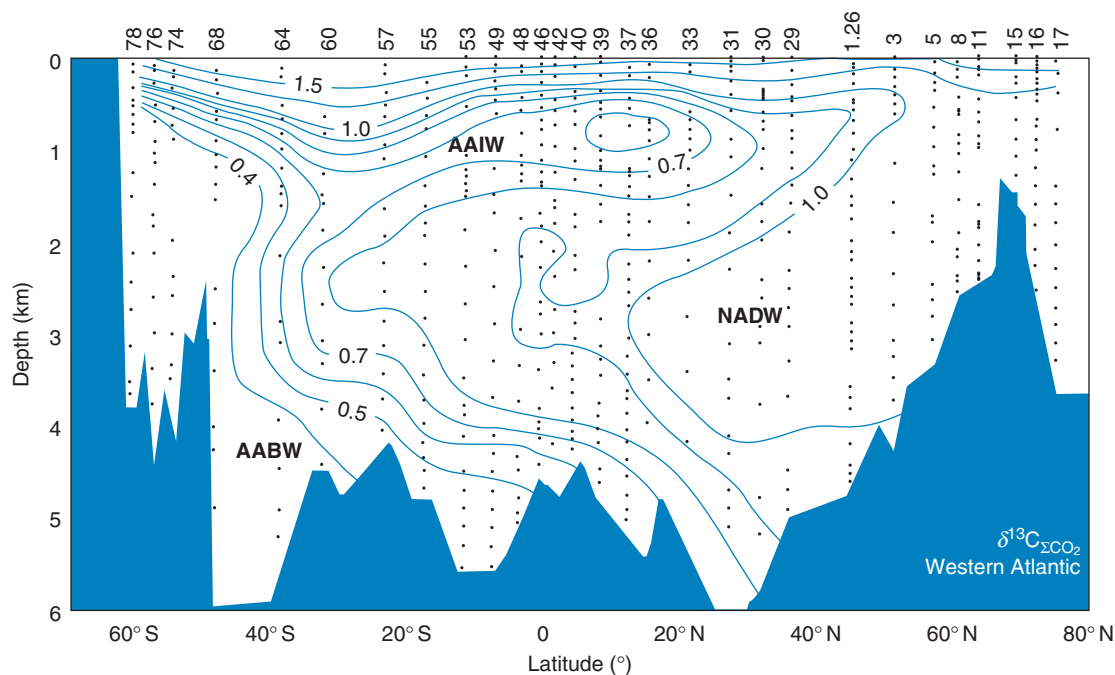**Figure 2**  Meridional section of the $\delta^{13}C$ of DIC in the western Atlantic Ocean during the 1970s (reproduced from Kroopnick PM (1985) The distribution of $^{13}C$ of $\Sigma CO_2$ in the world oceans. *Deep-Sea Research* 32: 57–84). Major water masses are indicated, and the numbers at the top refer to oceanographic cruise stations. Preindustrial $\delta^{13}C$ values were slightly higher at the sea surface and in the North Atlantic, shallower than $\sim 2$ km (Olsen and Ninnemann, 2010).

(LGM, $\sim 20$ ka BP), for which meridional Atlantic $\delta^{13}C$ sections have been created. Such reconstructions suggest that low-$\delta^{13}C$ AABW expanded into the North Atlantic and that its boundary with high-$\delta^{13}C$ NADW shoaled from a water depth of 4 to $\sim 2$–3 km (**Figure 3**; Curry and Oppo, 2005; Duplessy et al., 1988). This reorganization was long assumed to be due to a reduction in the formation rate of NADW, but other more rate-sensitive proxies have since underscored the fact that paleonutrients constrain only the spatial extent of water masses and not their fluxes. The glacial form of NADW, dubbed Glacial North

Atlantic Intermediate Water (GNAIW), likely formed significantly southward of its modern deep convection regions. This migration may therefore have cooled high latitudes even if formation rates were not reduced. On longer Quaternary timescales, the $\delta^{13}C$ gradient between the North Atlantic and Pacific has been used to monitor NADW extent. As during the LGM, NADW volume was apparently reduced during all Northern Hemisphere glaciations.

