Nutrient Proxies

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Introduction

The past distribution of marine nutrients 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 ΣCO_2, is composed of three dominant species in seawater: dissolved carbon dioxide ($CO_2(aq)$), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}), with 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:

$$\delta^{13}C = [(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard} - 1]^*1000 \qquad (1)$$

where the standard is a calcium carbonate, usually referenced to the PeeDee Belemnite (PDB) 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 like phosphate and nitrate, resulting in a water column $\delta^{13}C$ profile that is inversely correlated with these nutrients (Fig. 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 (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-$p CO_2$ North Atlantic, therefore experience $\delta^{13}C$ depletion. Areas that emit CO_2 to the atmosphere, such as the high-$p CO_2$ 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).

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 record 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 bottom waters due to organic matter remineralization (Zahn et al., 1986). However, the $\delta^{13}C$ of even epifaunal species may be lower than from bottom waters in regions where organic matter rain rates are very high (Mackensen et al., 1993).

Benthic foraminifera provide a picture of the past distribution of deep water masses. Biogeochemical
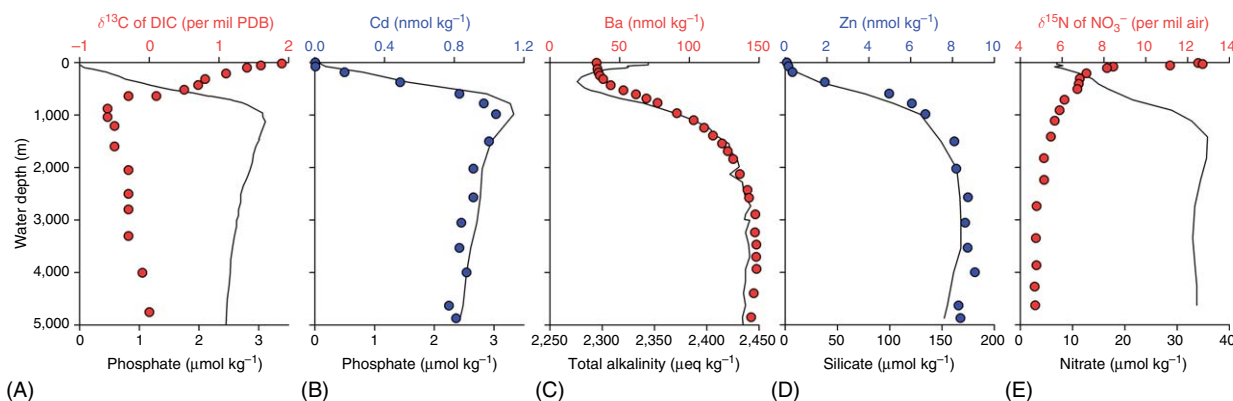
Figure 1 Modern seawater profiles of the main nutrient proxies. (A) δ^{13}C of DIC (Kroopnick, 1985) compared to dissolved phosphate (Broecker *et al.*, 1982) in the central North Pacific; (B) Dissolved Cd compared to dissolved phosphate in the eastern North Pacific (Bruland, 1980); (C) Dissolved Ba (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) δ^{15}N of dissolved nitrate compared to dissolved nitrate in the Indian sector of the Southern Ocean (Sigman *et al.*, 1999).

cycling and air–sea exchange cause most surface waters, particularly those stripped of nutrients, to be enriched in δ^{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-δ^{13}C signature (**Fig. 2**). In contrast, Antarctic Bottom Water (AABW) and Antarctic Intermediate Water (AAIW) are formed from poorly ventilated surface waters and therefore carry low-δ^{13}C signatures. Lowest δ^{13}C values are today found in the deep North Pacific, far from the well-ventilated NADW source.

