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# Effect of iron limitation on the cadmium to phosphorus ratio of natural phytoplankton assemblages from the Southern Ocean

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*Abstract*

There is considerable interest in the biogeochemical cycling of cadmium (Cd) and phosphate ($PO_4$) in surface waters, driven in part by the ongoing development of a paleonutrient proxy that utilizes Cd preserved in fossil planktonic foraminifera to determine past $PO_4$ utilization efficiencies in ocean surface waters. The present article reports the results of a field study into the effects of Fe limitation on the Cd : P composition of natural assemblages of marine phytoplankton in the Antarctic Zone of the Pacific sector of the Southern Ocean. Iron enrichment to shipboard incubation bottles led to increases in community growth rate and final biomass. After 10.7 d of incubation, the climax community was dominated by large diatoms of the genus *Fragillariopsis, Pseudonitzschia,* and *Nitzschia.* Direct measurements of phytoplankton metal : P ratios from controlled shipboard experiments indicate that Cd : P, Co : P, and Zn : P ratios decreased from control values with increasing initial dissolved Fe concentrations in the incubation bottles, by factors of ~2–10 at highest Fe additions. We suggest that the effect of Fe limitation on resident diatoms is to decrease growth rate, leading to elevated cellular Cd content. The dissolved Cd : P ratio in iron-limited surface waters of the Southern Ocean may, therefore, respond to the supply of Fe to the resident phytoplankton community, which has implications for the developing paleonutrient proxy. We suggest that the biological uptake of Cd and P is independent of the dissolved Cd : $PO_4$ ratio. As a consequence, the results argue against the use of empirical Rayleigh fractionation models or models with fixed phytoplankton uptake ratios to account for regional variability in surface water dissolved Cd : $PO_4$.

The distribution of cadmium in the ocean mimics that of the algal nutrient phosphate ($PO_4$) (Boyle et al. 1976; Bruland et al. 1978; de Baar et al. 1994). Like $PO_4$, vertical distributions are typified by surface depletions that increase rapidly to maximum concentrations in the main thermocline and remain relatively constant with depth. The strength of the correlation between Cd and $PO_4$, combined with Cd : Ca ratios in fossil foraminiferal tests, has been used to reconstruct empirically past $PO_4$ concentrations in deep water (Boyle 1988) and more recently in surface water (Elderfield and Rickaby 2000). In contrast to deep waters, well-documented deviations from the average Cd : $PO_4$ trend exist in surface waters of the modern ocean (Martin et al. 1989; Rutgers van der Loeff et al. 1997) especially in Fe-limited, high nutrient–low chlorophyll (HNLC) areas of the Southern Ocean, where waters exhibit relatively high concentrations of dissolved Cd, Zn, and the major nutrients N, P, and Si (Martin and Fitzwater 1990; Martin et al. 1990; Frew and Hunter 1992, 1995; Nolting and de Baar 1994; Löscher et al. 1998). The mechanism behind these deviations is not known.

Reconstructions of past $PO_4$ concentrations using foraminiferal Cd : Ca ratios depend on, among other factors, accurate knowledge of the modern dissolved Cd : $PO_4$ relationship (de Baar et al. 1994; Löscher et al. 1997), and our

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ability to model how this ratio changes temporally and spatially in the ocean (Saager and de Baar 1993; Löscher et al. 1998; Elderfield and Rickaby 2000). To account for variations in surface water dissolved $Cd:PO_4$ in the global ocean, Saager and de Baar (1993) have modeled global $Cd:PO_4$ distributions under the assumption of regionally constant uptake ratios by the plankton. In contrast, Elderfield and Rickaby (2000) have applied a Rayleigh fractionation model that assumes a constant fractionation factor between seawater (SW) and particulate organic matter (POM) ($\alpha_{Cd:P} = Cd:P_{POM}/Cd:P_{SW} \cong 2.5$). Although both approaches are fairly successful at describing the distribution of $Cd:PO_4$ in the modern ocean, they provide no mechanistic understanding of processes controlling the relative rates of Cd and $PO_4$ removal from the upper ocean or why regional differences in phytoplankton Cd:P might exist. Without a mechanistic understanding of the surface water variability of dissolved $Cd:PO_4$ ratios, we have to question the accuracy of glacial $Cd:PO_4$ distributions derived from modeling studies and, by extension, the accuracy of $PO_4$ concentration reconstructions based on planktonic foraminiferal Cd:Ca estimates.

The biogeochemical cycles of Cd and $PO_4$ are thought to be linked through their uptake by phytoplankton in surface waters and subsequent remineralization at depth when sinking organic material is destroyed by heterotrophs in the main thermocline. The factors controlling the uptake of Cd relative to $PO_4$ and the resulting Cd:P ratio of the sinking material are only poorly characterized. Evidence from controlled laboratory studies of Cd uptake by marine diatoms suggests that Cd can supplement or substitute for Zn in the enzyme carbonic anhydrase (Price and Morel 1990; Morel et al. 1994; Lee and Morel 1995) or can be used directly in a Cd-specific form of the enzyme (Cullen et al. 1999; Lane and Morel 2000*a*,*b*). In addition, laboratory studies with coastal diatoms have demonstrated that cellular Cd content increases with the free ion concentration of Cd in the medium and decreases with increasing Zn and Mn free ion concentrations, likely because of competitive inhibition at cellular uptake sites (Sunda and Huntsman 1996, 1998, 2000).

Experiments with Fe-limited populations of the oceanic diatom *Thalassiosira oceanica* (Sunda and Huntsman 2000) have indicated that cellular Cd content increases with decreasing Fe availability, which is apparently caused by a ~50% decrease in growth rate, at constant Cd uptake rate, according to the equation

$$\rho = \mu Q$$

where $\rho$ is the normalized cellular uptake rate (mol Cd cell$^{-1}$ time$^{-1}$), $\mu$ is the specific growth rate (time$^{-1}$), and $Q$ is the cellular quota (mol Cd cell$^{-1}$). In contrast, a recent study of Cd uptake in response to a mesoscale Fe addition south of the Polar Front along 140°E (Frew et al. 2001) concluded that increased Fe availability leads to increased Cd:P ratios in the plankton.