One interesting aspect of the glacial $\delta^{13}C$ distribution is that the lowest values occurred in the deep Southern Ocean, rather
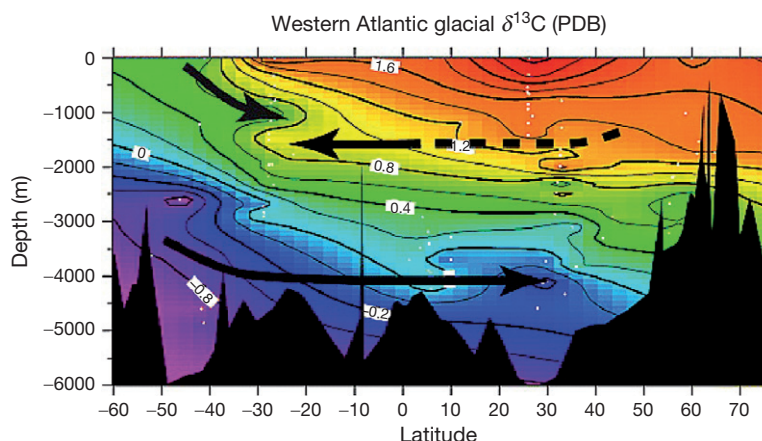
**Figure 3** Meridional section of benthic foraminiferal $\delta^{13}$C for the LGM western Atlantic (Curry and Oppo, 2005). Arrows indicate presumed flow directions of AAIW, GNAIW, and AABW, and small white dots show locations of sediment cores used in the reconstruction.

than in the North Pacific as they do today. Glacial production of a North Pacific Deep Water could explain the pattern, but such a water mass is difficult to document, in part because of the poor preservation of calcite in the North Pacific. Some have attributed low Southern Ocean $\delta^{13}$C values to an organic matter microhabitat effect (Mackensen et al., 1993), noting that Cd/Ca (see Section 'Cadmium') does not support a very high-nutrient glacial AABW (Boyle, 1992). However, the relative uniformity of glacial $\delta^{13}$C in the Atlantic sector of the Southern Ocean suggests that the values are probably reliable (Ninnemann and Charles, 2002). Independent estimates of deep sea salinity and temperature require glacial AABW to have been particularly dense, so perhaps GNAIW avoided extensive mixing in the Southern Ocean en route to the North Pacific, leaving AABW anomalously low in $\delta^{13}$C. Reduced vertical mixing between these two water masses is supported by an enhanced oxygen isotope vertical gradient in the deep Atlantic (Lund et al., 2011).

The $\delta^{13}$C pattern in the glacial Atlantic implies that there was a net shift of DIC from the upper ocean into the deep ocean. A comparable $\delta^{13}$C shift has been documented in the glacial Indian Ocean, and although data coverage in the Pacific is comparatively poor, an intermediate- to mid-depth $\delta^{13}$C gradient is generally supported (Herguera et al., 2010). Glacial DIC deepening may have acted to lower atmospheric $CO_2$, through both the direct effect of decreased surface ocean DIC and the compounding effect of increased oceanic alkalinity due to greater dissolution of seafloor $CaCO_3$ (Sigman et al., 2010).

Reconstruction of surface water $\delta^{13}$C appears to be more complicated than deep-water work because of confounding influences on planktonic foraminiferal $\delta^{13}$C (Keigwin and Boyle, 1989; Spero, 1998). For example, culture work shows that photosymbionts, respiration, and carbonate chemistry affect the $\delta^{13}$C of various taxa. Nevertheless, planktonic–benthic comparisons may record past shifts of DIC partitioning between the upper and deep oceans, with the implications for atmospheric $CO_2$ mentioned earlier (Shackleton et al., 1983). A widespread planktonic $\delta^{13}$C minimum during the last deglaciation may represent the release of DIC that was

stored in the isotopically light and isolated AABW during glacial times (Spero and Lea, 2002).

On glacial–interglacial timescales, the partitioning of carbon between land and ocean must also be considered. It is estimated from benthic Foraminifera that the average $\delta^{13}$C value of the world's oceans was 0.3‰ lower during the LGM (Duplessy et al., 1988). This estimate is subject to considerable error because of the scarcity of data in some regions, particularly the North Pacific. Assuming an average terrestrial carbon isotopic composition of $-25$‰, the glacial lowering could be explained by a transfer of 400–500 Gt ($10^{15}$ g) of carbon from land into the ocean, or about 20% of the terrestrial biomass (Crowley, 1995). Independent reconstructions of the LGM terrestrial biosphere, based on paleoecological data, argue for a greater reduction, by up to two or three times that inferred from mean ocean $\delta^{13}$C. Factors that might reconcile these disparate estimates include glacial carbon storage on exposed continental shelves or in isotopically light methane hydrates.

## Trace Metals: Cadmium, Barium, and Zinc

Numerous dissolved trace elements in the ocean exhibit vertical profiles that resemble those of nutrients. That is, they are at low concentrations in surface waters and at greater concentrations at depth. In some cases, this behavior is linked to the element's importance as a micronutrient. For example, iron is essential for the synthesis of chlorophyll and various algal proteins and is the limiting nutrient in some regions of the ocean. In other cases, nutrient-like behavior may result simply from adsorption onto particulate organic matter in the photic zone and co-remineralization in the deep sea. Regardless of biogeochemical mechanisms, such elements may be useful as nutrient and water mass tracers. Paleoreconstruction relies on the fact that various elements are incorporated into foraminiferal calcite during precipitation. In particular, divalent cations are believed to substitute for calcium in the calcite crystal matrix. Three divalent trace metals have been developed as paleonutrient tracers: cadmium (Cd), barium (Ba), and zinc (Zn).

