



The Zn/Si and isotopic composition of diatom frustules, a proxy for Zn availability in surface seawater

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Zinc is an essential micronutrient for certain phytoplankton and, 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 CO₂ during glacial periods. The preferential incorporation of light Zn isotopes into phytoplankton organic material [1] 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 recording the surface seawater Zn isotope composition.

We have tested the reliability of diatom opal as a recorder of the Zn isotopic composition of surface seawater, and have measured Zn concentration and isotopic compositions in cleaned diatom frustules from a sequence of core-top samples across the Pacific sector of the Southern Ocean [2]. 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 Zn²⁺ content in surface water [2], 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. These results show that Zn isotopes in diatom frustules record the availability of Zn in HNLC zones.

We will present Zn/Si ratios and Zn isotope compositions in cleaned diatom opal from down-core samples from the Southern Ocean, extending back into the last glacial period. The data shows a correlation between the Zn/Si ratios, the Zn isotope composition and relative opal burial rates at the measured sites. Thus this new data yield information on the link between the degree of Zn availability and opal productivity in the Southern Ocean since the last glacial period.

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

[2] Andersen et al. (2011) *EPSL*, 301, 137-145.