Herein we report the results of a shipboard incubation study that investigated the effect of Fe and Zn availability on the metal:P ratio of natural assemblages of phytoplankton collected from surface waters of the Southern Ocean. The results suggest that relaxing growth limitation by Fe may lead to reduced uptake of Cd (as well as Co and Zn) relative to P by diatoms. If a widespread eolian deposition of Fe led to increased diatom growth during the last glacial maximum (Martin 1990; Martin et al. 1990), estimations of surface water $PO_4$ concentrations that assume a constant fractionation factor (Elderfield and Rickaby 2000) or regionally fixed phytoplankton Cd:P ratios (Saager and de Baar 1993) similar to the modern ocean could systematically overestimate surface nutrient inventories. The lack of a clear physiological link between phytoplankton Cd:P ratios and the dissolved $Cd:PO_4$ ratio in the ambient seawater argues against the use of empirical Rayleigh fractionation models and $\alpha_{Cd:P}$ to account for regional variations in surface water dissolved $Cd:PO_4$.

## Materials and methods

*Shipboard incubations*—The incubation experiment was performed during the U.S. JGOFS Southern Ocean survey II cruise (8 Jan–8 Feb 1998) aboard R/V *Roger Revelle.* Trace metal clean methodology was used throughout, to minimize potential contamination during sample collection and subsequent handling.

Near-surface water (20 m) for the incubations was collected using acid-cleaned, 30-liter Teflon-coated GO-Flo bottles (General Oceanics) suspended on a Kevlar wire (Bruland et al. 1979), south of the Antarctic Polar Front, at 67.8°S, 170.1°W, on 18 January 1998. The mixed layer depth was 19.8 m at the time of SW collection. Polycarbonate carboys (20 liters) that were subjected to rigorous acid cleaning (according to the method of Martin et al. 1991) were used for the incubation experiments. Each carboy was equipped with Nalgene filling/venting closures with three built-in tubing ports (Coale 1991). After collection, eight 20-liter polycarbonate carboys were rinsed and then filled with unfiltered SW in the clean laboratory van at the sampling site, using the methodology described in Coale (1991). Incubation carboys were filled serially from each GO-Flo bottle, in an effort to assure homogeneity. For Fe treatments, a stock solution (1,000 ppm Fe stock solution; Fisher Scientific) was added to incubation carboys to achieve final concentrations of 0.2, 0.5, 1.0, and 2.5 nmol L$^{-1}$. There were also two Zn treatments—one carboy received Zn alone (10 nmol L$^{-1}$; from a 1,000 ppm Zn stock solution; Fisher Scientific) and another received Zn (10 nmol L$^{-1}$) and Fe (2.5 nmol L$^{-1}$). Two carboys incubated without metal additions served as controls. All carboys were triple bagged and incubated on deck at in situ temperature and light levels that were ~20% higher than in situ irradiance, so photoinhibition may have been a factor during the first day of the experiment.

Initial samples for chlorophyll *a*, nutrients, particulate organic carbon (POC), particulate organic nitrogen (PON), dissolved and particulate trace elements, and phytoplankton species counts were drawn directly from the GO-Flo bottles. An initial sample for dissolved Fe and Zn was drawn from each enrichment carboy directly into an acid-cleaned low-density polyethylene bottle and immediately acidified to pH <1.6 with 4 ml quartz-distilled 6 N HCl.

Subsamples (100 ml) were removed at regular intervals for analysis of nutrient and chlorophyll concentrations. After

Table 1. Surface water properties at 67.8°S, 170.1°W at the time of incubation water collection.

| Element | Dissolved (<0.4 μm) | Particulate (>0.45 μm) | $pCO_2$ Pa | Chl *a* (μg $L^{-1}$) | Temperature (°C) | Salinity |
|---|---|---|---|---|---|---|
| Cd (nmol $kg^{-1}$) | 0.34 | 0.34 | 39.9 | 0.91 | 0.5 | 34.14 |
| Co (nmol $kg^{-1}$) | 0.02 | 0.04 | | | | |
| Cu (nmol $kg^{-1}$) | 1.78 | 0.38 | | | | |
| Fe (nmol $kg^{-1}$) | 0.03 | 0.26 | | | | |
| Mn (nmol $kg^{-1}$) | 0.08 | 0.44 | | | | |
| Zn (nmol $kg^{-1}$) | 1.01 | 2.91 | | | | |
| $NO_3^-$ (μmol $L^{-1}$) | 25.1 | — | | | | |
| $PO_4^{3-}$ (μmol $L^{-1}$) | 1.54 | 0.26 | | | | |
| $SiO_2$ (μmol $L^{-1}$) | 60 | — | | | | |

10.7 d, 900-ml subsamples from each incubation bottle were filtered onto 0.45 μm 47 mm polysulfone-ester filters (Gelman Supor™) in a Class 100 laminar flow hood and stored at −20°C until they could be analyzed for particulate trace elements in the laboratory at Rutgers University.

*Analytical methods*—Trace metal concentrations in seawater were analyzed at Moss Landing Marine Laboratories using organic extraction with ammonium 1-pyrrolidinedithiocarbamate/diethylammonium diethyldithiocarbamate (APDC/DDDC) into chloroform (Bruland et al. 1979). Macronutrients (N, P, and Si) were analyzed by standard autoanalytical methods on board the ship. The concentration of Chl *a* was measured in acetone extractions using a Turner Design fluorometer (Model 10-AU). POC and PON were determined on precombusted 25-mm GF/F Whatman filters in the lab using a Control Equipment Corporation 440 Elemental analyzer.

