Cadmium and phosphate in coastal Antarctic seawater: implications for Southern Ocean nutrient cycling

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1 Abstract

Cadmium is a biologically important trace metal that co-varies with phosphate (PO_4^{3-} or Dissolved Inorganic Phosphate, DIP) in seawater. However, the exact nature of Cd uptake mechanisms and the relationship with phosphate and other nutrients in global oceans remains elusive. Here, we present a time series study of Cd and PO_4^{3-} from coastal Antarctic seawater, showing that Cd co-varies with macronutrients during times of high biological activity even under nutrient and trace metal replete conditions. Our data imply that Cd/PO_4^{3-} in coastal surface Antarctic seawater is higher than open ocean areas. Furthermore, the sinking of some proportion of this high Cd/PO_4^{3-} water into Antarctic Bottom Water, followed by mixing into Circumpolar Deep Water, impacts Southern Ocean preformed nutrient and trace metal composition. A simple model of endmember water mass mixing with a particle fractionation of Cd/P ($\alpha_{Cd\text{-}P}$) determined by the local environment can be used to account for the Cd/PO_4^{3-} relationship in different parts of the ocean. The high Cd/PO_4^{3-} of the coastal water is a consequence of two factors: the high input from terrestrial and continental shelf sediments and changes in biological fractionation with respect to P during uptake of Cd in regions of high Fe and Zn. This implies that the Cd/PO_4^{3-} ratio of the Southern Ocean will vary on glacial-interglacial timescales as the proportion of deep water originating on the continental shelves of the Weddell Sea is reduced during glaciations because the ice shelf is pinned at the edge of the continental shelf. There could also be variations in biological fractionation of Cd/P in the surface waters of the Southern Ocean on these timescales as a result of changes in atmospheric inputs of trace metals. Further variations in the relationship between Cd and PO_4^{3-} in seawater arise from changes in population structure and community requirements for macro- and micronutrients.

Keywords: cadmium, phosphate, coastal, nutrients, Southern Ocean

2 Introduction

Major nutrients (macronutrients) carbon (C), nitrate (NO_3^-), phosphate (PO_4^{3-}) and, in the case of siliceous organisms, silicic acid (Si or $Si(OH)_4$), are taken up into the organic and skeletal material of marine phytoplankton in the euphotic zone, repackaged by zooplankton and exported as dead cells and fecal pellets. Over 86% of the carbon flux at 100 m is remineralised by 1000 m depth, such that macronutrients exhibit characteristic vertical gradients (Martin et al., 1987). In addition to these macronutrients, trace amounts of other elements (micronutrients) are essential for phytoplankton growth. Although studies into micronutrient biogeochemical cycling have focused on Fe availability, other metals, such as Cd, may be biologically important. Cd is a labile nutrient associated with organic matter and has similar spatial distribution patterns to PO_4^{3-} in open ocean deep and surface waters (Boyle, 1988; Figure 1). The exact nature of the relationship between Cd and P has been discussed extensively in the literature, and has been modelled either as a combination of two linear relationships separated by a "kink" at ~1.3 μmol kg^{-1} PO_4^{3-} as a result of basin specific processes (Cullen, 2006; de Baar et al, 1994; Frew and Hunter, 1992; Yeats, 1998) or a non-linear fractionation curve (Elderfield and Rickaby, 2000).

There is increasing evidence that Cd is a biologically important trace metal, actively taken up by phytoplankton in productive surface waters. Firstly, Cd is known to substitute into the metalloenzyme Carbonic Anhydrase (CA), which catalyses the uptake of bicarbonate (HCO_3^-) from seawater providing a source of inorganic C for photosynthesis i.e. the Carbon Concentrating Mechanism or CCM (Morel and Price,

2003). Cd may substitute for Zn in CA such that Cd added to Zn-limited diatoms leads to an increase in cellular CA activity and growth rate (Lane and Morel, 2000; Lee and Morel, 1995; Morel et al., 1994; Price and Morel, 1990). Recent sequencing and primary characterisation has confirmed the presence of a Cd specific CA, i.e. Cd-CA; (Lane et al., 2005; Xu et al., 2008). Cd has also been implicated in the formation of Polyphosphate Bodies (PPBs) in the giant kelp, *Macrocystis pyrifera*. PPBs are ubiquitous to most organisms, and may be active in phytoplankton (Hunter and Boyd, 1997). Secondly, recent seawater analyses have shown that Cd isotopic fractionation occurs in seawater, with the greatest fractionation occurring in surface waters depleted in dissolved Cd suggesting a biological signature (Lacan et al., 2006; Ripperger et al., 2007).

Biological uptake, and thus changes in nutrient demands due to variations in environmental conditions and population structure, could have a significant impact on the relationship between Cd and P in seawater. In addition to providing insight into modern biogeochemical cycling, understanding the relationship between macro- and micronutrients has implications for the reconstruction of past PO_4^{3-} utilisation using Cd/Ca ratios in foraminiferal calcite, which relies on a predictable Cd/PO_4^{3-} ratio in seawater (Boyle, 1986; Rickaby & Elderfield, 1999; Elderfield & Rickaby, 2000). The chemistry of deep water masses could be influenced by continental shelf and coastal processes at the site of formation. Further, past changes in continental shelf inputs to deep water could impact past deep water Cd/PO_4^{3-}, and, consequently, the interpretation of benthic foraminiferal Cd/Ca ratios. Here, we investigate the seasonal uptake of Cd and macronutrients in a coastal environment off the West Antarctic Peninsula. We discuss our results in the context of Southern Ocean processes on a

wider spatial scale, and the implications of our results for seawater Cd/PO_4^{3-} over longer timescales.

3 Methods and materials

3.1 Field setting

Coastal seawater samples were collected from Ryder Bay, which forms the larger part of Marguerite Bay off Adelaide Island, near Rothera Research Station (British Antarctic Survey, BAS), West Antarctic Peninsula (WAP; Figure 2). As well as being ideally located in a climatically sensitive region (Meredith et al., 2004), this site is part of several long term monitoring projects (Clarke et al., 2008; Meredith et al., 2008; Smith et al., 1999). The Rothera Oceanographic and Biological Time-Series (RaTS) has been conducted by BAS since late 1997, following the end of the successful long term monitoring series at Signy, northern WAP, in 1994. Conductivity-Temperature-Depth (CTD) profiles, nutrient analysis and size fractionated pigment assays (to monitor biomass) are carried out on a regular basis throughout the year and further details are reported elsewhere (Clarke et al., 2008).