## Cadmium

Dissolved Cd has an oceanic distribution very similar to that of the major nutrient phosphate (**Figure 1**). Both are nearly completely removed from most surface waters and regenerated at depth, with an intermediate-depth concentration maximum near 1 km. Cd therefore behaves like a labile (easily reminer-alized) nutrient, and its concentration increases about fivefold between the deep North Atlantic and North Pacific. Although Cd has been linked to at least one important algal metalloen-zyme, it is not clear if this use is sufficient to explain its ocean-wide nutrient-like behavior. The global correlation between Cd and phosphate follows a slight curve that may be explained by preferential uptake of Cd over phosphate by particulate or-ganic matter (Elderfield and Rickaby, 2000).

Benthic foraminiferal Cd/Ca ratios reflect seawater Cd con-centrations (Boyle, 1992). The relationship between foraminif-eral Cd/Ca and seawater Cd is expressed in terms of the partition coefficient:

$$D_{Cd} = (Cd/Ca)_{foram}/(Cd/Ca)_{seawater} \qquad [2]$$

Calcitic benthic foraminiferal $D_{Cd}$ varies with water depth, from $\sim 1.3$ in the upper ocean to 2.9 below 3 km. The aragonitic benthic foraminifer *Hoeglundina elegans* has a $D_{Cd}$ of 1.0, invari-ant with depth. Calcitic partition coefficients also appear to be reduced in waters that are very undersaturated with respect to calcite, such as in the deep Pacific (McCorkle et al., 1995).

Cd/Ca generally supports $\delta^{13}C$ observations indicating that low-nutrient NADW was less extensive in the glacial Atlantic Ocean and was present as the shallower GNAIW (**Figure 4**; Boyle and Keigwin, 1987; Marchitto and Broecker, 2006). A notable difference between the two proxies is the already mentioned deep Southern Ocean discrepancy, where glacial $\delta^{13}C$ shows very low values in contrast to Cd/Ca, which is similar to the current value. An undersaturation effect on Cd/ Ca and/or a microhabitat effect on $\delta^{13}C$ might explain some of the difference. Alternatively, large-scale changes in deep-water ventilation might have decoupled the two tracers such that AABW was depleted in $\delta^{13}C$ without being significantly enriched in Cd.

The Southern Ocean problem highlights the fact that be-cause $\delta^{13}C$ and Cd behave somewhat differently in the modern ocean, unique information may be derived from paired measurements that is not available from either tracer alone. Specifically, air–sea exchange affects $\delta^{13}C$ but not Cd, so com-bining the two can potentially reveal past air–sea processes (Lynch-Stieglitz and Fairbanks, 1994). Paired measurements from various regions of the glacial ocean suggest that different deep-water masses had distinct air–sea signatures, allowing for the separation of biogeochemical aging and water mass mix-ing. LGM Atlantic observations may be largely explained by mixing between well-ventilated GNAIW and poorly ventilated AABW (Marchitto and Broecker, 2006).

Planktonic Foraminifera incorporate Cd with a similar range of partition coefficients as benthics (Delaney, 1989), but less paleoceanographic work has been done with plank-tonics. Cd/Ca from a polar species suggests that LGM nutrient levels in the high-latitude North and South Atlantic were not much different from today, arguing against changes in NADW and AABW end member properties as explaining the deep sea record (Keigwin and Boyle, 1989). Temperature appears to affect the incorporation of Cd in at least one planktonic species (Rickaby and Elderfield, 1999), and correction for this influ-ence implies that glacial Southern Ocean surface nutrient levels were elevated south of the modern Polar Front, but relatively unchanged north of it (Elderfield and Rickaby, 2000), seem-ingly in contradiction with $\delta^{15}N$ data (see Section 'Nitrate Utilization').