*Particulate metal : P determinations*—Subsamples (1.21 $cm^2$) of 0.45 μm 47 mm polysulfone-ester filters (Gelman Supor) were placed in 15-ml screw-cap Teflon vials (Savillex) (Cullen and Sherrell 1999). Cells were digested completely in 950 μl of 16 N $HNO_3$ and 50 μl 32 N HF, added to dissolve refractory inorganic phases, on a hot plate at 120°C for 4 h. Digests of samples and filter blanks and digest blanks (acid only) were analyzed for trace elements and P by magnetic sector high-resolution, inductively coupled plasma, mass spectrometer (HR-ICP-MS; Element, Finnigan-MAT) using a combination of internal and external standardization (Cullen et al. 2001). Concentrations of Cd, Co, Cu, Mn, P, and Zn in filter blanks were always <15% of the sample and were lowest for Cd (0.01%) and highest for Mn (15%).

*Calculation of phytoplankton growth rates*—Specific growth rates for phytoplankton genera and the phytoplankton community (μ $d^{-1}$) were calculated according to the following relationship:

$$\mu = \frac{\ln X_t - \ln X_0}{t}$$

where $X_t$ and $X_0$ are the total cell counts for the genus of interest or the entire phytoplankton community after and before the logarithmic phase of growth. The incubation time in days is represented by *t*. Cell counts were used to calculate specific growth instead of Chl *a*, POC, or PON, to avoid overestimation of true growth that could result from Fe-stimulated increases of phytoplankton Chl *a* content and variations in cellular C : N ratios.

A Michaelis-Menten equation was used to model the effects of increasing dissolved Fe concentrations ([Fe]) on phytoplankton growth rates (μ):

$$\mu = \mu_M \frac{[\text{Fe}]}{K_\mu + [\text{Fe}]}$$

where $\mu_M$ is the maximum growth rate and $K_\mu$ is the half-saturation constant for growth with respect to dissolved Fe. Fe concentrations were measured in the bottles at the beginning of experiments and were assumed not to change significantly during the incubations. Estimates of $\mu_M$ and $K_\mu$ were solved for iteratively using Microsoft Excel software. The resulting parameters and initial dissolved Fe concentrations were used to estimate in situ community growth rates.

## Results

The surface water chemical properties (20 m) on station at 67.8°S, 170.1°W on 18 January 1998 are given in Table 1.

*Effect of Fe and Zn additions on phytoplankton growth and species composition*—The addition of Fe to incubation bottles enhanced the growth of the resident phytoplankton community by a factor of ~2 from 0.15 $d^{-1}$ in control bottles (0.07 nmol $L^{-1}$ Fe measured in bottle) to a maximum of 0.28 $d^{-1}$ in the highest Fe treatment bottles (2.5 nmol $L^{-1}$ Fe) (Table 2). Community growth rates increased with increasing Fe additions and saturated at an added Fe concentration of ~1 nmol $L^{-1}$. The greatest growth response, determined by increase in cell numbers, to the 2.5 nmol $L^{-1}$ Fe addition was measured for the groups *Phaeocystis* (0.45 $d^{-1}$), *Pseudonitzschia* (0.34 $d^{-1}$), and *Chaetoceros* (0.33 $d^{-1}$). Phytoplankton growth rates in bottles supplemented with Zn without Fe were less than ~50% of rates measured in high Fe treatments and equal to the control treatment. Species composition was similar across Fe treatments, with the diatoms of the genera *Fragillariopsis, Pseudonitzschia,* and *Nitzschia* dominating the biomass of the communities in the

Table 2. Community growth rate and particulate metal concentrations (>0.45 $\mu$m) on day 10.7 of the incubations. SD represents the analytical uncertainty of the measurement.

| | | Incubation experiments: added Fe (nmol $L^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Initial | Control, 0 | 0.2 | 0.5 | 1 | 2.5 | +Zn | +Fe+Zn |
| $\mu$ ($d^{-1}$) | 0.11 | 0.15 | 0.19 | 0.25 | 0.28 | 0.28 | 0.15 | 0.27 |
| P ($\mu$mol $L^{-1}$) | 0.26 | 0.62 | 0.80 | 1.08 | 1.12 | 1.59 | 0.32 | 1.16 |
| ± SD | 0.01 | 0.01 | 0.02 | 0.04 | 0.03 | 0.07 | 0.003 | 0.002 |
| Cd (nmol $L^{-1}$) | 0.34 | 0.38 | 0.42 | 0.44 | 0.49 | 0.57 | 0.30 | 0.54 |
| ± SD | 0.002 | 0.004 | 0.001 | 0.004 | 0.0001 | 0.003 | 0.003 | 0.002 |
| Co (nmol $L^{-1}$) | 0.04 | 0.18 | 0.05 | 0.10 | 0.11 | 0.03 | 0.01 | 0.06 |
| ± SD | 0.0002 | 0.004 | 0.002 | 0.005 | 0.004 | 0.002 | 0.001 | 0.003 |
| Cu (nmol $L^{-1}$) | 0.38 | 0.32 | 0.49 | 0.58 | 0.67 | 0.71 | 0.22 | 0.64 |
| ± SD | 0.020 | 0.003 | 0.006 | 0.037 | 0.007 | 0.019 | 0.016 | 0.012 |
| Mn (nmol $L^{-1}$) | 0.44 | 0.38 | 0.56 | 0.71 | 0.79 | 0.84 | 0.27 | 0.76 |
| ± SD | 0.025 | 0.008 | 0.023 | 0.056 | 0.049 | 0.042 | 0.016 | 0.020 |
| Zn (nmol $L^{-1}$) | 2.91 | 2.46 | 2.70 | 2.73 | 3.25 | 3.40 | 3.81 | 7.04 |
| ± SD | 0.069 | 0.038 | 0.061 | 0.103 | 0.062 | 0.126 | 0.111 | 0.084 |

bottles. Using the Michaelis-Menten model with $\mu_M = 0.25$ $d^{-1}$ and $K_\mu = 0.038$ and the initial dissolved Fe concentration measured in surface waters at the station, 0.03 nmol $L^{-1}$, we estimate that the initial community growth rate was 0.11 $d^{-1}$.