NADW today transports a large amount of heat into the North Atlantic, and past changes in its formation are believed to have strongly impacted regional climate. The most extensively studied period in this regard is the Last Glacial Maximum (LGM, ~20 kyr BP), for which meridional Atlantic δ^{13}C sections have been created. Such reconstructions suggest that low-δ^{13}C AABW expanded into the North Atlantic and that its boundary with high-δ^{13}C NADW shoaled from 4 km to ~2–3 km water depth (Duplessy *et al.*, 1988; Curry and Oppo, 2005) (**Fig. 3**). 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 offer no direct measure of water mass fluxes, only their spatial extent. 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 δ^{13}C gradient between the North Atlantic and Pacific has been used as a monitor of NADW extent. As during the LGM,

NADW volume was apparently reduced during all Northern Hemisphere glaciations.

One interesting aspect of the glacial δ^{13}C distribution is that lowest values occurred in the deep Southern Ocean, rather than the North Pacific as today. Glacial production of a North Pacific Deep Water could explain the pattern, but there is no good evidence for such a water mass. Localized (microhabitat) lowering of δ^{13}C caused by high organic carbon flux to the sea floor and subsequent remineralization could also explain low δ^{13}C at some sites. Some have attributed the low Southern Ocean values to an organic matter microhabitat effect, noting that Cd/Ca (see below) does not support a very high-nutrient glacial AABW (Boyle, 1992; Mackensen *et al.*, 1993). However, the relative uniformity of glacial δ^{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 that glacial AABW was particularly dense, so perhaps GNAIW avoided extensive mixing in the Southern Ocean, leaving AABW anomalously low in δ^{13}C.

The δ^{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 δ^{13}C shift has been documented in the glacial Indian Ocean, and although data coverage in the upper Pacific is comparatively poor, an intermediate to mid-depth δ^{13}C gradient is generally supported. Glacial DIC deepening may have acted to lower atmospheric CO_2, both through the direct effect of decreased surface ocean DIC and the compounding effects of lowered deep sea CO_3^{2-}, sea-floor dissolution of $CaCO_3$, increased oceanic alkalinity, and therefore decreased pCO_2 (Sigman and Boyle, 2000; Marchitto *et al.*, 2005).
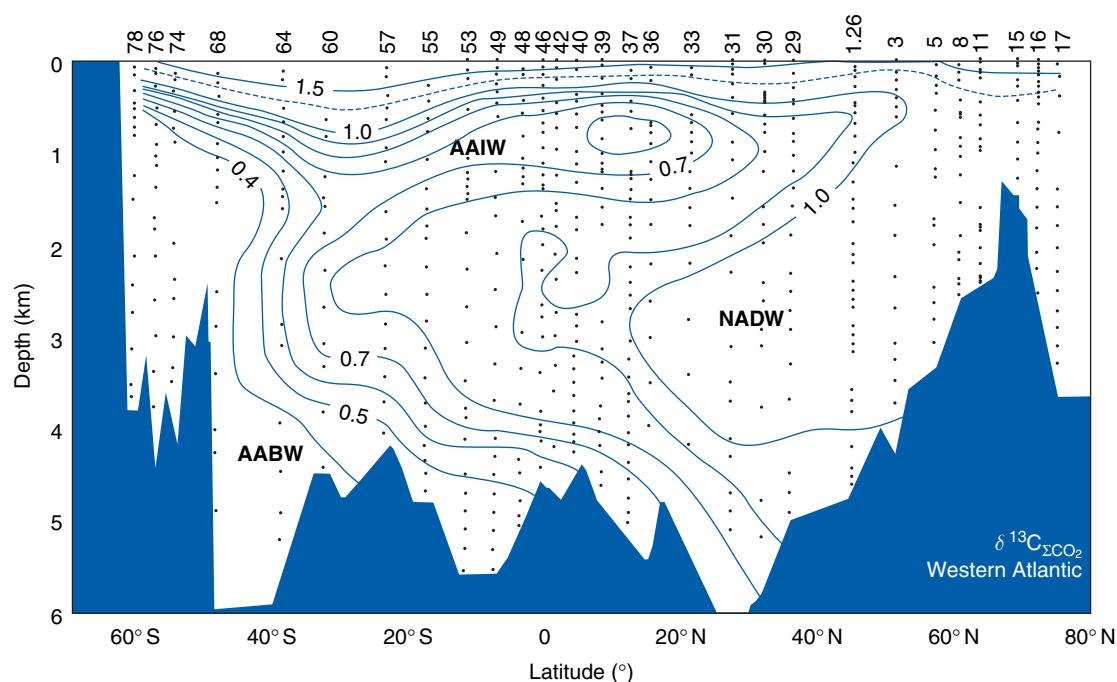
Figure 2 Meridional section of modern $\delta^{13}C$ of DIC in the western Atlantic Ocean (after Kroopnick, 1985). Major water masses are indicated, and numbers at top refer to oceanographic cruise stations.
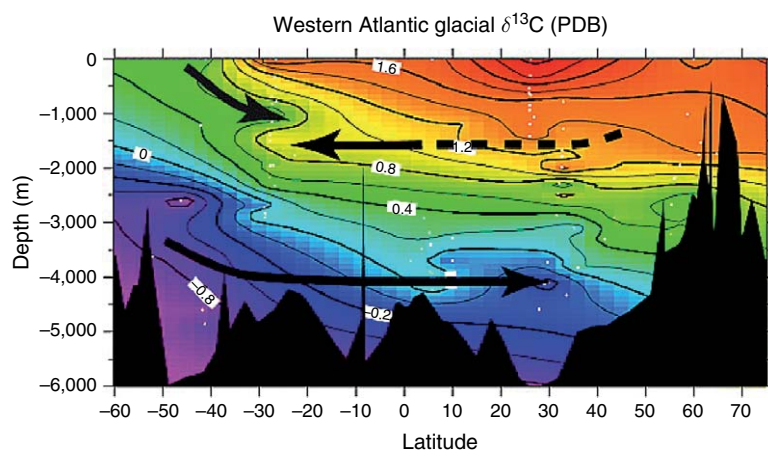
Figure 3 Meridional section of benthic foraminiferal $\delta^{13}C$ for the LGM western Atlantic (Curry and Oppo, 2005). Arrows indicate presumed flow directions of AAIW, GNAIW, and AABW, and small white dots show locations of sediment cores used in the reconstruction.