## Barium

Dissolved Ba is moderately depleted in surface waters and reaches maximum concentrations below $\sim 2$ km (**Figure 1**). Its distribution resembles that of alkalinity, but the association is coincidental (Lea and Boyle, 1989). Ba is removed from shallow waters mainly by barite formation in decaying organic matter, while alkalinity is removed mainly by $CaCO_3$ forma-tion. Both are regenerated at depth as their carrier phases dissolve, and deep-water masses have characteristic Ba and alkalinity values, with Ba increasing about threefold between the deep North Atlantic and North Pacific. Due to its refractory (less easily remineralized) behavior, Ba may offer information that is distinct from the more labile Cd. Ba is incorporated into several taxa of calcitic benthic Foraminifera with a partition coefficient of $\sim 0.4$ (Lea and Boyle, 1989), and there is
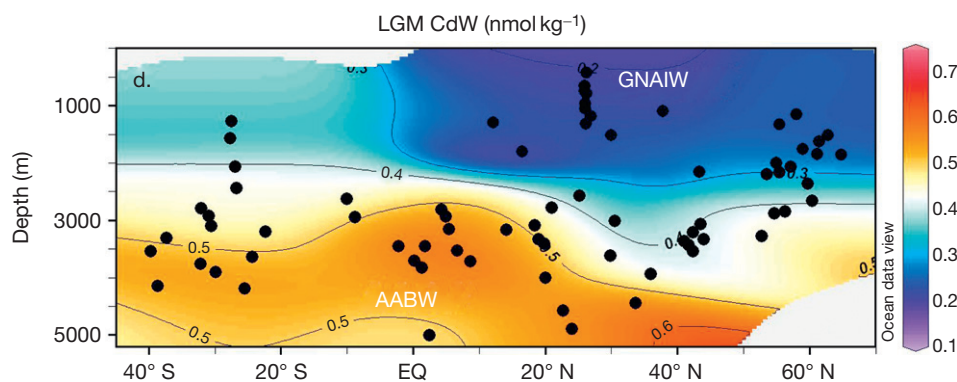


**Figure 4** Meridional section of seawater Cd concentration in the LGM Atlantic, reconstructed from benthic foraminiferal Cd/Ca (Marchitto and Broecker, 2006). Black dots show locations of sediment cores used in the reconstruction.
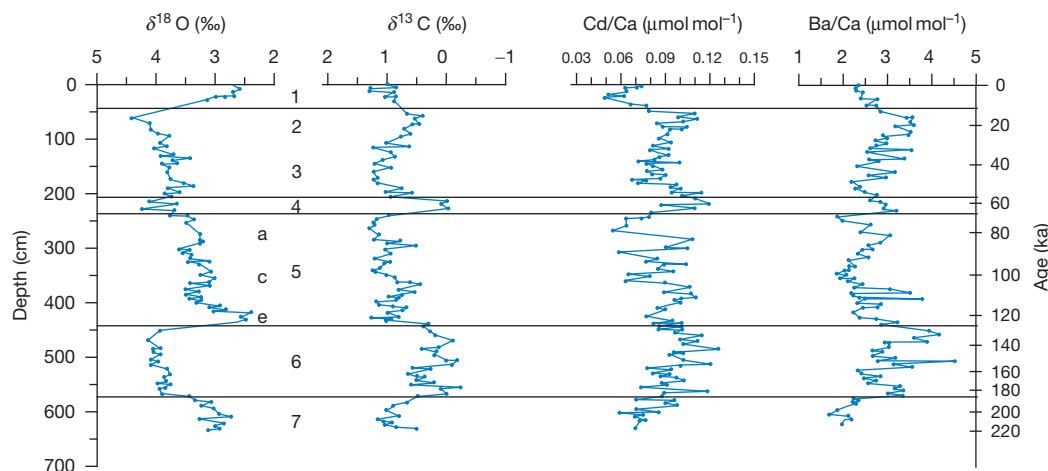
**Figure 5** Records of benthic foraminiferal $\delta^{18}O$, $\delta^{13}C$, Cd/Ca, and Ba/Ca in a sediment core from the deep North Atlantic spanning the past 210 ka (Lea and Boyle, 1990a). Low $\delta^{13}C$ and high Cd/Ca and Ba/Ca generally occur during glacial stages (indicated by high $\delta^{18}O$ and labeled as marine isotope stages 2, 4, and 6), indicative of high nutrients and the presence of AABW. Note the reversed scales for $\delta^{18}O$ and $\delta^{13}C$.

evidence that this value is reduced in strongly undersaturated waters (McCorkle et al., 1995).

For the LGM Atlantic, benthic Ba/Ca supports the view that low-nutrient NADW was replaced by the shallower GNAIW (**Figure 5**; Lea and Boyle, 1990b). Low intermediate-depth Ba/Ca also appears to rule out the Mediterranean Sea as an important contributor to GNAIW, since water from that basin carries high Ba concentrations. In contrast to $\delta^{13}C$ and Cd/Ca, however, there was no apparent glacial Ba gradient between the deep Atlantic and the Pacific. Deep ocean Ba may have become decoupled from the other nutrient tracers because of an increase in barite regeneration at the seafloor, possibly associated with increased productivity (Lea and Boyle, 1990b).