The Antarctic Circumpolar Current (ACC) pumps nutrient rich, oxygen poor, warm water from the Upper Circumpolar Deep Water (UCDW) onto the continental shelf along the WAP below 200 m and into Marguerite Bay several times a year (Meredith et al., 2004). Vertical mixing of this water occurs largely as a result of bathymetric features and is the principal heat transfer process at depth. Above 100-150 m, the highly seasonal Antarctic Surface Water (ASW) dominates in shelf waters, including Marguerite Bay. In the summer months, the surface water is separated from deeper

120 water by a strong pycnocline, which develops as a result of warming and freshening
121 and can be defined by a Mixed Layer Depth (MLD). This pycnocline isolates a
122 remnant of the water column, which is well mixed in winter, termed the Winter Water
123 Mass (WW) (Clarke et al., 2008; Meredith et al., 2008; Meredith et al., 2004).
124

125 ## *3.2 Field methods*

126 Water column samples were collected 2-3 times a week from January to March in
127 2005 and 2006 at the RaTS site (Figure 2). The samples were collected from 15 m,
128 the average chlorophyll maximum in Ryder Bay (Clarke et al., 2008), filtered using
129 0.2 μm polycarbonate membranes (Whatman), acidified to pH 1.7-1.9 using sub-
130 boiling quartz distilled HNO_3 under trace metal clean conditions and stored at 4°C.
131 All plasticware used during collection, filtration and analysis was acid-cleaned by
132 soaking in 1 N HNO_3 (AnalaR) for at least 24 hours and rinsing thoroughly in 18 MΩ
133 cm Milli-Q water. Laboratory blanks of 18 MΩ cm Milli-Q water were run through
134 the complete protocol outlined to test for contamination in the laboratory.
135 Additional samples were filtered for silicic acid and phosphate analysis. Glass fibre
136 filters (Whatman GF/F; nominal pore size 0.8μm) are routinely used to filter seawater
137 for N and P analysis. Silica free polycarbonate 0.2 μm filter membranes (Whatman)
138 were used to filter seawater for silicic acid (Si) analysis to avoid contamination by any
139 Si released from the glass fibres of the GF/F membranes. Samples for NO_3^- and PO_4^{3}
140 analysis were stored at -20°C; samples for silicic acid analysis were stored at 4°C.

141 ## *3.3 Laboratory methods*

142 *i) Initial Cd determinations by standard addition*

Approximate trace metal concentrations were measured on a Perkin Elmer Elan 6100DRC Quadrupole Inductively Coupled Plasma Mass Spectrometer (Q-ICP-MS) using a standard addition method. Five aliquots of acidified seawater were diluted ten-fold with 1% sub-boiling quartz-distilled HNO_3 and added to incremental amounts of spike solutions (Greyhound Chromatography). A machine blank was initially run for each batch of five solutions. Pulse intensity was measured six times for each aliquot, the mean value corrected for isobaric interferences and machine blank, and sample concentration calculated by regression.

Cd intensities were measured using ^{114}Cd (28.73% natural Cd). Isobaric interference from ^{114}Sn (0.65% natural Sn) was corrected for by measuring ^{118}Sn, and $^{98}Mo^{16}O^{+}$ was corrected for by monitoring ^{98}Mo intensities. $^{98}Mo^{16}O^{+}/^{98}Mo^{+}$ formation in the plasma is 0.2 to 0.4%. The external precision and accuracy were assessed using two independent seawater standards (Table 1). These approximate concentrations were used to determine the optimal quantities of Cd spike that were to be added to the samples, to avoid large error magnification factors in the application of the isotope dilution method. Laboratory blanks were also measured by standard addition, and were below the Limit of Detection (LoD for Cd ~ 0.01 ppb).

ii) Isotope dilution method

The small variations in Cd concentrations during the 2006 austral summer were subsequently measured by single-spike isotope dilution after pre-concentration of Cd by $Mg(OH)_2$ co-precipitation (Wu and Boyle, 1997). An appropriate amount of spike, which had been previously calibrated (Ripperger and Rehkämper, 2007a; Ripperger and Rehkämper, 2007b), was weighed into Teflon containers. Error magnification was reduced by keeping the sample-to-spike mass ratio for Cd approximately equal to

unity. As the co-precipitation method is pH sensitive, the concentration and acidity of the spike were adjusted after weighing. Approximately 13 ml of acidified seawater was weighed in 15 ml acid-cleaned polypropylene centrifuge tubes (5 point balance ± 0.01 mg) and spiked with 400 μl of enriched ^{110}Cd spike solution was added. Previous experiments have shown that the equilibration is rapid, and there is no significant difference between samples equilibrated for 2 minutes and 2 days (Wu and Boyle, 1997). FEP distilled aqueous NH_3 (500-2000 μl) was added to precipitate $Mg(OH)_2$; the amount added was determined empirically to allow ~ 7% Mg to precipitate to minimise matrix effects during analysis (Mg ~ 1000 ppm; (Wu and Boyle, 1997)). Cd is preferentially taken up into the precipitate, resulting in ~ 30% Cd yields. After NH_4OH addition, the sample was left for two minutes before centrifugation at 6000 rpm for 4 minutes. The supernatant was discarded and the precipitate was redissolved in 0.5 ml 5% HNO_3 (sub-boiling distilled HNO_3 in Milli-Q water), diluted with 0.5 ml Milli-Q and analysed for Cd isotopes by ICP-MS.