Reconstruction of surface water $\delta^{13}C$ may 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 above-mentioned implications for atmospheric CO_2 (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 we must also consider the partitioning of carbon between land and ocean. It is estimated from benthic foraminifera that the average $\delta^{13}C$ value of the world ocean 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 upper Pacific Ocean. 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 δ^{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 major nutrients. That is, they are at low concentrations in surface waters and 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 simply result 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. Paleo-reconstruction 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 (Fig. 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 remineralized) nutrient, and its concentration increases about five-fold between the deep North Atlantic and North Pacific. Although Cd has been linked to at least one important algal metalloenzyme, 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 by particulate organic matter (Elderfield and Rickaby, 2000).

Benthic foraminiferal Cd/Ca ratios reflect seawater Cd concentrations (Boyle, 1992) (Fig. 4). The relationship between foraminiferal 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, reaching a maximum value of 2.9 below 3,000 m and a minimum of 1.3 above 1,150 m. The aragonitic benthic foraminifer *Hoeglundina elegans* has a D_{Cd} of 1.0, invariant 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).

Early Cd/Ca work supported contemporaneous indications from δ^{13}C that low-nutrient NADW was less extensive in the glacial Atlantic Ocean and was present as the shallower GNAIW (Boyle and Keigwin, 1987) (Fig. 5). As LGM ocean coverage increased for the two proxies, they were found to broadly agree in most regions, but some differences have emerged (Boyle, 1992). Most notable is the above-mentioned Southern Ocean discrepancy, where glacial δ^{13}C shows very low values in contrast to Cd/Ca that is similar to today. An undersaturation effect on Cd/Ca and/or a microhabitat effect on δ^{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 δ^{13}C without being significantly enriched in Cd.