### Zinc

Dissolved Zn has an oceanic distribution very similar to that of the nutrient silica (**Figure 1**). Both are nearly completely removed from most surface waters, but unlike the labile Cd and phosphate, they lack intermediate-depth concentration maxima. Zn therefore behaves like a refractory nutrient, with maximum concentrations below $\sim 1$–2 km water depth. Zn is an essential micronutrient for many marine organisms, second only to iron among the biologically important trace metals. In particular, its use by diatoms (algal protists with siliceous shells) in the enzyme carbonic anhydrase may explain its oceanic association with silica. Zn concentrations increase more than tenfold between the deep North Atlantic and North Pacific, and there is a sevenfold meridional increase within the deep Atlantic alone. Zn/Ca may therefore be a very sensitive tracer of past interactions between NADW and AABW (Marchitto et al., 2002).

At least two species of calcitic benthic Foraminifera incorporate Zn with a partition coefficient that depends strongly on the saturation state. In sufficiently supersaturated waters $D_{Zn}$ is $\sim 9$, but it may be as low as $\sim 4$ in the corrosive deep Pacific. The glacial increase in deep North Atlantic Zn due to the increased presence of AABW was therefore partially muted in Zn/Ca because of AABW's lower saturation state (Marchitto et al., 2002). Nevertheless, paired Zn/Ca and Cd/Ca measurements provide
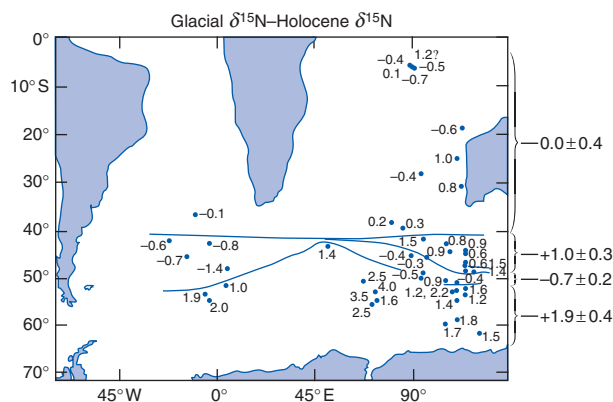


**Figure 6** Difference between LGM and Holocene bulk sediment $\delta^{15}N$ in the Southern Ocean and Indian Ocean (Francois et al., 1997). Numbers at right show mean values for four regions. There was an increase in $\delta^{15}N$ south of the modern Polar Front ($\sim 50^\circ$ S) during the LGM, suggesting increased $NO_3^-$ utilization due to reduced nutrient upwelling.

strong evidence for glacial AABW expansion, and not some independent change in NADW nutrient content.

### Nitrogen-15

#### Nitrate Utilization

Along with carbon and phosphate, nitrate ($NO_3^-$) is an essential major nutrient for marine primary production, and is often the limiting nutrient in the open ocean. Like carbon, nitrogen has two stable isotopes: $^{14}N$ (99.6%) and $^{15}N$ (0.4%). Fractionation is again expressed in delta notation:

$$\delta^{15}N = \left[ \left(^{15}N/^{14}N\right)_{sample} / \left(^{15}N/^{14}N\right)_{standard} - 1\right] \times 1000 \quad [3]$$

where the standard is atmospheric $N_2$. Phytoplankton preferentially incorporate the lighter isotope, leading to $\delta^{15}N$ enrichment of the remaining dissolved $NO_3^-$ pool. In regions where

the $NO_3^-$ supply is heavily utilized, the surface ocean isotopic enrichment can be relatively large (order of 10‰; Figure 1), and organic matter $\delta^{15}N$ increases in parallel. To the first order, the $\delta^{15}N$ of sedimentary organic matter may therefore be used to reconstruct past surface ocean $NO_3^-$ $\delta^{15}N$, and thus the degree of $NO_3^-$ utilization (Altabet and Francois, 1994). There are indications that sedimentary bulk organic matter $\delta^{15}N$ may be subject to diagenetic alteration in some environments, which might be avoidable by measuring diatom-bound $\delta^{15}N$ (Robinson and Sigman, 2008).

Past $NO_3^-$ utilization is of particular interest in the Southern Ocean, the largest area of incomplete consumption of $NO_3^-$ and phosphate by phytoplankton in the modern oceans. Here, deep waters charged with nutrients and DIC upwell to the surface, but they are subducted again before their nutrient load can be efficiently extracted, resulting in a missed opportunity for the ocean's 'biological pump' to sequester $CO_2$ (Sigman et al., 2010). Hypothetically, the resulting leak of $CO_2$ into the atmosphere could have been stemmed during glacial times either by increased biological productivity or by reduced vertical mixing. Both processes would be recorded as increases in $\delta^{15}N$ due to a more complete $NO_3^-$ utilization. South of the modern Polar Front, $\delta^{15}N$ data indeed suggest that $NO_3^-$ utilization was enhanced during the last glaciation (Figure 6), and proxy evidence for reduced export production confirms that this change was related to reduced upwelling and/or stronger surface stratification (Francois et al., 1997; Robinson and Sigman, 2008). North of the modern Polar Front, export production increased, but $NO_3^-$ utilization apparently did not rise as much as it did south of the front, implying that the



