1 **Cadmium and phosphate in coastal Antarctic**

2 **seawater: implications for Southern Ocean nutrient**

3 **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 (α_{Cd-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.

2   Introduction

51 Major nutrients (macronutrients) carbon (C), nitrate (NO_3^-), phosphate (PO_4^{3-}) and, in

52 the case of siliceous organisms, silicic acid (Si or $Si(OH)_4$), are taken up into the

53 organic and skeletal material of marine phytoplankton in the euphotic zone,

54 repackaged by zooplankton and exported as dead cells and fecal pellets. Over 86% of

55 the carbon flux at 100 m is remineralised by 1000 m depth, such that macronutrients

56 exhibit characteristic vertical gradients (Martin et al., 1987). In addition to these

57 macronutrients, trace amounts of other elements (micronutrients) are essential for

58 phytoplankton growth. Although studies into micronutrient biogeochemical cycling

59 have focused on Fe availability, other metals, such as Cd, may be biologically

60 important. Cd is a labile nutrient associated with organic matter and has similar

61 spatial distribution patterns to PO_4^{3-} in open ocean deep and surface waters (Boyle,

62 1988; Figure 1). The exact nature of the relationship between Cd and P has been

63 discussed extensively in the literature, and has been modelled either as a combination

64 of two linear relationships separated by a "kink" at ~1.3 μmol kg^{-1} PO_4^{3-} as a result of

65 basin specific processes (Cullen, 2006; de Baar et al, 1994; Frew and Hunter, 1992;

66 Yeats, 1998) or a non-linear fractionation curve (Elderfield and Rickaby, 2000).

67 There is increasing evidence that Cd is a biologically important trace metal, actively

68 taken up by phytoplankton in productive surface waters. Firstly, Cd is known to

69 substitute into the metalloenzyme Carbonic Anhydrase (CA), which catalyses the

70 uptake of bicarbonate (HCO_3^-) from seawater providing a source of inorganic C for

71 photosynthesis i.e. the Carbon Concentrating Mechanism or CCM (Morel and Price,

72 2003). Cd may substitute for Zn in CA such that Cd added to Zn-limited diatoms

73 leads to an increase in cellular CA activity and growth rate (Lane and Morel, 2000;

74 Lee and Morel, 1995; Morel et al., 1994; Price and Morel, 1990). Recent sequencing

75 and primary characterisation has confirmed the presence of a Cd specific CA, i.e. Cd-

76 CA; (Lane et al., 2005; Xu et al., 2008). Cd has also been implicated in the formation

77 of Polyphosphate Bodies (PPBs) in the giant kelp, *Macrocystis pyrifera*. PPBs are

78 ubiquitous to most organisms, and may be active in phytoplankton (Hunter and Boyd,

79 1997). Secondly, recent seawater analyses have shown that Cd isotopic fractionation

80 occurs in seawater, with the greatest fractionation occurring in surface waters depleted

81 in dissolved Cd suggesting a biological signature (Lacan et al., 2006; Ripperger et al.,

82 2007).

83 Biological uptake, and thus changes in nutrient demands due to variations in

84 environmental conditions and population structure, could have a significant impact on

85 the relationship between Cd and P in seawater. In addition to providing insight into

86 modern biogeochemical cycling, understanding the relationship between macro- and

87 micronutrients has implications for the reconstruction of past PO_4^{3-} utilisation using

88 Cd/Ca ratios in foraminiferal calcite, which relies on a predictable Cd/PO_4^{3-} ratio in

89 seawater (Boyle, 1986; Rickaby & Elderfield, 1999; Elderfield & Rickaby, 2000).

90 The chemistry of deep water masses could be influenced by continental shelf and

91 coastal processes at the site of formation. Further, past changes in continental shelf

92 inputs to deep water could impact past deep water Cd/PO_4^{3-}, and, consequently, the

93 interpretation of benthic foraminiferal Cd/Ca ratios. Here, we investigate the seasonal

94 uptake of Cd and macronutrients in a coastal environment off the West Antarctic

95 Peninsula. We discuss our results in the context of Southern Ocean processes on a

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

97   longer timescales.