The Southern Ocean problem highlights the fact that because δ^{13}C and Cd behave somewhat differently in the modern ocean, unique information may
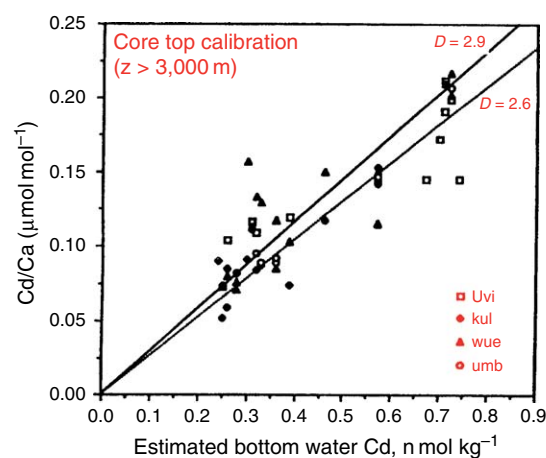
Figure 4 Deep sea core-top calibration for Cd/Ca in four taxa of benthic foraminifera (after Boyle (1992)). The slope of the line reveals the partition coefficient, and the lines show two possible values. Some data implying partition coefficients significantly lower than 2.9 may be affected by seawater undersaturation with respect to calcite (McCorkle et al., 1995).

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 combining 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 mixing.

Planktonic foraminifera incorporate Cd with a similar range of partition coefficients as benthics (Delaney, 1989), but less paleoceanographic work has been done with planktonics. Cd/Ca from a polar species suggests that LGM nutrient levels in the high-latitude North and South Atlantic were not much different than 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 influence 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), seemingly in contradiction with $\delta^{15}N$ data (see below).

Barium

Dissolved Ba is moderately depleted in surface waters and reaches maximum concentrations below ~2 km (Fig. 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, whereas alkalinity is removed mainly by $CaCO_3$ formation.

Both are regenerated at depth as their carrier phases dissolve, and deep-water masses have characteristic Ba and alkalinity values, with Ba increasing about three-fold 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 ~0.4 (Lea and Boyle, 1989), and there is 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 (Lea and Boyle, 1990b) (Fig. 5). Low intermediate depth Ba/Ca also appears to rule out the Mediterranean Sea as an important contributor to GNAIW, since waters 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 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 (Fig. 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 ~1–2 km water depth. Zn is an essential micronutrient for many marine organisms,
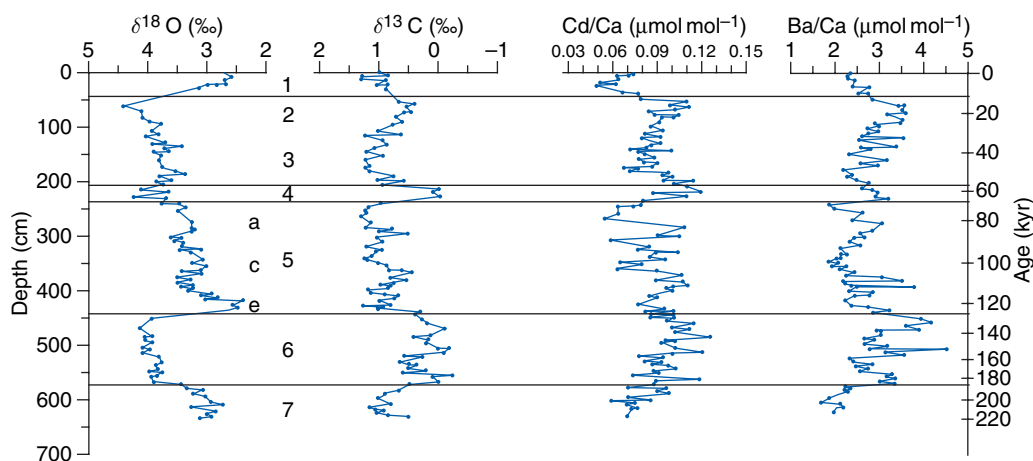
Figure 5 Records of benthic foraminiferal $\delta^{18}O$, $\delta^{13}C$, Cd/Ca, and Ba/Ca in a sediment core from the deep North Atlantic spanning the past 210 kyr (Lea DW and Boyle EA (1990). Low $\delta^{13}C$ and high Cd/Ca and Ba/Ca generally occur during glacial stages (indicated by high $\delta^{18}O$ and labeled as Marine Isotope Stages 2, 4, and 6), indicative of high nutrients and the presence of AABW. Note reversed scales for $\delta^{18}O$ and $\delta^{13}C$.

second only to iron among the biologically important trace metals. In particular, its use by diatoms (algal protists with siliceous skeletons) 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 meridioal 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 saturation state. In sufficiently supersaturated waters D_{Zn} is ~9, but it may be as low as ~4 in the 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 strong evidence for glacial AABW expansion, and not some independent change in NADW nutrient content.

