## Preliminary evidence for a decrease in vertical mixing in the upper water column of the Southern Ocean during the last glacial maximum

R. Francois M.A. Altabet E.-F. Yu M.P. Bacon L.D. Labeyrie Department of Marine Chemistry and Geochemistry, W.H.O.I., Woods Hole, MA 02543, USA.

Centre des Faibles Radioactivits, Laboratoire Mixte, CNRS/ CEA, Gif-sur-Yvette, France.

## Approach

We have made combined  $^{230}$ Th,  $^{231}$ Pa, and  $\delta^{15}$ N measurements in several southern ocean cores to evaluate paleoceanographic changes which accompanied the last deglaciation in this region. We have used normalization to ex.<sup>230</sup>Th (whose flux to the seafloor approximates its production rate) to reconstruct past changes in pelagic rain rates to the seafloor, <sup>231</sup>Pa/<sup>230</sup>Th ratio as an index of scavenging intensity associated with particle fluxes and bulk sediment  $\delta^{15}N$  to estimate changes in surface nitrate utilization. We have also made preliminary calculations based on <sup>230</sup>Th-normalized biogenic Ba fluxes to quantify past variations in export production. By combining these different tracers, we have attempted to evaluate the rate of supply of nitrate to the euphotic zone, and constrain past changes in vertical mixing and surface nutrient concentration in the upper water column.

For the southern ocean, the mixed layer can be represented by a simple box (Fig. 1) in which new nitrate is added by deep mixing  $(F_{NO_3}^{in})$ . A fraction of the new nitrate is utilized by phytoplankton  $(F_{NO_3}^{util})$ , resulting in the produc-





tion of suspended particulate nitrogen ( $PN_{susp}$ ). The unutilized nitrate is removed by mixing ( $F_{NO_3}^{out}$ ). Suspended PN is processed through the food chain, resulting in particulate nitrogen sinking out of the euphotic zone ( $F_{sink}$ ) and excretion of isotopically light ammonia. The latter is then taken up by phytoplankton ( $F_{NH_3}$ ), thereby sustaining recycled production.

Since the sedimentary record integrates signals from surface water processes over long periods of time, we can assume steady-state for its interpretation, and a balanced nitrogen budget for the euphotic zone, i.e.:

$$F_{NO_3}^{in} = F_{NO_3}^{out} + F_{sink}$$
(1)

Given  $[NO_3]_{surf.}$  and  $[NO_3]_{int.}$  the nitrate concentrations in surface and intermediate waters, u the fraction of new nitrate utilized by phytoplankton, and  $V_{mix}$  the mixing rate between intermediate and surface waters:

$$\mathbf{F}_{\text{sink}} = \mathbf{V}_{\text{mix}} \left( [\text{NO}_3]_{\text{int.}} - [\text{NO}_3]_{\text{surf.}} \right)$$
(2)

$$[NO_3]_{surf.}/[NO_3]_{int.} = 1-u$$
 (3)  
Hence:

$$V_{mix} [NO_3]_{surf.} = F_{sink} ((1-u)/u)$$
 (4)

If we can evaluate  $F_{sink}$  from radionuclides and Ba sediment profiles, and u from bulk sediment  $\delta^{15}N$ , we will be able to constrain the rate of nitrate supply to the mixed layer. If, in addition, surface nutrient concentrations can be estimated from Cd/Ca or  $\delta^{13}C$  in planktonic foraminifera, one could also constrain  $V_{mix}$  and [NO<sub>3</sub>]<sub>int</sub>.

## **Initial results**

 $^{230}$ Th-normalized fluxes and  $^{231}$ Pa/ $^{230}$ Th ratios were found to be significantly lower in the glacial section of cores collected in the Atlantic and

Western Indian sector of the southern ocean (Kumar et al., 1993; Francois et al., 1993), suggesting lower export production during LGM in this section of the southern ocean. Bulk sediment  $\delta^{15}N$  in the same cores was heavier during LGM (Francois et al., 1993), suggesting that a larger fraction of the nitrate supplied to the euphotic zone was utilized by phytoplankton. If our interpretation of these two observations is correct, it implies a significantly reduced rate of nitrate supply to the euphotic zone during LGM in this region. In contrast, these large glacial/ interglacial changes in export production were not recognized in the <sup>230</sup>Th-normalized fluxes and <sup>231</sup>Pa/<sup>230</sup>Th ratios of a sediment core collected in the Eastern Indian sector of the southern ocean (Yu, 1994). Likewise, the changes in bulk sediment  $\delta^{15}$ N were small (Francois *et al.*, 1992), suggesting the mechanism responsible for reducing nutrient supply to the euphotic zone during LGM dissipated eastward from the Atlantic sector.

We have made a first attempt at quantifying these observations. Our conclusions, however, must still be considered tentative, in view of the uncertainties that remain regarding the quantitative interpretation of these different tracers.