The POC : Chl *a*, C : N (Coale et al. 2003) and C : P (calculated from measurements of POC and HR-ICP-MS determined P on separate filters) ratios in the control bottle changed little over the course of the experiment. The initial POC : Chl *a* ratio was 206 g $g^{-1}$ and increased slightly by day 9 to 220 g $g^{-1}$. C : N and C : P ratios were initially 6.1 and 66 mol $mol^{-1}$ in the control bottle and decreased to 6 and 63 mol $mol^{-1}$, respectively, by the end of the incubation. Similar data were not available for the treatment bottles.

*Effect of Fe and Zn additions on particulate metal and P concentrations*—Initial particulate metal and P concentrations in the starting water and the concentrations after 10.7 d of incubation in the presence of varying Fe and Zn additions are shown in Table 2. Supplementing the incubation carboys with Fe led to progressive increases in the concentration of particulate P from an initial value of 0.26 ± 0.01 nmol $L^{-1}$ to a maximum value of 1.59 ± 0.07 nmol $L^{-1}$ in the 2.5 nmol $L^{-1}$ Fe treatment (Table 2). Similar to particulate P, particulate metal concentrations in the bottles generally increased in response to increasing Fe additions. Particulate Cd increased from the initial value of 0.34 ± 0.002 nmol $L^{-1}$ to 0.57 ± 0.003 nmol $L^{-1}$ in the highest Fe treatment. Particulate Cu, Mn, and Zn were slightly lower in the control treatment relative to the initial starting water concentrations but were progressively higher with increasing Fe additions. Unlike the other metals, after 10.7 d, the concentrations of particulate Co in the incubation bottles showed no systematic relationship to the amount of dissolved Fe added. The lowest particulate Co concentrations were measured in the +10 nmol $L^{-1}$ Zn treatment (0.01 ± 0.001 nmol $L^{-1}$), and the highest concentrations were present in the control bottle (0.18 nmol $L^{-1}$).

*Effect of Fe and Zn additions on the metal : P ratio of phytoplankton assemblages*—Additions of Fe increased the growth rates and final biomass of incubations and were accompanied by significant decreases in the Cd : P, Co : P, Cu : P, Mn : P, and Zn : P (nmol $\mu$$mol^{-1}$) ratios of the phytoplankton (Table 3; Fig. 1). Particulate material collected from surface waters on station had an initial Cd : P ratio of 1.29 ±

Table 3. Particulate metal : P ratios (>0.45 $\mu$m) for natural phytoplankton assemblages collected after 10.7 days of incubation. SD represents the analytical uncertainty of the measurement.

| Metal : P (nmol $\mu$$mol^{-1}$) | | Incubation experiments: added Fe (nmol $L^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Initial | Control, 0 | 0.2 | 0.5 | 1.0 | 2.5 | +Zn | +Fe+Zn |
| Cd : P | 1.29 | 0.62 | 0.53 | 0.41 | 0.44 | 0.36 | 0.93 | 0.47 |
| ± SD | 0.07 | 0.01 | 0.01 | 0.02 | 0.01 | 0.02 | 0.01 | 0.002 |
| Co : P | 0.15 | 0.29 | 0.06 | 0.09 | 0.10 | 0.02 | 0.04 | 0.05 |
| ± SD | 0.01 | 0.01 | 0.003 | 0.01 | 0.004 | 0.001 | 0.003 | 0.002 |
| Cu : P | 1.44 | 0.51 | 0.61 | 0.54 | 0.60 | 0.45 | 0.70 | 0.55 |
| ± SD | 0.11 | 0.01 | 0.02 | 0.04 | 0.01 | 0.02 | 0.05 | 0.01 |
| Mn : P | 1.68 | 0.61 | 0.70 | 0.66 | 0.70 | 0.53 | 0.85 | 0.65 |
| ± SD | 0.13 | 0.02 | 0.03 | 0.06 | 0.05 | 0.03 | 0.05 | 0.02 |
| Zn : P | 11.09 | 3.96 | 3.39 | 2.53 | 2.91 | 2.14 | 11.96 | 6.06 |
| ± SD | 0.67 | 0.09 | 0.11 | 0.14 | 0.09 | 0.12 | 0.37 | 0.07 |

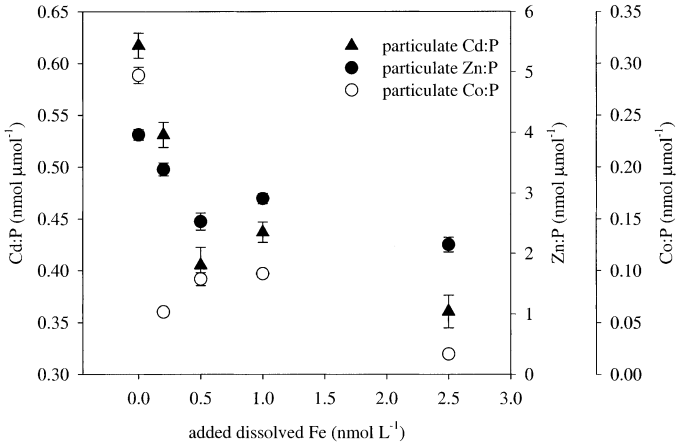


Fig. 1. The Cd : P, Co : P, and Zn : P ratio (nmol $\mu$mol$^{-1}$) of POM (>0.45 $\mu$m) vs. dissolved Fe added to the incubation bottles. Samples were filtered on day 10.7 of the incubation. Error bars represent the analytical uncertainty calculated from particulate metal and P measurements.