98

99   **3   Methods and materials**

100   *3.1   Field setting*

101   Coastal seawater samples were collected from Ryder Bay, which forms the larger part

102   of Marguerite Bay off Adelaide Island, near Rothera Research Station (British

103   Antarctic Survey, BAS), West Antarctic Peninsula (WAP; Figure 2).   As well as

104   being ideally located in a climatically sensitive region (Meredith et al., 2004), this site

105   is part of several long term monitoring projects (Clarke et al., 2008; Meredith et al.,

106   2008; Smith et al., 1999).   The Rothera Oceanographic and Biological Time-Series

107   (RaTS) has been conducted by BAS since late 1997, following the end of the

108   successful long term monitoring series at Signy, northern WAP, in 1994.

109   Conductivity-Temperature-Depth   (CTD)   profiles,   nutrient   analysis   and   size

110   fractionated pigment assays (to monitor biomass) are carried out on a regular basis

111   throughout the year and further details are reported elsewhere (Clarke et al., 2008).

112

113   The Antarctic Circumpolar Current (ACC) pumps nutrient rich, oxygen poor, warm

114   water from the Upper Circumpolar Deep Water (UCDW) onto the continental shelf

115   along the WAP below 200 m and into Marguerite Bay several times a year (Meredith

116   et al., 2004).   Vertical mixing of this water occurs largely as a result of bathymetric

117   features and is the principal heat transfer process at depth.   Above 100-150 m, the

118   highly seasonal Antarctic Surface Water (ASW) dominates in shelf waters, including

119   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*

143 Approximate trace metal concentrations were measured on a Perkin Elmer Elan

144 6100DRC Quadrupole Inductively Coupled Plasma Mass Spectrometer (Q-ICP-MS)

145 using a standard addition method. Five aliquots of acidified seawater were diluted

146 ten-fold with 1% sub-boiling quartz-distilled HNO_3 and added to incremental amounts

147 of spike solutions (Greyhound Chromatography). A machine blank was initially run

148 for each batch of five solutions. Pulse intensity was measured six times for each

149 aliquot, the mean value corrected for isobaric interferences and machine blank, and

150 sample concentration calculated by regression.

151 Cd intensities were measured using ^{114}Cd (28.73% natural Cd). Isobaric interference

152 from ^{114}Sn (0.65% natural Sn) was corrected for by measuring ^{118}Sn, and ^{98}Mo^{16}O$^+$

153 was corrected for by monitoring ^{98}Mo intensities. ^{98}Mo^{16}O$^+$/^{98}Mo$^+$ formation in the

154 plasma is 0.2 to 0.4%. The external precision and accuracy were assessed using two

155 independent seawater standards (Table 1). These approximate concentrations were

156 used to determine the optimal quantities of Cd spike that were to be added to the

157 samples, to avoid large error magnification factors in the application of the isotope

158 dilution method. Laboratory blanks were also measured by standard addition, and

159 were below the Limit of Detection (LoD for Cd ~ 0.01 ppb).

160

161 *ii) Isotope dilution method*

162 The small variations in Cd concentrations during the 2006 austral summer were

163 subsequently measured by single-spike isotope dilution after pre-concentration of Cd

164 by $Mg(OH)_2$ co-precipitation (Wu and Boyle, 1997). An appropriate amount of spike,

165 which had been previously calibrated (Ripperger and Rehkämper, 2007a; Ripperger

166 and Rehkämper, 2007b), was weighed into Teflon containers. Error magnification

167 was reduced by keeping the sample-to-spike mass ratio for Cd approximately equal to

168   unity. As the co-precipitation method is pH sensitive, the concentration and acidity of

169   the spike were adjusted after weighing. Approximately 13 ml of acidified seawater

170   was weighed in 15 ml acid-cleaned polypropylene centrifuge tubes (5 point balance $\pm$

171   0.01 mg) and spiked with 400 μl of enriched ^{110}Cd spike solution was added.