The standards and samples were analysed using an Element II magnetic sector ICP-MS (Thermo Finnigan), introduced in conjunction with a Cetac ASX-100 microautosampler. The ICP-MS was run in low resolution mode to optimise counting statistics; using medium resolution reduces the signal by a factor of 15. Even though $Mg(OH)_2$ co-precipitation significantly lowers the matrix load of the seawater samples, elements that potentially interfere with Cd isotopes, such as Mo, Sn and Pt, are precipitated along with Cd and need to be monitored. Standards were measured for mass bias and oxide corrections. Two standard solutions were used: 1) a 1 ppb "Alfa Cd Zürich" Cd standard (Ripperger and Rehkämper, 2007b), the isotopic composition of which is known accurately and precisely and is very similar to that of the bulk silicate Earth (Table 2); 2) "Ryder06", an in-house standard of seawater from

193 Ryder Bay that has undergone the sample preparation procedures, and therefore
194 represents an unspiked version of the samples.
195 Each sample was bracketed with a blank, and the "Alfa Cd Zürich" Cd standard was
196 run every 3 samples. The standard "Ryder06" was spiked with various amounts of In,
197 Mo and Cd to obtain signal corrections within a matrix similar to that of the samples
198 (see below for details). It was also measured at the beginning of each run without any
199 additives to test the validity of the blank and oxide corrections on the Cd signals
200 discussed below.
201 The ion beam intensities of ^{110}Cd, ^{111}Cd, ^{112}Cd, ^{114}Cd were measured and ^{106}Pd, ^{95}Mo,
202 ^{98}Mo and ^{118}Sn were monitored for interference corrections. Analytical conditions are
203 listed in Table 3. An extended E-Scan range of 30% was used, which allowed rapid
204 scanning without magnet jumps, hence a more efficient duty cycle and better
205 precision. The tuning of the instrument was optimised for maximum Cd intensity and
206 low oxide formation rates. Molybdenum oxides provided the most significant
207 polyatomic interferences (Table 4), with $^{98}Mo^{16}O^{+}/^{98}Mo^{+}$ values of 0.07-0.10%.
208 Further corrections were made by assessing the interferences on standards before the
209 samples were measured. A solution of "Ryder06" that had been spiked with 10 ppm
210 Mo was measured prior to each run to assess MoO^{+} formation. A pure Mo standard
211 was measured before each run to determine mass bias corrections for MoO
212 compounds that were not measured in the actual sample run (such as ^{94}MoO+ and
213 ^{96}MoO+); these interferences were then corrected using either ^{95}Mo or ^{98}Mo count
214 rates. ^{114}Cd and ^{112}Cd were corrected for ^{114}Sn and ^{112}Sn by measuring ^{118}Sn and using
215 the natural $^{114}Sn/^{118}Sn$ and $^{112}Sn/^{118}Sn$ ratios, respectively.

^{110}Pd interference on ^{110}Cd was corrected by monitoring ^{106}Pd after Mo and Sn corrections, and after correcting ^{106}Pd for ^{106}Cd based on ^{111}Cd signals as follows (Equations 1-2):

$$^{110}Cd_{corr} = {}^{110}Cd^{*} - {}^{106}Pd_{corr} / A_{106Pd} \times A_{110Pd} \quad (1)$$

$$^{106}Pd_{corr} = {}^{106}Cd^{*} - {}^{111}Cd^{*} / A_{111Cd} \times A_{106Cd} \quad (2)$$

where A_x = natural abundance if isotope, and the superscript * denotes count rates corrected for blank and MoO contributions.

The strong matrix effect of the sample solutions (about 1000 ppm each of Mg and Na) obtained by co-precipitation samples results in a suppression of the instrument blank signal. This suppression, and so the true instrument blank, was assessed by measuring the intensity of an In spike added to both 2% HNO_3 and the in-house standard 'Ryder06' standard and then applying Equation 3:

$$B = \frac{In_{Ryder06}}{In_{2\%}} \times B_{2\%} \quad (3)$$

where $In_{Ryder06}$ = In intensity in Ryder06

$In_{2\%}$ = In intensity in 2% acid

$B_{2\%}$ = Machine blank for 2% acid

Blank contributions were about 5% of the signal for all Cd isotopes except ^{112}Cd ca. 40%. Mass bias (Δ_M) was corrected by measuring the isotope ratio of a 1 ppb solution of "Alfa Cd Zürich" and applying Equation 4:

$$\Delta_M = \frac{\left[\frac{^{110}Cd}{^{111}Cd}\right]_{measured}}{\left[\frac{^{110}Cd}{^{111}Cd}\right]_{real}} - 1 \quad (4)$$

The natural sample ratio (or the ratio of the in-house Ryder06 standard) may not be exactly equal to the ratio of the Alfa Cd Zürich standard. Natural Cd isotopic fractionation in seawater occurs as a result of closed system biological uptake and ranges from $\varepsilon^{114/110}$ Cd = ±3 to ±36 (Ripperger et al., 2007). However, the greatest fractionations occurs in Cd-depleted surface waters in the North Pacific ([Cd] ~ 0.003 nmol kg^{-1}). The [Cd] concentration of the Ryder Bay surface waters are higher, suggesting a lower degree of Cd isotopic fractionation, and are replenished regularly by deep water ($\varepsilon^{114/110}$ Cd = ±3.3 ± 0.5; (Ripperger et al., 2007)). Hence, the maximum error associated with assuming $\varepsilon^{114/110}$ Cd = 0 is approximately 0.03%.

The external reproducibility of the isotope analysis was established by repeat measurements of unspiked standard "Ryder06", and was found to be approximately 2% (Figure 3). The reproducibility for spiked samples should be as good as or better than 2% due to the greater proportion of ^{110}Cd. The accuracy of the isotope dilution method was determined based on duplicate measurements of the reference standard NASS-5, which yielded concentrations of 0.0221 ± 0.0004 (~2%) and 0.021 ± 0.006 (~30%) ppb using ^{110}Cd/^{114}Cd and ^{110}Cd/^{111}Cd respectively (certified value 0.023 ± 0.003; measured as 0.02224 ± 0.00004 by double spiked isotope dilution, (Ripperger and Rehkämper, 2007b)). ^{110}Cd/^{114}Cd and ^{110}Cd/^{111}Cd agree well for the samples (Figure 4), but due to the greater precision on the former ratio, only concentrations determined via ^{110}Cd/^{114}Cd ratios are quoted in the results section.