**Figure 7**    Sedimentary $\delta^{15}N$ records from off southern Chile (c) (Robinson et al., 2007), California (d) (Hendy et al., 2004), and Oman (e) (Altabet et al., 2002), compared to $\delta^{18}O$ of ice (a proxy for air temperature) in Greenland (a) and Antarctica (b). Numbers at the top indicate marine isotope stages, and gray bars denote millennial-scale warm events in Antarctica. Also shown (on a reversed scale) is $\delta^{15}N$ in the subantarctic zone of the Southern Ocean (f). Reproduced from Robinson RS, Mix A, and Martinez P (2007) Southern Ocean control on the extent of denitrification in the southeast Pacific over the last 70 ka. *Quaternary Science Reviews* 26: 201–212.

enhanced productivity could have resulted from increased up-welling. It has been suggested that the changes south of the Polar Front had a greater impact on the atmosphere, contributing to glacial $CO_2$ lowering.

## Denitrification

A second important influence on the $\delta^{15}N$ of dissolved $NO_3^-$ is water column denitrification, which represents an important loss of fixed nitrogen from the oceans. Under suboxic conditions, $NO_3^-$ may be used by certain bacteria as an electron acceptor during organic matter degradation, producing $N_2O$ and $N_2$. Like $NO_3^-$ utilization, this process preferentially uses $^{14}N$ and results in $\delta^{15}N$ enrichment of the remaining $NO_3^-$ pool. While well-oxygenated deep waters are typically $\sim 5-6‰$ in $\delta^{15}N$, denitrification may drive the values above $18‰$. Today, denitrification occurs primarily in the intermediate-depth oxygen minimum zones (OMZs) of the eastern tropical North and South Pacific, and the Arabian Sea.

Along the western Mexico continental margin, bulk sediment $\delta^{15}N$ was about $2-3‰$ lower during late Quaternary glacial intervals, indicative of reduced denitrification in this region (Ganeshram et al., 2002). Other sediment cores from the eastern tropical North Pacific exhibit reduced organic carbon content and increased bioturbation during glacial times, consistent with erosion of the regional OMZ. Arabian Sea sedimentary $\delta^{15}N$ was similarly reduced (Altabet et al., 2002), suggesting that global rates of denitrification were significantly lower during glacial periods. This may have resulted in an increased oceanic inventory of $NO_3^-$, possibly stimulating primary production in oligotrophic (subtropical gyre) regions and contributing to the glacial drawdown of atmospheric $CO_2$. However, phosphate limitation likely became important, reducing overall $NO_3^-$ fixation and limiting the biological impact of reduced denitrification (Ganeshram et al., 2002).

OMZ weakening during glacial periods may have resulted from decreased upwelling-driven productivity in those regions, and/or increased ventilation by high-oxygen intermediate waters. In the Arabian Sea, sediment $\delta^{15}N$ also decreased during millennial-scale intervals corresponding to the Northern Hemisphere cold stages of the last Ice Age, the so-called Dansgaard–Oeschger stadials (Figure 7(a) and (e); Altabet et al., 2002). Reduced denitrification at these times was likely due to reduced summer upwelling and productivity in response to a weakened southwest Indian monsoon. $\delta^{15}N$ off southern Chile also displayed millennial-scale variability during the last Ice Age, but with a timing that more closely mimics the temperature history of Antarctica (Figure 7(b) and (c); Robinson et al., 2007). $\delta^{15}N$ records from the eastern North Pacific OMZ appear to transition from Antarctic-like timing near the equator to Greenland-like timing further north (Figure 7(d); Hendy et al., 2004; Robinson et al., 2007; Pichevin et al., 2010), pointing to some combination of southern and northern forcing along this margin. Enhanced ventilation of Subantarctic Mode Water during Antarctic cold phases may have delivered more oxygen to the eastern tropical and South Pacific OMZs, resulting in less denitrification. Furthermore, if enhanced $NO_3^-$ utilization occurred in the Subantarctic Southern Ocean during cold phases, as suggested

by higher diatom-bound $\delta^{15}N$ (Figure 7(f); Robinson et al., 2007), then nutrient delivery to the low-latitude world ocean would have been reduced, leading to lower productivity and less demand for oxygen in the regions of the modern OMZs. In contrast to the Southern Ocean, changes in upwelling and productivity above the low-latitude OMZs are believed to exert little leverage on atmospheric $CO_2$ because nutrients upwelled there are completely utilized eventually (Sigman et al., 2010).

