The Zn isotopic composition of diatom frustules, a proxy for Zn availability in ocean surface seawater

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Zinc is among the essential trace-metal micronutrients for phytoplankton. In common with some other bio-active trace metals, Zn concentrations are highly depleted in those parts of the surface ocean that are replete in the major nutrients (so-called High Nutrient-Low chlorophyll, or HNLC, zones), including the Southern Ocean. The release of these HNLC zones from trace metal limitation may be key for explaining lower atmospheric CO_2 during glacial periods. The preferential incorporation of light Zn isotopes into phytoplankton organic material is expected to leave residual surface seawater Zn isotopically heavy. Thus the degree of trace metal depletion in surface oceans in the past could be tested with a suitable archive of surface seawater Zn isotopes.

We are investigating the reliability of diatom opal as a recorder of the Zn isotopic composition of surface seawater, and have measured Zn isotopic compositions in cleaned diatom frustules from a sequence of core-top samples across the Southern Ocean. All diatom opal exhibits heavy Zn isotopic compositions, as expected from surface waters in highly trace metal-depleted HNLC zones, and the Zn isotope composition tracks decreasing diatom opal burial rates with progressively heavier Zn isotope compositions. Furthermore the measured Zn isotope and Zn/Si ratios, a potential proxy for the free Zn^{2+} content in surface water, are consistent with a model of Zn isotope evolution of the surface ocean in response to the fractionation of Zn isotopes into phytoplankton organic material as measured in experiments [1]. These results suggest that Zn isotopes in diatom frustules record trace metal availability in HNLC zones. Our initial down-core results also show a clear correlation between Zn isotopes and opal burial rates.

[1] John *et al*. (2007) *Limnol Oceanogr.* **52**, 2710-2714.

Sedimentary $^{231}Pa/^{230}Th$ ratios are not a proxy for Atlantic meridional overturning circulation

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Sedimentary $^{231}Pa/^{230}Th$ ratios are receiving growing use as a kinematic proxy to estimate changes in the rate of Atlantic Meridional Overturning Circulation (AMOC). We will present evidence that this use is misdirected. In the Atlantic Ocean today, dissolved $^{231}Pa/^{230}Th$ ratios in deep waters increase from north to south, as expected given that water masses are ventilated in the north and deep waters age as they move southward. However, in contrast to the southward increase in dissolved $^{231}Pa/^{230}Th$ ratios, a survey of core top samples shows that the highest sedimentary $^{231}Pa/^{230}Th$ ratios generally occur in the northernmost North Atlantic, in the region of best-ventilated deep waters. Furthermore, at mid latitudes, sedimentary $^{231}Pa/^{230}Th$ ratios off NW Africa are nearly twice as large as at corresponding latitudes off North America. Overall, the spatial pattern of sedimentary $^{231}Pa/^{230}Th$ ratios indicates control by biological productivity; specifically, by diatom productivity and by the flux of biogenic opal exported to the deep ocean. This relationship is governed by the strong preference for scavenging of dissolved Pa by biogenic opal. Sedimentary $^{231}Pa/^{230}Th$ ratios do not reflect AMOC in the modern Atlantic and should not be used as a quantitative proxy for past changes in the rate of overturning circulation.

We do not contend that AMOC was unaffected during Heinrich Events. To the contrary, we propose that it was the reduction of AMOC that allowed the North Atlantic to be flooded with Si-rich water supplied from the Southern Ocean. If winter mixing penetrated deep enough to entrain Si-rich southern-source water, then this source of Si to surface waters would have stimulated the production of diatoms and increased the flux of opal that enhanced the scavenging of Pa from the water column. This view is supported by the peak during Heinrich Event 1 in the accumulation rate of diatoms in Bermuda Rise sediments [1] that coincided with the interval of elevated $^{231}Pa/^{230}Th$ ratios there [2].

[1] Gil, Keigwin & Abrantes (submitted) *Paleoceanography*.
[2] McManus *et al*. (2004) *Nature* **428**, 834-837.