Macronutrients were measured using a Skalar Autoanalyser (Kirkwood, 1996). The detection limit for NO_3^-, PO_4^{3-} and Si analyses were 0.1, 0.05 and 0.1 μmol l^{-1} respectively. The percentage error for all nutrient analyses was less than 5% relative to Ocean Scientific International (U.K.) standards. This results in a propagated error of ~ 5.5% on Cd/PO_4^{3-} values.

4 Results and discussion

Our time series shows a consistent pattern of biological utilisation, with seasonal depletion in macronutrients NO_3^- and PO_4^{3-} during periods of high biomass (Figure 5). Cd co-varies with macronutrients (using all available data, Cd versus PO_4^{3-}, $r^2 = 0.70$, n = 18) with depletions occurring during the peaks of the summer bloom. However, the relationship between total chlorophyll *a* (chl *a*) and both macronutrients and Cd is not statistically significant ($r^2 < 0.1$ for chl *a* versus $Si(OH)_4$, PO_4^{3-}, NO_3^- and Cd). This suggests that chl *a*, a measure of biomass, may not in this situation provide a reliable measure of nutrient utilisation *per se*. This could be because 1) phytoplankton utilise a range pigments in addition to chl *a*; 2) biomass does not relate to total nutrient drawdown because of grazing and remineralisation processes; 3) abiological/physical factors, such as storminess and water column mixing, influence the distribution of nutrients (Clarke et al., 2008).

4.1 Comparison between open ocean and coastal Cd/ PO_4^{3-}: implications for Southern Ocean chemistry

The "global relationship" between Cd and P reflects various interactions between mixing of water masses containing different preformed nutrients and surface water biological fractionation. The non-linear nature of the relationship is not fully understood and may be a result of several different mechanisms (Cullen, 2006). The new Cd and PO_4^{3-} data from Ryder Bay presented here (Figure 5, 6) are consistent with other published coastal datasets and appear offset towards higher Cd/P compared to the global open ocean trend (Frew, 1995; Jones and Murray, 1984; Van Geen and Luoma, 1993). Here, we suggest the Cd/PO_4^{3-} of a parcel of surface seawater is determined by the initial Cd/PO_4^{3-}, set by inputs from upwelling and terrestrial runoff, and the subsequent fractionation trajectory of biological utilisation. The initial offset towards higher Cd values in coastal regions is a result of input from continentally derived sediments and the high Cd/PO_4^{3-} composition of upwelling water. The biological utilisation trajectory in these coastal regions follows a curve with reduced uptake of Cd with respect to PO_4^{3-} compared to open ocean regions (Figure 6). Variability in the extent of such enrichment in Cd over that expected for a given PO_4^{3-} concentration is most likely to relate to spatial variation in the micronutrient content of the water column due to variations in upwelling, phytoplankton nutrient requirements and community structure.

4.1.1 Initial Cd/ PO_4^{3-} of upwelling water: continental input and water mass mixing

The most likely sources of high Cd/P inputs to our coastal setting are continental shelf sediments and terrestrial runoff from glaciers. Coastal and Continental Shelf Waters

307 (CCSW) contain higher Fe and Al inputs as a result of shelf sediment remineralisation
308 and terrestrial input (Measures, pers. com.). In contrast to Fe and Al, Cd precipitates
309 from porewaters and becomes concentrated in reducing sediments (Gobeil et al.,
310 1997). However, in oxic layers at the sediment-water interface, the decomposition of
311 organic matter can release Cd, which is largely mobile (Nolting et al., 1999). The
312 surface layers of Antarctic continental sediments are generally organic rich and
313 oxygenated, and these sediments, possibly with direct input from glacial runoff, will
314 be a significant source of Cd to seawater.
315
316 We can assess the influence of these high Cd/PO_4^{3-} coastal waters on the deep waters
317 that emanate from the Weddell Sea using a mixing model of endmember water
318 masses. Antarctic Bottom Water (AABW) forms largely on the Antarctic continental
319 shelf and shows a correspondingly high Cd/PO_4^{3-} value. The upwelling of
320 Circumpolar Deep Water (CDW), formed from a mixture of aged North Atlantic Deep
321 Water (NADW) and AABW, can be observed in measurements of Cd and PO_4^{3-}
322 measurements from open ocean regions of the Southern Ocean (Figure 6). We can
323 use a simple mass balance calculation to quantify the impact of shelf water on CDW.
324 Assuming endmember compositions of NADW and CCSW have [Cd] of 0.3 and 0.8
325 nM and PO_4^{3-} of 1.6 and 2.3 μM respectively (from Figure 6), Modern CDW can be
326 explained by entrainment of shelf waters in a mixing ratio of 40:60 NADW:CCSW
327 (Figure 6). This mixing ratio is also supported by the oxygen isotope signature of
328 AABW and Weddell Sea waters (Frew et al., 1995) and a simple mass balance
329 calculation based on salinity. Assuming NADW and CCSW have salinities of 34.9
330 and 34.6 psu respectively (Adkins et al., 2002; Clarke et al., 2008; Meredith et al.,

2008), then a 40:60 ratio of NADW:CCSW explains the Modern CDW salinity of 34.7 psu.

4.1.2 Biological fractionation

The subsequent biological fractionation of the mixed water upwelling to the surface in the Southern Ocean will depend on environmental conditions. In open ocean regions the fractionation of Cd with respect to P follows a simple fractionation trend given by Equation 6, where Cd_T and P_T are the total Cd and P available in the ocean, Cd_{sw} and P_{sw} is the concentration of Cd and P in seawater, and $\alpha_{Cd\text{-}P}$ is the fractionation factor as defined in Equation 5 (Elderfield and Rickaby, 2000).

$$\alpha_{Cd-P} = \frac{\left(\frac{Cd}{P}\right)_{organic}}{\left(\frac{Cd}{PO_4^{3-}}\right)_{seawater}} \quad (5)$$

$$Cd_{sw} = Cd_T \Big/ \left\{ \alpha_{Cd-P} \left(\frac{P_T}{PO_4^{3-}{}_{sw}} - 1 \right) + 1 \right\} \quad (6)$$