172   Previous experiments have shown that the equilibration is rapid, and there is no

173   significant difference between samples equilibrated for 2 minutes and 2 days (Wu and

174   Boyle, 1997). FEP distilled aqueous NH_3 (500-2000 μl) was added to precipitate

175    $Mg(OH)_2$; the amount added was determined empirically to allow ~ 7% Mg to

176   precipitate to minimise matrix effects during analysis (Mg ~ 1000 ppm; (Wu and

177   Boyle, 1997)). Cd is preferentially taken up into the precipitate, resulting in ~ 30%

178   Cd yields. After NH_4OH addition, the sample was left for two minutes before

179   centrifugation at 6000 rpm for 4 minutes. The supernatant was discarded and the

180   precipitate was redissolved in 0.5 ml 5% HNO_3 (sub-boiling distilled HNO_3 in Milli-

181   Q water), diluted with 0.5 ml Milli-Q and analysed for Cd isotopes by ICP-MS.

182   The standards and samples were analysed using an Element II magnetic sector ICP-

183   MS (Thermo Finnigan), introduced in conjunction with a Cetac ASX-100

184   microautosampler. The ICP-MS was run in low resolution mode to optimise counting

185   statistics; using medium resolution reduces the signal by a factor of 15. Even though

186    $Mg(OH)_2$ co-precipitation significantly lowers the matrix load of the seawater

187   samples, elements that potentially interfere with Cd isotopes, such as Mo, Sn and Pt,

188   are precipitated along with Cd and need to be monitored. Standards were measured

189   for mass bias and oxide corrections. Two standard solutions were used: 1) a 1 ppb

190   "Alfa Cd Zürich" Cd standard (Ripperger and Rehkämper, 2007b), the isotopic

191   composition of which is known accurately and precisely and is very similar to that of

192   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.

216 ^{110}Pd interference on ^{110}Cd was corrected by monitoring ^{106}Pd after Mo and Sn

217 corrections, and after correcting ^{106}Pd for ^{106}Cd based on ^{111}Cd signals as follows

218 (Equations 1-2):

219 $$^{110}Cd_{corr} = {}^{110}Cd^* - {}^{106}Pd_{corr} / A_{106Pd} \times A_{110Pd} \qquad (1)$$

220 $$^{106}Pd_{corr} = {}^{106}Cd^* - {}^{111}Cd^* / A_{111Cd} \times A_{106Cd} \qquad (2)$$

221 where A_x = natural abundance if isotope, and the superscript * denotes count rates

222 corrected for blank and MoO contributions.

223

224 The strong matrix effect of the sample solutions (about 1000 ppm each of Mg and Na)

225 obtained by co-precipitation samples results in a suppression of the instrument blank

226 signal. This suppression, and so the true instrument blank, was assessed by measuring

227 the intensity of an In spike added to both 2% HNO_3 and the in-house standard

228 'Ryder06' standard and then applying Equation 3:

229 $$B = \frac{In_{Ryder06}}{In_{2\%}} \times B_{2\%} \qquad (3)$$

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

231 $In_{2\%}$ = In intensity in 2% acid

232 $B_{2\%}$ = Machine blank for 2% acid

233

234 Blank contributions were about 5% of the signal for all Cd isotopes except ^{112}Cd ca.

235 40%. Mass bias (Δ_M) was corrected by measuring the isotope ratio of a 1 ppb solution

236 of "Alfa Cd Zürich" and applying Equation 4:

237

238 $$\Delta_M = \frac{\left[\dfrac{^{110}Cd}{^{111}Cd}\right]_{measured}}{\left[\dfrac{^{110}Cd}{^{111}Cd}\right]_{real}} - 1 \tag{4}$$

239

240   The natural sample ratio (or the ratio of the in-house Ryder06 standard) may not be

241   exactly equal to the ratio of the Alfa Cd Zürich standard. Natural Cd isotopic

242   fractionation in seawater occurs as a result of closed system biological uptake and

243   ranges from $\varepsilon^{114/110}$ Cd $= \pm3$ to ±36 (Ripperger et al., 2007). However, the greatest

244   fractionations occurs in Cd-depleted surface waters in the North Pacific ([Cd] ~ 0.003

245   nmol kg^{-1}). The [Cd] concentration of the Ryder Bay surface waters are higher,

246   suggesting a lower degree of Cd isotopic fractionation, and are replenished regularly

247   by deep water ($\varepsilon^{114/110}$ Cd $= \pm3.3 \pm 0.5$; (Ripperger et al., 2007)). Hence, the

248   maximum error associated with assuming $\varepsilon^{114/110}$ Cd $= 0$ is approximately 0.03%.