The strong relationship between benthic Zn/Ca and saturation state may allow for reconstruction of the latter. Past changes in saturation state depend mainly on the movement of DIC and alkalinity within the oceans, with important implications for surface ocean pCO_2 and atmospheric CO_2 concentrations. $\delta^{13}C$, Cd/Ca, and Ba/Ca suggest that glacial–interglacial changes in deep Pacific nutrient content were modest, so large down-core changes in Zn/Ca may be mainly attributable to changes in saturation state. A notable deep Pacific Zn/Ca peak during the last deglaciation is consistent with a transient CO_3^{2-} rise and increased $CaCO_3$ preservation due to deglacial removal of DIC from the deep sea (Marchitto et al., 2005).

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:

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

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 10‰) (Fig. 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 et al., 2005).

Past NO_3^- utilization is of particular interest in the Southern Ocean, the largest area of incomplete utilization of NO_3^- and phosphate by phytoplankton in the modern ocean. The supply of these nutrients by deep upwelling is enough to support a significantly larger primary biomass than is present, but production is limited by other factors, the most important of which is probably the lack of dissolved iron. One prominent hypothesis to explain the drawdown of atmospheric CO_2 during Quaternary glacial periods is that increased iron supply to the Southern Ocean, carried by terrestrial dust, may have stimulated production and led to a greater export of carbon out of the surface ocean and therefore out of the atmosphere. $\delta^{15}N$ data indeed suggest that overall Southern Ocean NO_3^- utilization was enhanced during the last glaciation (Francois et al., 1997; Robinson et al., 2005) (Fig. 6). However, various paleoproductivity indicators argue against a large glacial increase in Southern Ocean export production, particularly south of the modern Polar Front. This implies that greater NO_3^- utilization may have resulted in part from decreased upwelling of deep
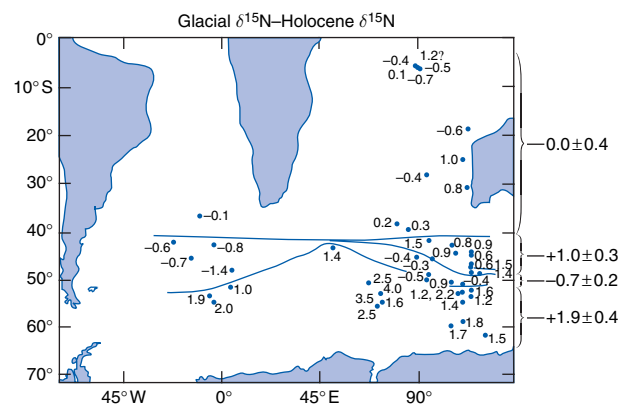
Figure 6 Difference between LGM and Holocene bulk sediment $\delta^{15}N$ in the Southern Ocean and Indian Ocean (Francois et al., 1997). Numbers at right show mean values for four regions. There was an overall increase in Southern Ocean $\delta^{15}N$ during the LGM, suggesting increased NO_3^- utilization due to iron fertilization and/ or reduced nutrient upwelling.

waters around Antarctica, a mechanism that could also have contributed to lower atmospheric CO_2 (Sigman and Boyle, 2000).

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 bacteria as an electron receptor 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 intermediate water NO_3^- pool. Whereas well-oxygenated deep waters are typically ~5–6‰ in $\delta^{15}N$, denitrification may drive values above 18‰. Denitrification today occurs primarily in the intermediate-depth oxygen minimum zones of the eastern tropical North and South Pacific, and 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 weakening of the regional oxygen minimum zone. 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 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).