In the CCSZ (e.g. this study and the Princess Elizabeth Trough, (Frew, 1995)), the relative requirements of Cd with respect to PO_4^{3-} are diminished, $\alpha_{Cd\text{-}P}$ is reduced (Equation 7) and there is a stock of Cd that is not appear to be utilised ("Cd_{xs}").

$$Cd_{sw} = \left(Cd_T - Cd_{xs}\right) \Big/ \left\{ \alpha_{Cd-P} \left(\frac{P_T}{PO_4^{3-}{}_{sw}} - 1 \right) + 1 \right\} + Cd_{xs} \quad (7)$$

This reduction in relative Cd requirements in coastal regions with respect to the open ocean may be due to differences in the activity of metalloenzymes, such as CA. The activity of CA is affected by the availability of macronutrients (Wang and Dei, 2001), micronutrients (Cullen et al., 2003; Cullen and Sherrell, 2005; Sunda and Huntsman, 1998) and pCO_2 (Cullen and Sherrell, 2005). Coastal regions show depleted seawater CO_2 in summer compared to the open Southern Ocean, suggesting variations in pCO_2 cannot provide a mechanism to explain the observed seawater Cd/PO_4^{3-} (Álvarez et al., 2002; Bakker et al., 1997; Gibson and Trull, 1999; Hoppema et al., 2000; Takahashi et al., 2002). Hence, the most likely explanation for the lower utilisation of Cd is that the higher micronutrient conditions in coastal waters influences CA activity, Cd requirements or uptake mechanisms. It has been postulated that the non-linear relationship between Cd and PO_4^{3-} is a result of two different fractionation relationships between Cd and PO_4^{3-} in Fe replete and deficient conditions (Cullen et al., 2003). Under high Fe conditions, Cd/P uptake into cellular material is reduced, possibly due to a competing Fe-Cd cellular transporter (Armbrust, 2004; Cullen, 2006). Furthermore, the substitution of Zn into the Cd-CA structure influences the enzyme activity, such that CA activity and Cd requirements vary with Zn concentrations in the ambient medium (Park et al., 2007; Xu et al., 2008).

In Fe and Zn deficient regions (e.g. Subantarctic Zone), uptake of Cd with respect to P follows a simple trend given by Equation 6 with a constant fractionation factor, $\alpha_{Cd\text{-}P}$ = 3.5. In Fe and Zn replete conditions of the CCSZ (e.g. Table 5) uptake of Cd follows a trend with a lower fractionation factor ($\alpha_{Cd\text{-}P}$ = 2; Figure 6). Phytoplankton grown under such conditions have lower Cd requirements (Cullen, 2006), which could

provide a mechanism behind the lower value of $\alpha_{Cd\text{-}P}$ in coastal waters. Further, competitive interaction between metals (Sunda and Huntsman, 1998) or biologically produced ligands (Lee et al., 1996) can modulate uptake of Cd. For example, production of metal-binding polypeptides, phytochelatins, is activated in cultured diatoms under high internal and external Cd concentrations (Lee et al., 1996). Increased production of phytochelatins under higher micronutrient conditions could explain the reduction in uptake of Cd in coastal zones.

4.2 Seasonal variability and population structure

Our data show some scatter about the linear relationship between Cd and PO_4^{3-} in Ryder Bay (Figure 6), which reflects seasonal variations in seawater Cd/PO_4^{3-} due to changes in diatom species composition and environmental conditions. Such population related variations may also influence large scale global cycling of macro- and micronutrients in seawater given the predictable geographical variation in plankton types and sizes.

Surface Cd/PO_4^{3-} of Ryder Bay has an initial background of ~ 0.4-0.5 nmol/μmol (Figure 5). Although this estimate is based on approximate concentrations measured using standard addition, it agrees well with other Antarctic coastal regions, e.g. Deception Island ~ 0.6; Palmer Station 0.3-0.35; (Sañudo-Wilhelmy et al., 2002). These values are also similar to the upper estimates of Cd/PO_4^{3-} for UCDW, 0.35-0.5 nmol/μmol (Löscher et al., 1998). This is consistent with coastal Antarctic seawater being influenced by high Cd/PO_4^{3-} waters from upwelling UCDW (Meredith et al., 2004).

401

402 During the first bloom (Jan-Feb 2006), the Cd/PO_4^{3-} ratio in seawater increases as the
403 uptake of P increases proportionately more than Cd with growth rate. As the early
404 bloom declines, both Cd and P are remineralised and replaced by upwelling water
405 restoring the Cd/PO_4^{3-} to near background levels. Growth rates increase again during
406 the late bloom (Feb-Mar), resulting in an increase in Cd/PO_4^{3-}.
407 Cd requirements are lower with respect to PO_4^{3-} (i.e. Cd/PO_4^{3-} is higher) for the late
408 bloom than for the early bloom, which may reflect differences in community structure
409 or environmental conditions, such as changes in photoperiod and temperature.
410 Macro- and micronutrient requirements are a function of cell size (e.g. Ho et al.,
411 2003) and, in particular, it is thought that smaller plankton have lower Cd uptake rates
412 (Finkel et al., 2007) and greater PO_4^{3-} requirements and uptake efficiencies (Asknes
413 and Egge, 1991; Gligora et al., 2007; Wen et al., 1997). Indeed, in Ryder Bay, there
414 is a greater contribution to surface productivity by smaller pico- and nanoplankton (<
415 20 μm) with respect to microplankton (> 20 μm) during the late summer bloom
416 corresponding with higher Cd/PO_4^{3-} (Figure 5). In addition to size, a shift in
417 dominant phytoplankton community can also result in a shift in bulk community Cd
418 requirements. Further, these requirements can change with environmental conditions
419 to varying extents with different divisions. For example, laboratory cultures of
420 diatoms show an increase in Cd requirements (and steady state influx of Cd with
421 respect to PO_4^{3-}) with increasing temperature and irradiance; in contrast, cultures of
422 cyanobacteria show a reduction in Cd uptake under similar conditions (Finkel et al.,
423 2007). However, in this case although there is a change in cell size, there does not
424 appear to be a major shift in the phytoplankton divisions throughout the summer with
425 more than 55% of the population comprising diatoms. Preliminary population

analyses indicate there is a shift away from large centrics in the early summer towards smaller diatom species in the later bloom (Annett, pers. com.). In other words, these results show that a switch does not have to be between phytoplankton divisions during the bloom (e.g diatoms to flagellates) in order to influence the seawater Cd/PO_4^{3-} ratio but may be between phytoplankton genera within a division.

