Orbital period variations in $^{15}N/^{14}N$ ratio in the Arabian Sea: an indicator of past changes in denitrification

M. A. Altabet
R. Francois
D.W. Murray
W. Prell

Marine Chemistry and Geochemistry Dept., Woods Hole Oceanographic Inst., Woods Hole, MA 02345, USA
Geological Sciences, Brown University, Providence, Rhode Island 02912, USA

Introduction

The $^{15}N/^{14}N$ ratio (^{15}N) of particulate organic matter (POM) sinking out of the surface ocean is a function of the $\delta^{15}N$ of source NO_3^- and isotopic fractionation occurring during partial utilization by phytoplankton (e.g. Altabet, 1988; Altabet *et al.*, 1991). Recent results have shown this surface generated isotopic signal to be subsequently recorded in deep sea sediments (Altabet and Francois, 1994). In the equatorial Pacific and the Southern Ocean, large latitudinal gradients in $\delta^{15}N$ for both near-surface ocean POM and core top sediments are inversely correlated with surface $[NO_3^-]$. In the former case, it was found that:

$$\delta^{15}N_{sinking\ POM} = \delta^{15}NO^-_{3subsurf.} - \varepsilon_u \times \ln(1-u)$$

where ε_u is the fractionation factor associated with phytoplankton uptake and u is the relative utilization of NO_3^-. In these regions, variations in $\delta^{15}N$ are driven by u, whereas $\delta^{15}NO^-_{3subsurf.}$ is fairly constant throughout most of the ocean. However in oceanic regions with suboxic subsurface waters, denitrification (NO_3^- going to N_2) occurs also with substantial isotopic fractionation, leaving residual subsurface NO_3^- enriched in ^{15}N. Water column denitrification produces regional increases in $\delta^{15}NO^-_{3subsurf.}$ and thus can also influence the $\delta^{15}N$ of sinking POM and sediments in these domains.

We have examined 3 sites in the Arabian Sea, an important region for water column denitrification, to isolate past variations in these effects. Summer monsoon winds produce upwelling along the Oman coast out to about 400 km. There is a corresponding NW to SE gradient in NO_3^- concentration that may be reflected in spatial variations in $\delta^{15}N$. The Owen ridge (RC2761) and nearshore Oman margin sites are at the edge of the upwelling system and well within it, respectively. Past changes in the gradient in $\delta^{15}N$ between them would reflect changes in the spatial pattern of NO_3^- utilization (a function of both physical supply and biological removal). Changes in $\delta^{15}N$ occurring in concert, in contrast, would reflect changes in the $\delta^{15}N$ of subsurface NO_3^- and hence denitrification intensity. The two nearby cores on the Oman margin have been compared to check for effects of depositional environment on sedimentary $\delta^{15}N$. Core ODP 723B at 800 m depth is overlain by suboxic waters and core RC 2724, 24 km away at 1416 m water depth is overlain by oxic water.

Results and Discussion

Despite large differences in %N and sedimentary N accumulation rate between ODP 723B and RC 2724 (e.g. 1 *vs.* 0.45% at core top), $\delta^{15}N$ variations downcore are very similar (Fig. 1). For the late Holocene, values are indistinguishable. Considering that these sites are sufficiently close to receive the same input from near-surface waters, the differences in %N and N accumulation rate can only be due to contrasts in N preservation and/or along bottom transport or trapping of sediment. In either case, there appears to be little significant influence on the downcore $\delta^{15}N$ record due to depositional environment in this region. Throughout most of the last 150 kyr., the Owen Ridge core has $\delta^{15}N$ values higher than for the Oman Margin suggesting influence of surface nutrient utilization. A survey of surficial sediments in this region show a general NW to SW increase in $\delta^{15}N$ of 1 to 3 ‰. However, the predominant $\delta^{15}N$ events over the last 150 kyr. occur in near-synchrony in all 3 cores. The fact that maxima and minima do not overlap exactly can be attributed to age model uncertainties. Being regional in nature, the principal $\delta^{15}N$ events cannot reflect changes in surface ocean utilization and most likely reflect past changes in the $\delta^{15}N$ of subsurface NO_3^- and thus denitrification. While changes in the difference in $\delta^{15}N$ between the

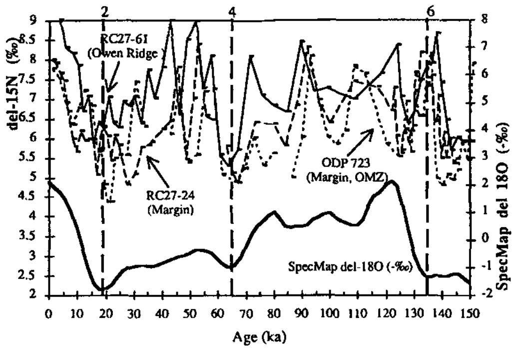

FIG. 1. Variation in sedimentary $\delta^{15}N$ over the last 150 kyr. from 3 cores in the NW Arabian Sea as compared to the SpecMap $\delta^{18}O$ stack. $\delta^{15}N$ is expressed relative to atmospheric N_2 with a precision of $\pm 0.2‰$.