*See also:* **Diatom Records:** Antarctic Waters. **Glacial Climates:** Thermohaline Circulation. **Paleoceanography:** Paleoceanography An Overview. **Paleoceanography, Biological Proxies:** Benthic Foraminifera; Planktic Foraminifera. **Paleoceanography, Physical and Chemical Proxies:** Carbon Cycle Proxies ($\delta^{11}B$, $\delta^{13}C_{calcite}$, $\delta^{13}C_{organic}$, Shell Weights, B/Ca, U/Ca, Zn/Ca, Ba/Ca); Dissolution of Deep-Sea Carbonates; Mg/Ca and Sr/Ca Paleothermometry from Calcareous Marine Fossils. **Paleoclimate Reconstruction:** Sub-Milankovitch (DO/Heinrich) Events.

## References

Altabet MA and Francois R (1994) Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization. *Global Biogeochemical Cycles* 8: 103–116.

Altabet MA, Higginson MJ, and Murray DW (2002) The effect of millennial-scale changes in Arabian Sea denitrification on atmospheric $CO_2$. *Nature* 415: 159–162.

Boyle EA (1992) Cadmium and $\delta^{13}C$ paleochemical ocean distributions during the stage 2 glacial maximum. *Annual Review of Earth and Planetary Science* 20: 245–287.

Boyle EA and Keigwin LD (1987) North Atlantic thermohaline circulation during the past 20,000 years linked to high-latitude surface temperature. *Nature* 330: 35–40.

Broecker WS, Spencer DW, and Craig H (1982) *GEOSECS Pacific Expedition*. Washington, DC: US Government Printing Office.

Bruland KW (1980) Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific. *Earth and Planetary Science Letters* 47: 176–198.

Crowley T (1995) Ice age terrestrial carbon changes revisited. *Global Biogeochemical Cycles* 9: 377–390.

Curry WB and Oppo DW (2005) Glacial water mass geometry and the distribution of $\delta^{13}C$ of $\Sigma CO_2$ in the western Atlantic Ocean. *Paleoceanography* 20: PA1017. http://dx.doi.org/10.1029/2004PA001021.

Delaney ML (1989) Uptake of cadmium into calcite shells by planktonic foraminifera. *Chemical Geology* 78: 159–165.

Duplessy JC, Shackleton NJ, Fairbanks RG, Labeyrie L, Oppo D, and Kallel N (1988) Deepwater source variations during the last climatic cycle and their impact on global deepwater circulation. *Paleoceanography* 3: 343–360.

Duplessy JC, Shackleton NJ, Matthews RK, et al. (1984) $\delta^{13}C$ record of benthic foraminifera in the Last Interglacial Ocean: Implications for the carbon cycle and the global deep water circulation. *Quaternary Research* 21: 225–243.

Elderfield H and Rickaby REM (2000) Oceanic Cd/P ratio and nutrient utilization in the glacial Southern Ocean. *Nature* 405: 305–310.

Francois R, Altabet MA, Yu E-F, et al. (1997) Contribution of Southern Ocean surface-water stratification to low atmospheric $CO_2$ concentrations during the last glacial period. *Nature* 389: 929–935.

Ganeshram RS, Pedersen TF, Calvert SE, and Francois R (2002) Reduced nitrogen fixation in the glacial ocean inferred from changes in marine nitrogen and phosphorous inventories. *Nature* 415: 156–159.

Hendy IL, Pedersen TF, Kennett JP, and Tada R (2004) Intermittent existence of a southern Californian upwelling cell during submillennial climate change of the last 60 kyr. *Paleoceanography* 19: PA3007. http://dx.doi.org/10.1029/2003PA000965.

Herguera JC, Herbert T, Kashgarian M, and Charles C (2010) Intermediate and deep water mass distribution in the Pacific during the Last Glacial Maximum inferred from oxygen and carbon stable isotopes. *Quaternary Science Reviews* 29: 1228–1245.

Keigwin LD and Boyle EA (1989) Late quaternary paleochemistry of high-latitude surface waters. *Palaeogeography, Palaeoclimatology, Palaeoecology* 73: 85–106.

Kroopnick PM (1985) The distribution of $^{13}C$ of $\Sigma CO_2$ in the world oceans. *Deep Sea Research* 32: 57–84.

Lea DW and Boyle EA (1989) Barium content of benthic foraminifera controlled by bottom-water composition. *Nature* 338: 751–753.

Lea DW and Boyle EA (1990a) A 210,000-year record of barium variability in the deep northwest Atlantic Ocean. *Nature* 347: 269–272.