The variation in Cd requirements with respect to macronutrients with population and size structure in seawater may also influence the "global relationship" between Cd and PO_4^{3-}. For example, high nutrient upwelling zones favour the growth of microplankton (in particular diatoms) with high Cd requirements. Temperate open ocean regions favour the growth of other larger phytoplankton. Conversely, tropical oligotrophic gyres favour the growth of picoplankton and autotrophic bacteria with lower Cd requirements. Further, there is an effective microbial loop in these regions that results in more rapid regeneration, which may mask the effect of biological fractionation (Alvain et al., 2005; Follows et al., 2007).

4.3 Implications for glacial-interglacial reconstructions

We have shown the non-linear relationship between Cd and PO_4^{3-} in seawater can be explained by a combination of 1) water mass mixing; 2) differential biological fractionation due to variation in micronutrient concentration, and 3) changes in phytoplankton community structure. These processes are likely to change on glacial-interglacial timescales, due to shifts in deep water formation processes and atmospheric inputs, resulting in long-term changes in the Cd/PO_4^{3-} ratio of Southern Ocean seawater.

1) Deep water formation processes

Currently, Atlantic Sector Southern Ocean deep water originates in the southern region of the Weddell Sea near the continental shelf. Hence, these waters are replete in micronutrients and Cd utilisation is lower than open ocean conditions, which results in a relatively high seawater Cd/PO_4^{3-}. However, benthic foraminifera stable isotopes have been used to infer a shift in the deep convection site during the last glaciation to the northern rim of the Weddell Sea because the ice sheet was pinned to the edge of the continental shelf (Mackensen et al., 1996; Mackensen et al., 2001). Consequently, the site of deep water formation may have had lower inputs of micronutrients and, thus, surface waters may have experienced higher Cd utilisation and a lower seawater Cd/PO_4^{3-}. Such a shift in deep water convection could have lowered the Cd inventory of Southern Atlantic deep waters, explaining, in part, the conflict between foraminiferal $\delta^{13}C$ and Cd/Ca data from the Southern Ocean LGM (Mackensen, 2001 and references therein).

2) Atmospheric inputs

A range of ice-core, terrestrial and marine records indicate an increase in dust supply to the Southern Ocean during the last glaciation (Kohfeld and Harrison, 2001; Petit, 1999). Although the link between biological productivity and atmospheric supply of micronutrients is poorly constrained and somewhat controversial (e.g. Maher and Dennis, 2001), it is possible that phytoplankton may have experienced Fe and Zn replete conditions in the Southern Ocean during the Last Glacial Maximum (LGM). Indeed, one model suggests that, although global dust deposition may not have increased dramatically, hydrological factors amplify the sensitivity of high latitude

476 regions to dust input resulting in over an order of magnitude enhancement in Fe
477 supply (Ridgwell and Watson, 2002). This would suggest growth conditions in the
478 LGM open Southern Ocean could have been analogous to the modern coastal system,
479 with lower Cd fractionation with respect to PO_4^{3-}.
480
481 *3) Phytoplankton community structure*
482 Changes in ocean stratification and sea-ice cover can shift phytoplankton community
483 structure (Abelmann et al., 2006; Arrigo, 1999) and, thus, changes in macro- and
484 micronutrient requirements (Arrigo, 2005). However, lack of constraint on
485 phytoplankton community structures over longer timescales further compounds the
486 ability to reconstruct past ocean nutrient budgets.
487
488 Shifts in the preformed Cd/PO_4^{3-} ratio of seawater, and changes in biological
489 fractionation in Southern Ocean surface waters, could have significantly altered the
490 relationship between Cd/Ca recorded in foraminiferal calcite and ambient phosphate
491 concentrations. For example, Cd/Ca foraminiferal records have previously been
492 interpreted as showing no change in PO_4^{3-} utilisation in the Subantarctic, and a lower
493 PO_4^{3-} utilisation (5%) in the Antarctic during the LGM compared to today (35%;
494 Elderfield & Rickaby, 2000). However, assuming that the open Southern Ocean at
495 the LGM exhibited Cd/PO_4^{3-} characteristics of modern coastal regions due to
496 enhanced atmospheric input, the same records imply PO_4^{3-} utilisation was higher in
497 the LGM Subantarctic compared to today. Further, a similar calculation suggests
498 PO_4^{3-} utilisation in the Antarctic Zone was lower than today (approximately 20%) but
499 declined less than previously calculated.
500

5 Summary and conclusions

We present a time series of Cd and macronutrient data from a coastal site adjacent to the West Antarctic Peninsula, which shows that Cd is taken up during periods of high biological productivity despite nearshore, micronutrient replete conditions. These Antarctic coastal waters show high Cd/PO_4^{3-} and can impact the preformed nutrient content of seawater in the open Southern Ocean through deep water formation and mixing with water masses originating further north. We have demonstrated that the non-linear relationship between Cd and PO_4^{3-} in seawater can be explained by a combination of 1) water mass mixing; 2) differential biological fractionation due to variation in micronutrient concentration, and 3) changes in phytoplankton community structure, which can vary within a season. These processes are likely to change on glacial-interglacial timescales, due to shifts in deep water formation processes and atmospheric inputs, resulting in long-term changes in the Cd/PO_4^{3-} ratio of Southern Ocean seawater. An understanding these shifts in the preformed Cd/PO_4^{3-} ratio of seawater, and changes in biological fractionation in Southern Ocean surface waters, could resolve discrepancies between benthic foraminiferal Cd/Ca records and other paleonutrient proxies.

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Figure 1: All seawater dissolved Cd and Dissolved Inorganic Phosphate (DIP) data for the global ocean (surface and deep waters in open symbols) for different ocean basins (Boyle et al., 1976; Bruland, 1980; Bruland & Franks, 1983; Danielsson et al., 1985; Sakamoto-Arnold et al., 1987; Hunter & Ho, 1991; Nolting & de Baar, 1994; Löscher et al., 1998; Fitzwater et al., 2000; Abe, 2001, 2002; Ellwood, 2004). Also included are data from semi-enclosed South China Sea (Chen et al,. 2005). Deep water data shown in closed symbols from de Baar et al., (1994).