Owen Ridge and Oman Margin sites may be interpreted as reflecting surface processes, here we will focus on their shared features. The seasonal nature of monsoonal upwelling is the likely reason that surface nutrient utilization does not leave a greater impact on the sedimentary record. In the Southern Ocean and equatorial Pacific, latitudinal gradients in nutrient utilization are perennial features giving rise to permanent gradients in the $\delta^{15}N$ of sinking POM reaching the sediments. In the Arabian Sea, seasonal variations in $\delta^{15}N$ rising from the annual onset and subsequent collapse of upwelling (Shafer and Ittekkot, 1993) will be integrated in the sedimentary record thereby damping the spatial gradients in $\delta^{15}N$ that would be observed during active upwelling.Inspection of the common downcore variations in sedimentary $\delta^{15}N$ and the SpecMap $\delta^{18}O$ stack (a record of ice volume and climate stage) indicates strong linkages. At core top, $\delta^{15}N$ values are near maximal, decreasing to minimal values about 20 kyr. ago (ice stage 2) indicating greatly reduced denitrification during this most recent glacial stage. At 65 kyr. (ice stage 4), a maximum in ice volume corresponds to another $\delta^{15}N$ minimum. The previous deglaciation (120 kyr. b.p.) is a also marked by rising $\delta^{15}N$ values but is punctuated by a $\delta^{15}N$ peak. In the Arabian Sea, an exact match with glacial cycles is not expected. For example, the summer monsoon, which is the dominant climatic phenomenon in this region, is much more closely linked to N. Hemisphere insolation than ice volume (Clemens *et al.*, 1991).

Our Owen Ridge $\delta^{15}N$ record goes back to 450 kyr. b.p. and spectral analysis of this data show significant peaks in power associated with the principal Milankovitch periods of variation in Earth's orbital parameters; 24, 40, and 100 kyr. A 16 kyr. peak in spectral power likely arises as a harmonic of the other periods of variations. ETP (eccentricity, tilt, precession) is an index of northern hemisphere insolation previously shown to have forced variations in the intensity of the summer monsoon. Cross-spectral analysis with the $\delta^{15}N$ record demonstrates significant coherency at the 100, 40, and 24 kyr. periods with $\delta^{15}N$ lagging ETP by 5 to 10 kyr. Similar cross-spectra with the %G. bulloides record also shows very strong coherency with $\delta^{15}N$ at the 40, 24 and 16 kyr. periods. The relative abundance of this planktonic foraminifera is considered an index of upwelling. The $\delta^{15}N$ record lags %G. bulloides by 1 to 6 kyr. suggesting denitrification responds to changes in upwelling intensity.

The picture that emerges is one of variations in denitrification in the Arabian Sea linked to changes in intensity of the summer monsoon and associated upwelling. It appears that with less upwelling, generally during periods of increased ice volume, water column denitrification was diminished. Since $\delta^{15}N$ drops to values as low as those found in regimes where denitrification does not occur, a complete collapse of denitrification is suggested. This change should also produce an ocean-wide change in average $\delta^{15}N$ for NO_3^-, albeit with much less magnitude. Such variations may have been previously detected (Altabet and Curry, 1990).

Water column denitrification requires the presence of an intense O_2 minimum zone (OMZ) and our $\delta^{15}N$ indirectly reflects changes in the volume of suboxic water in the Arabian Sea. The latter is a control upon a number chemical and biogeochemical processes (e.g. certain metals) both in the OMZ and the sediments it impinges. Some of these changes may have had global consequences. In the case of the nitrogen cycle, denitrification in the Arabian sea accounts for a large fraction of the ocean's loss of fixed nitrogen. Sharp reductions in its rate would produce a rise in the ocean's fixed nitrogen inventory and hence its fertility.

References

Altabet, M. A. (1988) *Deep-Sea Res.*, **35**, 535–54.

Altabet, M. A. and Curry, W. B. (1989) *Glob. Biogeochem. Cycles*, **3**, 107–19.

Altabet, M. A., Deuser, W. G., Honjo, S. and Stienen, S. (1991) *Nature*, **354**, 136–9.

Altabet, M. A. and Francois, R. (1994) *Glob. Biogeochem. Cycles*, **8**, 103–16.

Clemens, S., Prell, W., Murray, D., Shimmield, G. and Weedon, G. (1991) *Nature*, **353**, 720–5.

Schafer, P. and Ittekkot, V. (1993) *Naturwissenshaften*, **80**, 511–3.