From <sup>230</sup>Th-normalized biogenic Ba fluxes, we have estimated export production and  $F_{sink}$ . On Kerguelen Plateau, <sup>230</sup>Th-normalized biogenic Ba fluxes rose from c. 1 mg/cm<sup>2</sup>.ka during LGM to c. 3 mg/cm<sup>2</sup>.ka during the Holocene, confirming that there was a significant increase in export production during the Holocene. After correction for barite dissolution on the seafloor, using the equation proposed by Dymond *et al.* (1992), we have used the correlation between biogenic Ba and organic carbon fluxes measured in the modern ocean with sediment traps (Dymond *et al.*, 1992; Francois *et al.*, submitted) to arrive at estimates of export production ranging from 10 gC/m2.y (i.e.  $F_{sink} = 1.7$  gN/m<sup>2</sup>.y) during LGM to 42 gC/m2.y (i.e.  $F_{sink} = 7$  gN/m2.y) during the Holocene.

Our interpretation of downcore changes in bulk sediment  $\delta^{15}$ N in the southern ocean (Altabet and Francois, 1994) is based on the Raleigh fractionation equation describing changes in the  $\delta^{15}$ N of the accumulated particulate N sinking out of the euphotic zone ( $\delta_{sink}$ ) as a function of nitrate utilization (u), isotopic fractionation during nitrate uptake by phytoplankton ( $\epsilon_u$ ) and the  $\delta^{15}$ N of new nitrate ( $\delta_{NO_4}$ <sup>in</sup>):

$$\delta_{\text{sink}} = \delta_{\text{NO}_{e}}^{\text{in}} + (\epsilon_{u} (1-u) \ln(1-u)/u)$$
 (5)

When estimating  $\delta_{sink}$  from bulk sediment  $\delta^{15}N$ , we must also take into account the increase in  $\delta^{15}N$  resulting from early diagenesis. We have

measured  $\delta_{NOF}$  (4.5 per mil),  $\varepsilon_u$  (7.5 per mil) and u (0.2) on Kerguelen Plateau during australe summer 1991. By comparing the expected  $\delta_{sink}$  (-2 per mil) with the core top value in MD84-552 (2.5 per mil; Fig. 2c), we have estimated a diagenetic  $\delta^{15}N$  offset of c. 4.5 per mil. Hence, assuming that  $\delta_{NOF}$  and  $\varepsilon_u$  did not change with time:

7.5 (1-u)  $\ln(1-u) / u = \delta_{sed} - 9$  (6) where  $\delta_{sed}$  is the bulk sediment  $\delta^{15}N$ .

Applying equation (6) to the  $\delta^{15}N$  values measured in core MD84-552 (Fig. 2c) suggests that as much as 90% of the nitrate supplied to the euphotic zone during LGM was utilized by phytoplankton, in contrast to only 20% in modern ocean. A similar but smaller difference was also observed in a core further to the north (Francois et al., 1993). The low <sup>231</sup>Pa/<sup>230</sup>Th ratios and <sup>230</sup>Th-normalized biogenic Ba fluxes recorded during the LGM imply that nitrate depletion was not a result of enhanced productivity, and must have been driven by a decrease in the rate of supply of nitrate to the euphotic zone. From the above estimates of F<sub>sink</sub> and u, we can estimate the much reduced rate of nitrate supply to the mixed layer during LGM (0.13 moles/m<sup>2</sup>.y) compared to the Holocene (2.5 moles/ $m^2$ .y). If we assume that nitrate concentration in surface water did not change, we can evaluate  $V_{mix}$  (LGM: 0.5m/y; Holocene: 70m/y). This would however imply impossibly high nitrate concentrations in glacial intermediate water (280µM). We thus conclude that, in addition to reduced mixing in the upper water column, surface nutrient concentration in the surface waters of this region must have decreased substantially. Depending on the geographic extent of this phenomenon, such decrease in surface nutrients (and  $\Sigma CO_2$ ) may have had an important effect on atmospheric CO<sub>2</sub> (e.g. Sarmiento and Toggweiller, 1984 and others).

## Conclusions

We have interpreted the <sup>230</sup>Th, <sup>231</sup>Pa, Ba and  $\delta^{15}$ N profiles of several southern ocean cores as reflecting higher upper water column stratification during LGM which resulted in lower export production and surface nutrient concentration in the Atlantic and Western Indian sector of the southern ocean. These results are consistent with earlier planktonic foraminifera  $\delta^{18}$ O, SST and icerafted debris data (Labeyrie *et al.*, 1986), and with the distribution of *E. antarctica* (Burckle, 1984) which suggest the formation of a melt-water lid from melting icebergs following an eastward trajectory from the Weddell Sea towards the Western Indian sector during LGM.