Figure 2: Map of study site off the West Antarctic Peninsula, with the RaTS site shown by the grey box.

Figure 3: External reproducibility of 1 ppb Alfa Zürich standard and in-house standard ("Ryder06") using A) $^{110}Cd/^{111}Cd$ and B) $^{110}Cd/^{114}Cd$. Error bars show internal precision (±1.3%).

Figure 4: Comparison of methods for the analysis of dissolved Cd in seawater samples of using two different isotope ratios for isotope dilution (±1σ).

Figure 5: Pigment and nutrient concentrations from 15 m collected at the RaTS site from 2005-2006. A) Total chlorophyll *a* concentrations (grey square; B) size fractionated chl *a* (data courtesy of BAS); macronutrient concentrations C) nitrate (white triangles), D) silicic acid (black squares) and E) phosphate (white diamonds); micronutrient concentrations F) cadmium (measured by standard addition (SA; grey dots) and isotope dilution (ID; black circles) and G) Cd/PO_4^{3-}. (grey circles). N and P measurements carried out by Weston, UEA, and Carson, Edinburgh. All errors bars show ±2σ.

Figure 6: Fractionation of dissolved Cd and PO_4^{3-} or DIP in Southern Ocean waters. Upwelling CDW (cyan dashed line) is formed from a mixture of NADW and AABW. Endmember compositions shown in the large cyan circles (de Baar and al, 1994; Elderfield and Rickaby, 2000; Frew, 1995; Westerlund and Ohman, 1991). The mixing of these water masses can be observed in measurements of Cd and P measurements in Subantarctic Zone Waters (SAW, black circles), Polar Front regions (PF, red circles) and Antarctic Zone Waters (AAW, green circles). In open water regions (e.g. Subantarctic Zone, black circles), fractionation of Cd with respect to P follows a simple fractionation trend given by Equation 6 with a constant fractionation factor, $\alpha_{Cd\text{-}P} = 3.5$. In coastal conditions in the (CCSW e.g. this study, dark blue circles and the Princess Elizabeth Trough, PET, yellow circles) there is 1) stock of Cd, Cd_{xs}, that is not utilised (Equation 7), and 2) a lower fractionation factor, $\alpha_{Cd\text{-}P} = 2.0$. Utilisation and decay of nutrients follow trajectories given by the grey arrows. Note that the Cd/PO_4^{3-} of upwelling waters will depend on the depth of mixing due to the deeper regeneration cycle of Cd.

Standard	Quoted concentration (ppb)	Measured concentration
IAPSO K15	0.08-0.12	0.087 ± 0.010
NASS-5	*0.023 ± 0.003	0.024 ± 0.004

*Certified seawater reference material for trace metals, National Research Council Canada

Table 1: Cd analysis of reference seawater standards. Errors are ±2σ.

Solution	**^{110}Cd/^{111}Cd**	**^{110}Cd/^{114}Cd**
Alfa Cd Zürich (lot 901463E)	0.977047 (50)	0.438564 (50)
Spike	72.7346 (5072)	79.4532 (5540)

Table 2: Isotope ratios of standards (Ripperger and Rehkämper, 2007b). Uncertainties in brackets denote 2σ.

Instrument	Thermo Finnigan Element2 magnetic sector ICP-MS with Cetac ASX-100 autosampler
Isotopes measured	95, 98, 106, 110, 111, 112, 114, 118, all in Low Resolution mode
Scan parameters	mass window 5%, 400 samples/peak, segment duration 40 ms
E-Scan range	30%
Analysis time	4.00 min (10 runs × 73 passes)
Plasma power	1450 W
Sample gas	1.12 L/m
Sample uptake rate	ca. 100 µL/min

Table 3: Analytical parameters of ICP-MS analysis

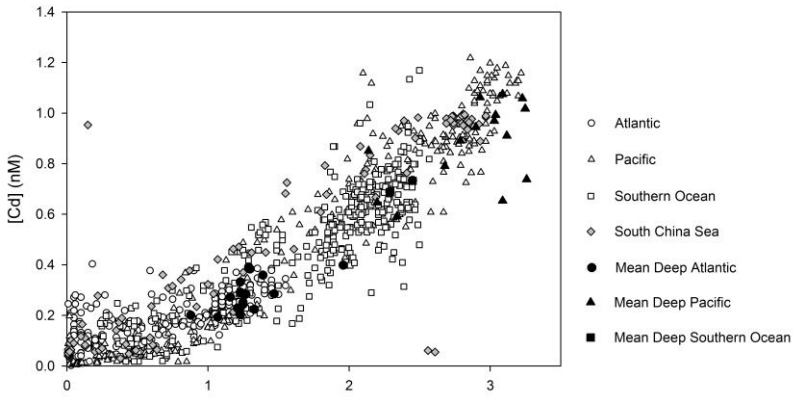
Isotope	% Abundance (natural)	Interferences	% signal
^{106}Cd	1.25	^{106}Pd	68
^{110}Cd	12.49	^{110}Pd, ^{94}MoO^{+}	6, 2
^{111}Cd	12.80	^{95}MoO^{+}	12
^{112}Cd	24.13	^{112}Sn, ^{96}MoO^{+}	3, 7
^{114}Cd	28.73	^{114}Sn, ^{98}MoO^{+}	2, 8

Table 4: Interferences on isotopes of cadmium, and mean percentage of the signal of each interference. The percent signal calculated as follows, and averaged for all samples measured:

% signal = (counts from interference at mass peak)/(total counts at mass peak) x 100.

