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Fe and Zn effects on the Si cycle and diatom community structure in two contrasting high and low-silicate HNLC areas

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Abstract

We compared the importance of Fe, Zn and Si availability for diatom growth and silicification through microcosm enrichment experiments in two contrasting HNLC systems of the Sub-Arctic and Sub-Antarctic Pacific. The Bering Sea was characterized by low Fe and Zn concentrations (<0.2 nM) but relatively high silicic acid (5.6–15.9 µM). The addition of 0.25 nM Fe induced a 2–7-fold increase in diatom cell abundance (*Pseudo-nitzschia* sp. and *Cylindrotheca closterium*), an increase in Chl *a*, biogenic silica, and particulate organic carbon and nitrogen, and a 2–3-fold decrease in the average cellular Si content. Zn had no impact on biomass parameters or diatom community structure in this region.

The Sub-Antarctic Zone (SAZ) was a low Si-HNLC system, with initial silicic acid levels of 0.45 µM and Fe and Zn concentrations <0.03 nM. Si was the proximate limiting factor controlling diatom growth, followed by a secondary role for Fe on non-siliceous phytoplankton. In this region, we also found evidence for Zn-mediated changes in diatom community structure. The presence of Zn ($+1$ nM) shifted the community away from a large colonial pennate (*Pseudo-nitzschia* sp.) towards a smaller and less silicified solitary pennate (*Cylindrotheca closterium*), potentially prone to more rapid silica dissolution in the surface layer.

Despite the dominance by the same two diatom genera, these two high-latitude regimes exhibited different nutrient limitation scenarios. Diatom growth in the Bering Sea was strongly Fe-limited, while the SAZ was mainly limited by Si and only secondarily by Fe.

Keywords: Iron; Zinc; Silicate; Diatoms; HNLC; HNLSiLC; Trace metal limitation

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1. Introduction

Carbon export to the deep ocean by the biological pump is often associated with diatom blooms. The contribution of diatoms to total primary production ranges from 35% in open ocean waters to 75% in coastal upwelling areas (Nelson et al., 1995), and this group tends to dominate new production and export fluxes in turbulent, nutrient rich areas (Margalef, 1978; Legendre and Le Fèvre, 1989). Diatoms use dissolved Si to build their cell wall through biomineralization, but once formed, biogenic silica (BSi) is less readily recycled in the surface layer than the more labile organic carbon, nitrogen or phosphorus compounds, and is thus preferentially exported out of the euphotic layer (Dugdale et al., 1995; Buesseler, 1998). The surface ocean is therefore largely undersaturated with silicic acid, which consequently can often be limiting for diatom growth.

Phytoplankton productivity is not sustained at its full capacity in some areas despite high major nutrient levels, keeping vast open ocean regions biologically poor. The High Nutrient Low Chlorophyll (HNLC) areas are secluded from land masses and receive low atmospheric fluxes of iron-rich dust particles, leading to iron limitation of phytoplankton growth (Martin and Fitzwater, 1988; Martin et al., 1991). Fe-limitation has been conclusively demonstrated in these HNLC areas through mesoscale in situ enrichment experiments and microcosm bottle experiments (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Bakker et al., 2001; Law et al., 2001; Gervais et al., 2002; Tsuda et al., 2003; Coale et al., 2004; Boyd, 2004). Fe limitation also controls community structure in these regions, preventing the growth of larger species with high half-saturation constants for Fe uptake (Gall et al., 2001; Sedwick et al., 2000; Timmermans et al., 2001).

Fe availability has far-reaching implications for the biogeochemical cycles of C, N, P, and Si. For instance, Fe can induce significant alterations of diatom Si:N and Si:C stoichiometric ratios (Hutchins and Bruland, 1998; Takeda, 1998; De La Rocha et al., 2000; Firme et al., 2003; Brzezinski et al., 2003; Leynaert et al., 2004; Timmermans et al., 2004). As Fe is required for photosynthetic carbon acquisition and the synthesis of nitrate reductase, Fe-starved diatoms exhibit dramatically reduced carbon fixation and nitrate uptake rates (Geider and La Roche, 1994) while continuing to take up Si at slightly lowered rates (De La Rocha et al., 2000). Depending on the degree of Fe limitation, increases in the dissolved Si:N drawdown ratio by a factor of 1.4–3 have been observed (Takeda, 1998; Hutchins and Bruland, 1998; De La Rocha et al., 2000; Leynaert et al., 2004).

While Fe has received a great deal of attention, there has also been interest in the possible role of Zn in phytoplankton productivity (Morel et al., 1994). Zinc is a required nutrient for growth and is a cofactor for approximately 300 enzymes involved in nearly all aspects of cell metabolism (Anderson et al., 1978; Vallee and Auld, 1990). These include critical enzymes like carbonic anhydrase (Morel et al., 1994), which catalyzes inorganic carbon acquisition by supplying CO_2 to RUBISCO, and alkaline phosphatase, which enables cells to acquire phosphorus from organic compounds under low P-conditions (Aksnes et al., 1994).

The potential role of Zn in controlling phytoplankton productivity and community structure is however less well documented. It typically occurs in concentrations $<0.1\,\mathrm{nM}$ in surface waters (Bruland and Franks, 1983) and several studies have suggested that free Zn^{2+} concentrations could be limiting in the oceans, as 98% of the total dissolved Zn is chelated by strong ligands (Bruland, 1980, 1989; Ellwood and van den Berg, 2000; Lohan et al., 2002). Laboratory experiments suggest that low free Zn^{2+} concentrations can limit the growth of coastal species (Anderson et al., 1978; Brand et al., 1983) leading to the formulation of the "Zn-hypothesis" by Morel et al. (1994). However, relatively few experiments have been conducted with natural assemblages, and in most cases have shown very minimal effects of Zn, if any, on the bulk phytoplankton community (Coale, 1991; Gall et al., 2001; Cochlan et al., 2002; Crawford et al., 2003; Coale et al., 2003).

Despite this, Zn availability could be low enough to control the growth of particular taxa