Oxygen minimum zone weakening during glacial periods may have resulted from decreased productivity and/or increased ventilation by high-oxygen intermediate waters. In the Arabian Sea, sediment $\delta^{15}N$ also decreased during intervals corresponding to the cold stadials of Marine Isotope Stage 3, the so-called Dansgaard–Oeschger oscillations (Altabet et al., 2002) (Fig. 7). Reduced denitrification at these times was likely due to reduced summer upwelling and productivity in response to a weakened
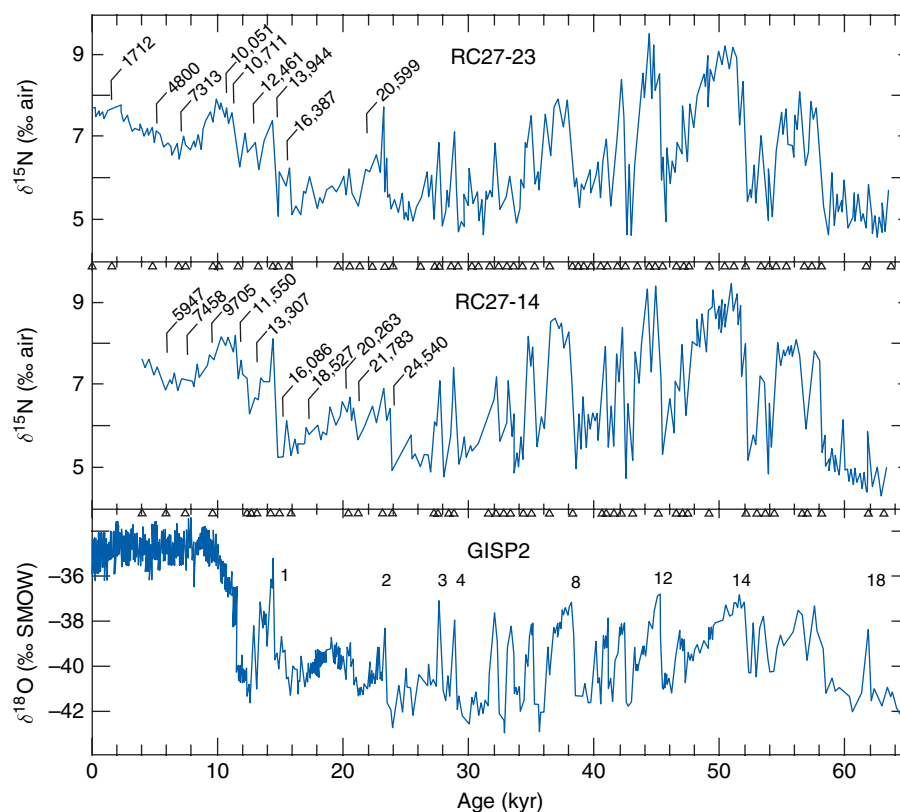
Figure 7 Bulk sediment $\delta^{15}N$ in two cores from the Oman Margin in the Arabian Sea, compared to $\delta^{18}O$ of Greenland ice (a proxy for air temperature) over the past 65 kyr (Altabet et al., 2002). Cold stadials in Greenland coincide with lower $\delta^{15}N$ and apparently reduced denitrification in the Arabian Sea. Marine productivity was likely reduced during stadials because of a weakened southwest Indian monsoon and reduced upwelling.

southwest Indian monsoon. On glacial–interglacial timescales, globally reduced denitrification has also been linked to enhanced NO_3^- utilization (nutrient reduction) in the sub-Antarctic Southern Ocean, since those waters feed nutrients into the intermediate-depth world ocean and therefore can modulate lower latitude productivity (Sigman and Boyle, 2000; Robinson et al., 2005).

See also: **Diatom Records**: Antarctic Waters. **Glacial Climates**: Thermohaline Circulation. **Paleoceanography**. **Paleoceanography, Biological Proxies**: Benthic Foraminifera; Planktic Foraminifera. **Paleoceanography, Physical and Chemical Proxies**: Carbon Cycle Proxies; Dissolution of Deep-Sea Carbonates; Mg/Ca and Sr/Ca Paleothermometry. **Paleoclimate Reconstruction**: Sub-Milankovitch (DO/Heinrich) Events.