Region	[Fe] (nM)	[Zn] (nM)	Reference
Palmer Station, WAP	4-6	4-5	(Sañudo-Wilhelmy et al., 2002)
King George Island, South Georgia		> 40	(Prendez and Carrasco, 2003; Prendez et al., 1996)
Weddell Sea	1-6	3-5	(Westerlund and Ohman, 1991)
Terra Nova Bay, Antarctica	3.5	5	(Sañudo-Wilhelmy et al., 2002)
Open Southern Ocean	0.2-0.5	0.2-0.5	(Abollino et al., 1995; Löscher et al., 1997; Löscher et al., 1998; Martin et al., 1990)

794 Table 5: Fe and Zn concentrations of some regions in the Southern Ocean and coastal
795 Antarctica.
796
797
798



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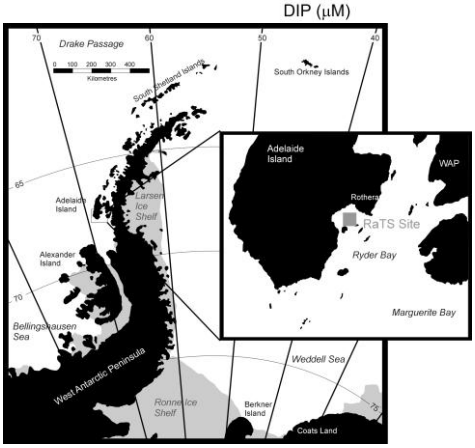

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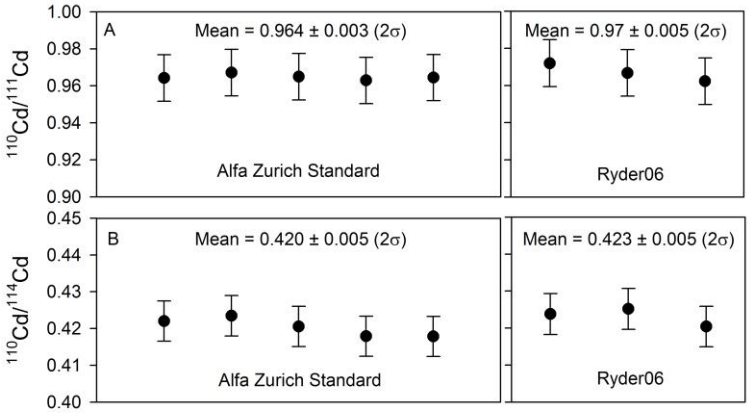
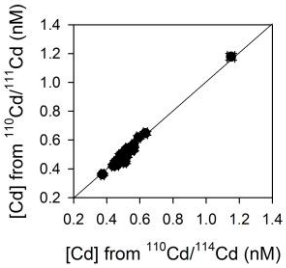

A
Mean = 0.964 ± 0.003 (2σ)
Mean = 0.97 ± 0.005 (2σ)
Alfa Zurich Standard
Ryder06
$^{110}Cd/^{111}Cd$
B
Mean = 0.420 ± 0.005 (2σ)
Mean = 0.423 ± 0.005 (2σ)
Alfa Zurich Standard
Ryder06
$^{110}Cd/^{114}Cd$

801


[Cd] from $^{110}Cd/^{111}Cd$ (nM)
[Cd] from $^{110}Cd/^{114}Cd$ (nM)

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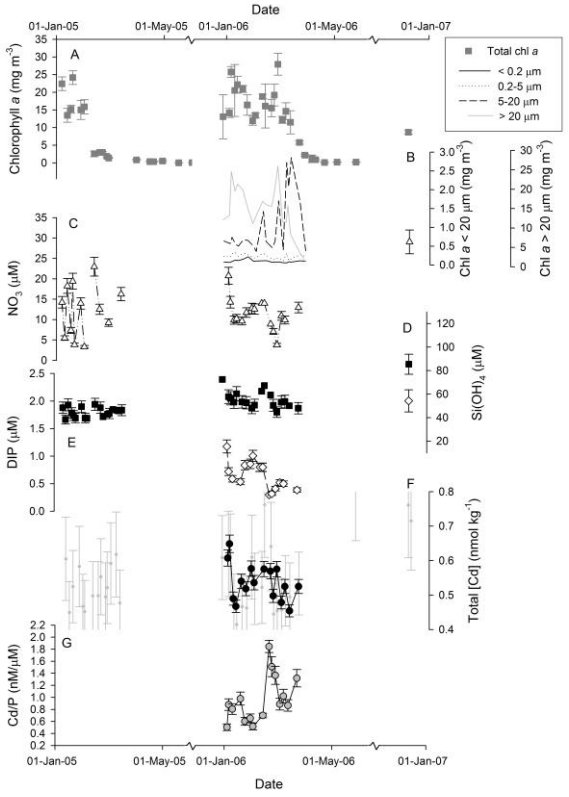
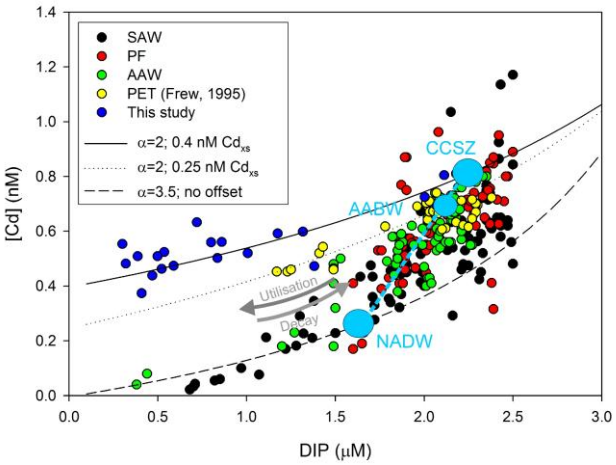

Date
Total chl a
< 0.2 µm
0.2-5 µm
5-20 µm
> 20 µm
Chlorophyll a (mg m-3)
Chl a < 20 µm (mg m-3)
Chl a > 20 µm (mg m-3)
NO3 (µM)
Si(OH)4 (µM)
DIP (µM)
Total [Cd] (nmol kg-1)
Cd/P (nM/µM)

803


SAW
PF
AAW
PET (Frew, 1995)
This study
α=2; 0.4 nM Cdxs
α=2; 0.25 nM Cdxs
α=3.5; no offset
CCSZ
AABW
NADW
Utilisation
Decay
[Cd] (nM)
DIP (μM)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0.5
1.0
1.5
2.0
2.5
3.0

804