0.07 nmol $\mu$mol$^{-1}$, which is substantially higher than the dissolved Cd : $PO_4$ ratio of 0.22 nmol $\mu$mol$^{-1}$. This particulate Cd : P ratio is high compared with reported values derived from the slope of dissolved Cd : $PO_4$ in the nutricline; however, there is precedent in the literature for similarly high particulate ratios (0.7–1.5 nmol $\mu$mol$^{-1}$ >0.45 $\mu$m; Sherrell 1989; Cullen et al. 1999; Kremling and Streu 2001). Our initial Cd : P ratio, derived from the analysis of Cd and P from the same filter, is in excellent agreement with the particulate Cd : P ratio (1.45 or 1.27 nmol $\mu$mol$^{-1}$) derived by taking the ratio of independent estimates of particulate Cd (data of K. Coale, http://usjgofs.whoi.edu/jg/dir/jgofs/southern/rr-kiwi_8) and particulate P (estimated from the particulate N data of W. O. Smith, http://usjgofs.whoi.edu/jg/dir/jgofs/southern/rr-kiwi_8, assuming either N : P = 16 or 14; de Baar et al. 1997) at this site.

As in previous Fe addition experiments (Coale 1991; Hutchins and Bruland 1998), control bottles in this experiment, to which no Fe was added, showed increases in growth rate and final biomass that may have resulted from relaxation of grazing pressure or increased mean irradiance. At the end of the incubation period (10.7 d), particulate Cd : P ratios in the control bottles were 0.62 ± 0.01 nmol $\mu$mol$^{-1}$, a factor of two lower than initial surface plankton ratios. We observed a progressive decrease in the particulate Cd : P ratio at 10.7 d with increasing Fe additions, from 0.62 ± 0.01 nmol $\mu$mol$^{-1}$ in the control bottle down to 0.36 ± 0.02 nmol $\mu$mol$^{-1}$ in the bottle incubated with an addition of 2.5 nmol L$^{-1}$ dissolved. Trends for particulate Co : P and Zn : P ratios were similar to that of Cd : P. Particulate Co : P ratios were highest in the initial and control treatments (0.15 ± 0.01 and 0.29 ± 0.01 nmol $\mu$mol$^{-1}$), decreasing to a minimum of 0.02 ± 0.003 nmol $\mu$mol$^{-1}$ in the highest Fe treatment. Zn : P ratios were 11.1 ± 0.67 nmol $\mu$mol$^{-1}$ in the initial sample but dropped to 3.96 ± 0.09 nmol $\mu$mol$^{-1}$ after 10.7 d in the control bottle. The Zn : P of the natural phytoplankton assemblage decreased with increasing dissolved Fe additions to a minimum of 2.14 ± 0.12 mmol mol$^{-1}$ in the 2.5 nmol L$^{-1}$ treatment. Initial samples for Cu : P and Mn : P were 1.44 ± 0.11 and 1.68 ± 0.13 nmol $\mu$mol$^{-1}$, respectively. After incubation, Cu : P and Mn : P in the control treatments (0.51 ± 0.01 and 0.61 ± 0.02 nmol $\mu$mol$^{-1}$) were significantly lower than in initial samples. Unlike for Cd : P and Zn : P, Fe-amended incubations had Cu : P and Mn : P ratios that did not decrease progressively in response to Fe additions. Cu : P and Mn : P were more variable across Fe treatments with the lowest ratios measured in bottles with the 2.5 nmol L$^{-1}$ Fe addition (0.45 ± 0.02 and 0.53 ± 0.03 nmol $\mu$mol$^{-1}$, respectively).

In incubation bottles to which 10 nmol L$^{-1}$ Zn was added on its own, final Cd : P, Cu : P, Mn : P, and Zn : P ratios were 0.93 ± 0.01, 0.70 ± 0.05, 0.85 ± 0.05, and 12 ± 0.37 nmol $\mu$mol$^{-1}$, respectively (Table 3). In bottles supplemented with Zn and 2.5 nmol L$^{-1}$ Fe, particulate Cd : P, Cu : P, Mn : P, and Zn : P ratios were 0.47 ± 0.002, 0.55 ± 0.01, 0.65 ± 0.02, and 6.06 ± 0.07 nmol $\mu$mol$^{-1}$, respectively. Unlike the other metals, Co : P ratios were lower in the Zn (0.04 ± 0.003 nmol $\mu$mol$^{-1}$) and Zn+Fe (0.05 ± 0.002 nmol $\mu$mol$^{-1}$) treatments than in initial samples or the control bottle (Table 3).

## Discussion

The present study used shipboard incubation experiments to investigate the effects of Fe fertilization on the metal : P ratios of natural phytoplankton assemblages in the HNLC Southern Ocean. The results indicate that Fe additions act to increase community growth rate and final biomass and to reduce Cd : P, Co : P, and Zn : P ratios of the diatom-dominated phytoplankton assemblages after 10.7 d of incubation.

Two possible mechanisms can be invoked to explain these results. First, there may be a direct physiological link between Cd (and Zn and Co) uptake and Fe availability, such that high dissolved Fe inhibits uptake of other metals. Second, the reduction in metal : P ratios at high dissolved Fe may be an indirect effect of increased growth rate with Fe amendment, leading to ''growth rate dilution'' of cellular metal concentrations.

In support of the first explanation, laboratory experiments with the centric coastal diatom *Thalassiosira weissflogii* have demonstrated competitive uptake inhibition between Cd and Fe (Foster and Morel 1982; Harrison and Morel 1983). In single-species cultures of this organism, Cd uptake was inhibited by ~2-fold, from 0.23 to 0.12 × 10$^{-18}$ mole cell$^{-1}$ d$^{-1}$ when pFe ($-\log[Fe^{3+}]$) increased from 19.6 to 18.6. The authors of that study suggested that this antagonism between the two elements could be attributed to competition between Fe and Cd for cell surface transport sites (Harrison and Morel 1983). We are not aware of similar studies that conclusively document competitive inhibition between Fe and Zn or between Fe and Co.