References

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

Altabet, M. A., Higginson, M. J., and Murray, D. W. (2002). The effect of millennial-scale changes in Arabian Sea denitrification on atmospheric CO_2. *Nature* **415**, 159–162.

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

Broecker, W. S., Spencer, D. W., and Craig, H. (1982). *GEOSECS Pacific Expedition.* US Government Printing Office, Washington, DC.

Bruland, K. W. (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, W. B., and Oppo, D. W. (2005). Glacial water mass geometry and the distribution of $\delta^{13}C$ of ΣCO_2 in the western Atlantic Ocean. *Paleoceanography* **20**, PA1017, (doi:10.1029/2004PA001021).

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

Duplessy, J. C., Shackleton, N. J., Fairbanks, R. G., Labeyrie, L., Oppo, D., and Kallel, N. (1988). Deepwater source variations during the last climatic cycle and their impact on global deep-water circulation. *Paleoceanography* **3**, 343–360.

Duplessy, J. C., Shackleton, N. J., Matthews, R. K., *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, R. E. M. (2000). Oceanic Cd/P ratio and nutrient utilization in the glacial Southern Ocean. *Nature* **405**, 305–310.

Francois, R., Altabet, M. A., 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, R. S., Pedersen, T. F., Calvert, S. E., and Francois, R. (2002). Reduced nitrogen fixation in the glacial ocean inferred from changes in marine nitrogen and phosphorous inventories. *Nature* **415**, 156–159.

Keigwin, L. D., and Boyle, E. A. (1989). Late Quaternary paleochemistry of high-latitude surface waters. *Palaeogeography, Palaeoclimatology, Palaeoecology* **73**, 85–106.

Kroopnick, P. M. (1985). The distribution of ^{13}C of ΣCO_2 in the world oceans. *Deep-Sea Research* **32**, 57–84.

Lea, D. W., and Boyle, E. A. (1989). Barium content of benthic foraminifera controlled by bottom-water composition. *Nature* **338**, 751–753.

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

Lea, D. W., and Boyle, E. A. (1990b). Foraminiferal reconstruction of barium distributions in water masses of the glacial oceans. *Paleoceanography* **5**, 719–742.

Lynch-Stieglitz, J., and Fairbanks, R. G. (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, T. F., Broecker, W. S., and Fairbanks, R. G. (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 Fütterer, D. K. (1993). $\delta^{13}C$ in benthic foraminiferal tests of *Fontabia 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, T. M., Lynch-Stieglitz, J., and Hemming, S. R. (2005). Deep Pacific $CaCO_3$ compensation and glacial–interglacial atmospheric CO_2. *Earth and Planetary Science Letters* **231**, 317–336.

Marchitto, T. M., Oppo, D. W., and Curry, W. B. (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, (doi:10.1029/2000PA000598).

McCorkle, D. C., Martin, P. A., Lea, D. W., and Klinkhammer, G. P. (1995). Evidence of a dissolution effect on benthic foraminiferal shell chemistry: $\delta13C$, Cd/Ca, Ba/Ca, and Sr/Ca results from the Ontong Java Plateau. *Paleoceanography* **10**, 699–714.

Ninnemann, U. S., and Charles, C. D. (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.

Ostlund, H. G., Craig, H., Broecker, W. S., and Spencer, D. (1987). *GEOSECS Atlantic, Pacific and Indian Ocean Expeditions, Volume 7: Shorebased Data and Graphics.* US Government Printing Office, Washington, DC.

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

Robinson, R. S., Sigman, D. M., DiFiore, P. J., Rohde, M. M., Mashiotta, T. A., and Lea, D. W. (2005). Diatom-bound $^{15}N/^{14}N$: New support for enhanced nutrient consumption in the ice age subantarctic. *Paleoceanography* **20**, PA3003, (doi:10.1029/2004PA001114).

Shackleton, N. J., Hall, M. A., 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, D. M., Altabet, M. A., McCorkle, D. C., 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, D. M., and Boyle, E. A. (2000). Glacial/interglacial variations in atmospheric carbon dioxide. *Nature* **407**, 859–869.