Lea DW and Boyle EA (1990b) Foraminiferal reconstruction of barium distributions in water masses of the glacial oceans. *Paleoceanography* 5: 719–742.

Lund DC, Adkins JF, and Ferrari R (2011) Abyssal Atlantic circulation during the Last Glacial Maximum: Constraining the ratio between transport and vertical mixing. *Paleoceanography* 26: PA1213. http://dx.doi.org/10.1029/2010PA001938.

Lynch-Stieglitz J and Fairbanks RG (1994) A conservative tracer for glacial ocean circulation from carbon isotope and palaeo-nutrient measurements in benthic foraminifera. *Nature* 369: 41–43.

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.

Mackensen A, Hubberten H-W, Bickert T, Fischer G, and Futterer DK (1993) $\delta^{13}$C in benthic foraminiferal tests of *Fontbotia wuellerstorfi* (Schwager) relative to $\delta^{13}$C of dissolved inorganic carbon in Southern Ocean deep water: Implications for Glacial ocean circulation models. *Paleoceanography* 8: 587–610.

Marchitto TM and Broecker WS (2006) Deep water mass geometry in the glacial Atlantic Ocean: A review of constraints from the paleonutrient proxy Cd/Ca. *Geochemistry, Geophysics, Geosystems* 7: Q12003. http://dx.doi.org/10.1029/2006GC001323.

Marchitto TM, Oppo DW, and Curry WB (2002) Paired benthic foraminiferal Cd/Ca and Zn/Ca evidence for a greatly increased presence of Southern Ocean Water in the glacial North Atlantic. *Paleoceanography* 17: 1038. http://dx.doi.org/10.1029/2000PA000598.

McCorkle DC, Martin PA, Lea DW, and Klinkhammer GP (1995) Evidence of a dissolution effect on benthic foraminiferal shell chemistry: $\delta^{13}$C. *Cd/Ca, Ba/Ca, and Sr/Ca results from the Ontong Java Plateau, Paleoceanography* 10: 699–714.

Ninnemann US and Charles CD (2002) Changes in the mode of Southern Ocean circulation over the last glacial cycle revealed by foraminiferal stable isotopic variability. *Earth and Planetary Science Letters* 201: 383–396.

Olsen A and Ninnemann US (2010) Large $\delta^{13}$C gradients in the preindustrial North Atlantic revealed. *Science* 330: 658–659.

Ostlund HG, Craig H, Broecker WS, and Spencer D (1987) GEOSECS Atlantic, Pacific and Indian Ocean expeditions. *Shorebased Data and Graphics*, vol. 7. Washington, DC: US Government Printing Office.

Pichevin LE, Ganeshram RS, Francavilla S, Arellano-Torres E, Pedersen TF, and Beaufort L (2010) Interhemispheric leakage of isotopically heavy nitrate in the eastern tropical Pacific during the last glacial period. *Paleoceanography* 25: PA1204. http://dx.doi.org/10.1029/2009PA001754.

Rickaby REM and Elderfield H (1999) Planktonic foraminiferal Cd/Ca: Paleonutrients or paleotemperature? *Paleoceanography* 14: 293–303.

Robinson RS, Mix A, and Martinez P (2007) Southern Ocean control on the extent of denitrification in the southeast Pacific over the last 70 ka. *Quaternary Science Reviews* 26: 201–212.

Robinson RS and Sigman DM (2008) Nitrogen isotopic evidence for a poleward decrease in surface nitrate within the ice age Antarctic. *Quaternary Science Reviews* 27: 1076–1090.

Shackleton NJ, Hall MA, Line J, and Shuxi C (1983) Carbon isotope data in core V19-30 confirm reduced carbon dioxide concentration in the ice age atmosphere. *Nature* 306: 319–322.

Sigman DM, Altabet MA, McCorkle DC, Francois R, and Fischer G (1999) The $\delta^{15}$N of nitrate in the Southern Ocean: Consumption of nitrate in surface waters. *Global Biogeochemical Cycles* 13: 1149–1166.

Sigman DM, Hain MP, and Haug GH (2010) The polar ocean and glacial cycles in atmospheric $CO_2$ concentration. *Nature* 466: 47–55.

Spero HJ (1998) Life history and stable isotope geochemistry of planktonic foraminifera. In: Norris RD and Corfield RM (eds.) *Isotope Paleobiology and Paleoecology*, pp. 7–36. Paleontological Society.

Spero HJ and Lea DW (2002) The cause of carbon isotope minimum events on glacial terminations. *Science* 296: 522–525.

Zahn R, Winn K, and Sarnthein M (1986) Benthic foraminiferal $\delta^{13}$C and accumulation rates of organic carbon: *Uvigerina peregrina* group and *Cibicidoides wuellerstorfi*. *Paleoceanography* 1: 27–42.