*Growth rate dilution*—In the absence of a known biochemical link between Fe availability and the uptake of Cd, Zn, and Co and given the good relationship found here between growth rate and community Cd : P (Fig. 2), we believe that our incubation results are better explained by the effect of iron on growth rate through the ''growth rate dilution''

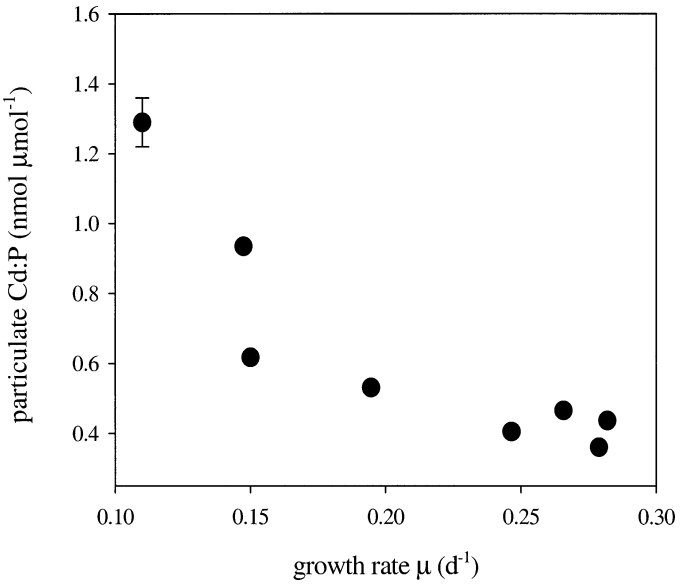


Fig. 2. Particulate Cd : P ratio (>0.45 $\mu$m) for the climax community (10.7 d) vs. the community growth rate calculated from the increase of cells numbers with time (except where noted in the text). Error bars represent analytical uncertainty in the measured ratio.

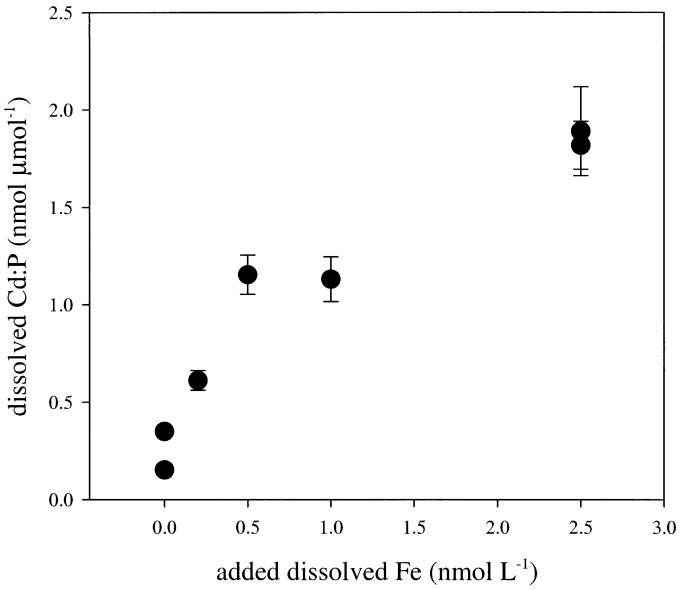


Fig. 3. Calculated dissolved Cd : $PO_4$ ratio on day 10.7 of the experiment vs. dissolved Fe added to the incubation bottles.

effect. This effect of growth rate, which has been observed in laboratory cultures (Kudo et al. 1996; Sunda and Huntsman 2000) can be described as a constant accumulation of metals combined with faster rates of accumulation of nonmetal biomass at higher growth rates. In semicontinuous batch cultures of the diatom *Phaeodactylum tricornutum*, where growth rate was controlled by the supply rate of fresh media, particulate Cd : P ratios decreased from 0.2 nmol $\mu$mol$^{-1}$ at a growth rate of 0.11 d$^{-1}$ down to 0.1 nmol $\mu$mol$^{-1}$ at 1.1 d$^{-1}$ (Kudo et al. 1996). Similar to those in our incubations, the decrease in particulate Cd : P in this diatom resulted from an increase in particulate P (biomass increase), whereas the particulate Cd content was largely invariant with increasing growth rate.

The effect of Fe additions on the partitioning of Cd and $PO_4$ in the incubation carboys at the end of the experiment, relative to the initial conditions, are reported in Table 4. Final dissolved Cd concentrations were calculated by assuming that the increase of particulate Cd was balanced by a decrease in the dissolved pool. Except where noted, all other parameters were directly measured in the bottles on day 10.7. Consistent with the growth rate dilution hypothesis, the decrease in dissolved $PO_4$ was proportionally greater than the draw-down of dissolved Cd in the Fe treatment bottles relative to the initial dissolved Cd : $PO_4$ ratio. The initial dissolved Cd : $PO_4$ ratio of 0.22 $\pm$ 0.02 nmol $\mu$mol$^{-1}$ increased with increasing Fe addition and community growth rate to a maximum of 1.88 $\pm$ 0.11 nmol $\mu$mol$^{-1}$ in the 2.5 nmol L$^{-1}$ Fe treatment (Table 4; Fig. 3).