Spero, H. J. (1998). Life history and stable isotope geochemistry of planktonic foraminifera. In *Isotope Paleobiology and Paleoecology* (R. D. Norris and R. M. Corfield, Eds.), pp. 7–36. Paleontological Society, Pittsburg, PA.

Spero, H. J., and Lea, D. W. (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.

Oxygen Isotope Stratigraphy of the Oceans

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Introduction

The Pleistocene, also known as the 'Ice Ages,' starts ~2.6 Ma. At the beginning of the nineteenth century, the first geological evidence of major Quaternary glacial episodes came from observations by Louis Agassiz of sediment deposits (moraine) and erosion features attributed to ancient glaciers in the Jura mountains of Western Europe. Up until about 1960, however, most of the Ice Age puzzle remained unexplained. One theory was very promising in explaining the Ice Ages: the astronomical theory of climate developed by a Serbian professor of mathematics, Milutin Milankovitch. Based on his calculations of seasonal and latitudinal distribution of solar energy at the surface of the Earth, Milankovitch (1930) proposed an orbital theory of Ice Ages in which waxing and waning of continental ice sheets are under the control of long-term, orbitally driven changes in summer insolation over the high latitudes of the Northern Hemisphere. One of the most interesting aspects of this theory was that it made it possible to test predictions about climatic records such as how many ice-age deposits geologists would find, and when these deposits had been formed during the past 650 kyr. During a few decades, however, the astronomical theory of climate was largely disputed because discussions were based on fragmentary geological records obtained on land and supported by incomplete, and frequently incorrect, radiometric age data. The key to unravel the mystery of the Ice Ages would come from the oceanic seafloor covered by continuous sedimentary sections that had recorded hundreds of thousands of years of the Earth climatic and oceanographic evolution.

A new branch of Earth's Sciences emerged in the 1950s: Paleoceanography. One of its major tools for reconstructing the climate evolution of the Earth are stable oxygen isotopes measured from the remains of marine calcareous organisms. This tool provides clues about past changes in seawater temperature and seawater isotopic composition, which is controlled by changes in waxing and waning of large continental ice sheets and is, therefore, directly linked to glacial/interglacial history of the Earth. This article presents the major steps in our understanding of oxygen isotope fluctuations in the Ocean and their use for stratigraphic purposes.

Oxygen Stable Isotopes in Marine Carbonate Remains, a Brief Overview

Oxygen Stable Isotopes and the δ-Notation

There are three stable isotopes of oxygen in nature: ^{16}O, ^{17}O, and ^{18}O, with relative natural abundances of 99.76%, 0.04%, and 0.20%, respectively. Because of the higher abundances and the greater mass difference between ^{16}O and ^{18}O, research on oxygen isotopic ratios deals normally with the $^{18}O/^{16}O$ ratio. The ratio of stable isotopes of oxygen in carbonates is analyzed by gas mass spectrometric determination of the mass ratios of carbon dioxide (CO_2) released during reaction of the sample with a strong acid, and are expressed with reference to a standard carbon dioxide of known composition. These differences in isotope ratios, known as δ-values and given in ‰, are calculated as follows:

$$\delta^{18}O = ((^{18}O/^{16}O_{sample} - {}^{18}O/^{16}O_{standard})/ \atop {}^{18}O/^{16}O_{standard}).1000 \qquad [1]$$

A sample enriched in ^{18}O relative to the standard will show a positive δ-value (with a corresponding negative value for a sample enriched in ^{16}O relative to the standard). The standard commonly used in carbonates is referred to as Pee Dee belemnite (PDB) (a cretaceous belemnite from the Pee Dee formation in North Carolina, USA). This standard is not available any longer; however, various international standards have been run against PDB for comparative purposes. Two standards are commonly used and distributed by the National Institute of Standards and Technology (NIST) in the USA, and the International Atomic Energy Agency (IAEA) in Vienna. They are NBS-18 (carbonatite) and NBS-19 (limestone), (Coplen, 1988, 1994).