

Metal uptake and sequestration within Southern Ocean diatom frustules: A significant sink for iron and zinc

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Diatoms, abundant and productive microbes present in all the Earth's seas, account for approximately 43% of annual global marine carbon sequestration. Data from three cruises in the Southern Ocean reveals substantial uptake of iron (Fe) and zinc (Zn) into the diatom's silicate exoskeleton, or frustule. Iron is a necessary nutrient with proven limitations on diatom productivity. Zinc is a critical element in some enzymes necessary for the growth of the diatom. Yet in the Southern Ocean, dissolved Fe and Zn concentrations are extremely limited. Hence, Fe and Zn availability act to limit primary productivity. Using the synchrotron at Argonne National Laboratory, the elemental concentrations of silicon (Si), Fe and Zn in diatoms have been investigated using X-ray micro-fluorescence at a 300nm resolution. An analysis of 300 diatoms from an extensive sample collection along the 67°S transect in the Pacific sector of the Southern Ocean, indicates a molar uptake ratio of 380 $\mu\text{mol Zn:mol Si}$ and a median value of 45 $\mu\text{mol Fe:mol Si}$. X-ray absorption near-edge structure (XANES) spectroscopy on a subset of these samples illustrates that Zn is bound to the silica frustule in 80% of the samples and preliminary data indicate that Fe occurs within the frustule as reduced Fe(II).

XANES spectral data, strong correlations between the Fe:Si and Zn:Si ratios, and results from chemical treatments of frustules indicate that these metals are incorporated into the silicate structure of the frustule, rather than existing as a collocated element or a surface coating. The frustule, relative to the labile organic cellular material, will achieve greater vertical transport prior to remineralization and will sink more quickly into the intermediate and bottom waters. These complementary mechanisms move the incorporated Fe and Zn into deeper waters and create global implications for the potential loss of these trace minerals from the surface ocean.