The effect of Zn additions with and without Fe on the Cd : P ratio of the phytoplankton assemblage lends support to the interpretation that reduced particulate Cd : P in the Fe treatments resulted from growth rate dilution. The surface water

Table 4. Cd and P partitioning in the initial sample and in carboys on day 10.7 of incubation SII-3. SD represents the analytical uncertainty of the measurement, except where indicated.

| Treatment | Particulate Cd (nmol L$^{-1}$) | $\pm$SD | Dissolved Cd (nmol L$^{-1}$)* | $\pm$SD† | Dissolved $PO_4$ ($\mu$mol L$^{-1}$) | Dissolved Cd : $PO_4$ (nmol $\mu$mol$^{-1}$) | $\pm$SD‡ | Particulate Cd : $PO_4$ (nmol $\mu$mol$^{-1}$) | $\pm$SD |
|---|---|---|---|---|---|---|---|---|---|
| Initial | 0.34 | 0.002 | 0.34 | 0.017 | 1.56 | 0.22 | 0.02 | 1.29 | 0.072 |
| 0 | 0.38 | 0.004 | 0.30 | 0.018 | 0.85 | 0.35 | 0.03 | 0.62 | 0.012 |
| 0.2 | 0.42 | 0.001 | 0.26 | 0.017 | 0.42 | 0.61 | 0.05 | 0.53 | 0.012 |
| 0.5 | 0.44 | 0.004 | 0.24 | 0.018 | 0.21 | 1.15 | 0.10 | 0.41 | 0.017 |
| 1 | 0.49 | 0.0001 | 0.19 | 0.017 | 0.17 | 1.13 | 0.12 | 0.44 | 0.010 |
| 2.5 | 0.57 | 0.003 | 0.11 | 0.017 | 0.16 | 0.67 | 0.11 | 0.36 | 0.016 |
| +Fe+Zn | 0.30 | 0.003 | 0.38 | 0.017 | 0.21 | 1.82 | 0.12 | 0.93 | 0.013 |
| +Zn | 0.54 | 0.002 | 0.14 | 0.017 | 0.92 | 0.15 | 0.02 | 0.47 | 0.002 |

* Calculated assuming that the increase in particulate Cd in the incubation bottles was balanced by the removal of dissolved Cd.
† Uncertainty was calculated by error propagation under the assumption of a 5% uncertainty in the initial dissolved Cd measurement.
‡ Uncertainty in the ratio was calculated by error propagation under the assumption of a 5% uncertainty in the measurement of dissolved phosphate.

geochemistry of Zn and Cd are closely linked through the physiological requirements of the phytoplankton. The fact that Cd can substitute for or supplement Zn in the enzyme carbonic anhydrase (CA) (Price and Morel 1990; Morel et al. 1994; Cullen et al. 1999; Lane and Morel 2000*b*) or as part of a Cd-specific CA (Lane and Morel 2000*a*) has been cited as the reason for the biological uptake of Cd in surface waters. Indeed, Zn-amended phytoplankton assemblages from Monterey Bay had lower Cd : P ratios than controls without added Zn (Cullen et al. 1999). This effect was independent of $CO_2$-driven Cd : P variations (Cullen et al. 1999) and was more consistent with competition at cell surface transport sites (Sunda and Huntsman 2000). Whatever the physiological basis for the Zn effect on algal Cd : P in culture and in the central California upwelling, in our Southern Ocean study, the addition of Zn to surface waters did not lead to a decrease in particulate Cd : P ratios. This is perhaps not surprising, given the relatively high surface water concentration of dissolved Zn at the study site (1.01 nmol $L^{-1}$), which may have been sufficient to meet the growth requirements of the resident phytoplankton community. Given that community growth rate was unaffected by Zn additions, the lack of a response of Cd : P to Zn additions is entirely consistent with our hypothesis of growth rate dilution and argues against a metal-metal antagonism at cell surface transport sites as the primary reason underlying reduced Cd uptake relative to P in the high Fe treatments.

*Comparison with a mesoscale iron fertilization experiment*—Frew et al. (2001), in the only existing study of the effect of Fe fertilization on surface water dissolved Cd : $PO_4$ ratios, investigated the uptake of Cd in response to a mesoscale Fe addition south of the Polar Front along 140°E. The authors concluded that Fe amendments lead to increased Cd : P ratios in the plankton and decreased dissolved Cd : $PO_4$. Similar to our incubations, Fe additions promoted the growth of diatoms, which drew down dissolved Cd and $PO_4$. Initial dissolved Cd : $PO_4$ outside the fertilized patch was 0.19 nmol $\mu$mol$^{-1}$. In contrast to our results, after four dissolved Fe infusions spaced over 7 d, the dissolved ratio had decreased to 0.10 nmol $\mu$mol$^{-1}$ by day 13 of the experiment. It is important to point out that Frew et al. (2001) did not measure particulate Cd and P directly in the same size fraction but calculated Cd : P by the draw-down of the dissolved species in filtered and unfiltered seawater. Our findings may be at odds because of this methodological difference or because of fundamental differences between bottle and in situ Fe addition experiments.

The differing environmental conditions (light fields, mixing rates, grazing pressure, etc.) experienced by the phytoplankton communities in our shipboard incubations versus the in situ patch conditions of the mesoscale study of Frew et al. (2001) may help explain the fundamental differences in the results. For example, more efficient Cd or less efficient P recycling in our shipboard incubations could help explain the higher dissolved Cd : $PO_4$ ratio in our high Fe treatments. Löscher et al. (1998) estimated that ~70% of Cd and 40% of P removed from surface waters in the Atlantic sector of the Southern Ocean by biological uptake were recycled within the mixed layer. It is possible that, in our onboard incubations, the conditions favored even more preferential recycling of Cd or that relaxed grazing pressure in the bottles reduced P recycling, driving the dissolved Cd : $PO_4$ higher. Another important difference between our study and that of Frew et al. (2001) is the degree of nutrient draw-down and amount of biomass produced in response to Fe fertilization. In the present study, our highest Fe treatment had a final biomass of ~12 $\mu$g Chl *a* $L^{-1}$ and removed 67% and 95% of the initial dissolved Cd and $PO_4$, respectively, after 10.7 d of incubation. Multiple infusions of Fe during the Frew et al. (2001) study produced ~4 $\mu$g Chl *a* $L^{-1}$ and removed 57% of initial dissolved Cd and only 17% of the available $PO_4$ by day 13 of the experiment (Boyd et al. 2000). The more intense biological response and P draw-down in our incubation carboys compared with the results of Frew et al. (2001) helps explain why dissolved Cd : $PO_4$ ratios increased in our bottles and decreased in the mesoscale experiment. It is known that, at day 13 in the Frew et al. (2001) study, the effects of Fe fertilization on the phytoplankton community were incomplete (Hannon et al. 2001) and that more phytoplankton growth and nutrient drawdown likely occurred up until day 60. It is not clear how phytoplankton Cd : P and dissolved Cd : $PO_4$ ratios evolved over that extended time period. What is clear is that a comprehensive study of the evolution of particulate and dissolved Cd : P ratios over the course of an Fe-stimulated phytoplankton bloom is needed to resolve the present contradiction.

*Implications for Cd and $PO_4$ biogeochemistry*—The preferential uptake of Cd by surface water biota and sinking of high Cd : P particulate matter has been proposed as the process driving the reduction of dissolved Cd : $PO_4$ ratios in ocean surface waters (Saager and de Baar 1993; Löscher et al. 1998; Cullen et al. 1999). The results of the present study suggest that, when natural assemblages of phytoplankton are released from Fe limitation, they may preferentially accumulate P relative to Cd, driving the residual dissolved Cd : $PO_4$ ratio higher. It is important to point out that our conclusion that P was taken up preferentially depends on our comparison between the particulate ratios and *calculated* dissolved ratios in our incubation bottles at the end of the experiment. Previous work has documented the preferential accumulation of P relative to Cd in cultures of the diatom *P. tricornutum* (Kudo et al. 1996), in natural populations of phytoplankton in Funka Bay, Japan (Abe and Matsunaga 1988), and in communities off the Oregon coast (Takesue and van Geen 2002). Our incubation study suggests that these earlier results can be reconciled with the prevailing view of preferential uptake of Cd relative to $PO_4$ by noting that the favorable growth conditions of the culturing experiment and the higher ambient dissolved trace nutrients in the coastal studies would suppress relative phytoplankton Cd uptake by promoting fast growth rates and through antagonistic interactions at cell surface transport sites. Although the present study is but one incubation experiment, barring any serious artifacts, it is possible that the preferential uptake of Cd by surface water biota (Saager and de Baar 1993; Löscher et al. 1998; Cullen et al. 1999) is not a general phenomenon in surface waters of the global ocean but may be re-

stricted to those regions where community growth rate is relatively slow.

The fact that Fe limitation of phytoplankton growth rates leads to substantial increases in particulate Cd : P ratios carries important implications for the biogeochemical link between dissolved Cd and $PO_4$ in Southern Ocean surface waters and for the reconstruction of past nutrient inventories using planktonic foraminiferal Cd : Ca (Rosenthal et al. 1997; Rickaby and Elderfield 1999; Elderfield and Rickaby 2000). Although we have demonstrated a convincing relationship between particulate Cd : P and the community growth rate, from these results alone we cannot derive an explicit relationship between the fractionation factor and growth rate, because we have not directly measured initial and final dissolved P and Cd concentrations in the incubation bottles. Nevertheless, from the above discussion, together with the results of Kudo et al. (1996) and Sunda and Huntsman (2000), it seems very likely that the fractionation factor or uptake ratio varies inversely with community growth rate. We calculate a $\alpha_{Cd:P}$ of 5.8 from the Cd : P ratios in SW (Cd : $P_{SW}$) and particles (Cd : $P_{POM}$) measured in ambient water collected at the study site. This fractionation factor is more than twice the global model-derived average cited by Elderfield and Rickaby (2000). This discrepancy can be explained on the basis of the demonstrated growth-rate dependence of particulate Cd : P ratios. That is, in the Southern Ocean, low temperatures, low Fe, and low light all conspire to produce low growth rates (Sunda and Huntsman 1997), which favor elevated particulate Cd : P ratios in the phytoplankton. The high particulate Cd : P ratios and associated high fractionation factor in Antarctic waters may well explain the anomalously low dissolved Cd : $PO_4$ ratio observed in sectors of this region (Frew and Hunter 1992; Nolting and de Baar 1994; Löscher et al. 1998).

More generally, the fact that phytoplankton Cd : P ratios vary with growth rate has important implications for the use of foraminiferal Cd : Ca ratios to reconstruct surface water $PO_4$ concentrations. To derive surface P from foraminiferal Cd : Ca, one needs to know, among other variables, the relationship between dissolved Cd and $PO_4$ in surface waters. The models of Elderfield and Rickaby (2000), with constant $\alpha_{Cd:P} = 2.5$, and Saager and de Baar (1993), with a fixed phytoplankton Cd : P uptake ratio, do reasonable jobs of capturing the global relationship between Cd and P in surface waters. However, these results cannot be taken as proof that $\alpha_{Cd:P}$ or the phytoplankton Cd : P ratio are in fact constant across all oceanic regimes (and glacial-interglacial cycles). Specifically, some other environmental variable(s) may covary with growth rate in such a way as to produce a seemingly correct model fit to the data. Given the lack of field-based estimates of the fractionation factor and the suggestion that $\alpha_{Cd:P}$ and phytoplankton Cd : P may be strongly dependent on growth rate, reconstructions of paleonutrient concentrations in surface waters based on the Cd : Ca proxy should be viewed with caution.

There is mounting evidence, and now field evidence, that phytoplankton Cd : P uptake ratios decrease with increasing growth rate, which necessarily affects residual dissolved ratios. Given the potential effects of environmental variables like temperature and nutrient concentrations on phytoplankton growth rates and the lack of a physiological mechanism linking Cd : P uptake to dissolved Cd : $PO_4$, we strongly caution against treating Cd and P as an analog of a true two-isotope Rayleigh fractionation system. To constrain temporal and spatial variability in surface ocean dissolved Cd : $PO_4$, we suggest more comprehensive investigations into the effect of Fe limitation on metal : nutrient ratios and more data coverage throughout the oceans of phytoplankton Cd : P as a function of dissolved Fe and the in situ growth rate.

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