249

250   The external reproducibility of the isotope analysis was established by repeat

251   measurements of unspiked standard "Ryder06", and was found to be approximately

252   2% (Figure 3). The reproducibility for spiked samples should be as good as or better

253   than 2% due to the greater proportion of ^{110}Cd. The accuracy of the isotope dilution

254   method was determined based on duplicate measurements of the reference standard

255   NASS-5, which yielded concentrations of 0.0221 ± 0.0004 (~2%) and 0.021 ± 0.006

256   (~30%) ppb using ^{110}Cd/^{114}Cd and ^{110}Cd/^{111}Cd respectively (certified value $0.023 \pm$

257   0.003; measured as 0.02224 ± 0.00004 by double spiked isotope dilution, (Ripperger

258   and Rehkämper, 2007b)). ^{110}Cd/^{114}Cd and ^{110}Cd/^{111}Cd agree well for the samples

259   (Figure 4), but due to the greater precision on the former ratio, only concentrations

260   determined via ^{110}Cd/^{114}Cd ratios are quoted in the results section.

262 Macronutrients were measured using a Skalar Autoanalyser (Kirkwood, 1996). The

263 detection limit for NO_3^-, PO_4^{3-} and Si analyses were 0.1, 0.05 and 0.1 µmol l$^-$

264 ^{1} respectively. The percentage error for all nutrient analyses was less than 5% relative

265 to Ocean Scientific International (U.K.) standards. This results in a propagated error

266 of ~ 5.5% on Cd/PO_4^{3-} values.

267

4 Results and discussion

268

269

270 Our time series shows a consistent pattern of biological utilisation, with seasonal

271 depletion in macronutrients NO_3^- and PO_4^{3-} during periods of high biomass (Figure 5).

272 Cd co-varies with macronutrients (using all available data, Cd versus PO_4^{3-}, $r^2 = 0.70$,

273 n = 18) with depletions occurring during the peaks of the summer bloom. However,

274 the relationship between total chlorophyll *a* (chl *a*) and both macronutrients and Cd is

275 not statistically significant ($r^2 < 0.1$ for chl *a* versus $Si(OH)_4$, PO_4^{3-}, NO_3^- and Cd).

276 This suggests that chl *a*, a measure of biomass, may not in this situation provide a

277 reliable measure of nutrient utilisation *per se*. This could be because 1)

278 phytoplankton utilise a range pigments in addition to chl *a*; 2) biomass does not relate

279 to total nutrient drawdown because of grazing and remineralisation processes; 3)

280 abiological/physical factors, such as storminess and water column mixing, influence

281 the distribution of nutrients (Clarke et al., 2008).

282

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.,

331   2008), then a 40:60 ratio of NADW:CCSW explains the Modern CDW salinity of

332   34.7 psu.

333   **4.1.2 Biological fractionation**

334   The subsequent biological fractionation of the mixed water upwelling to the surface in

335   the Southern Ocean will depend on environmental conditions. In open ocean regions

336   the fractionation of Cd with respect to P follows a simple fractionation trend given by

337   Equation 6, where Cd_T and P_T are the total Cd and P available in the ocean, Cd_{sw} and

338   P_{sw} is the concentration of Cd and P in seawater, and α_{Cd-P} is the fractionation factor as

339   defined in Equation 5 (Elderfield and Rickaby, 2000).

340

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

342   (5)

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

344   (6)

345   In the CCSZ (e.g. this study and the Princess Elizabeth Trough, (Frew, 1995)), the

346   relative requirements of Cd with respect to PO_4^{3-} are diminished, α_{Cd-P} is reduced

347   (Equation 7) and there is a stock of Cd that is not appear to be utilised ("Cd_{xs}").

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

349   (7)

350

351

352   This reduction in relative Cd requirements in coastal regions with respect to the open

353   ocean may be due to differences in the activity of metalloenzymes, such as CA. The

354   activity of CA is affected by the availability of macronutrients (Wang and Dei, 2001),

355   micronutrients (Cullen et al., 2003; Cullen and Sherrell, 2005; Sunda and Huntsman,

356   1998) and pCO_2 (Cullen and Sherrell, 2005). Coastal regions show depleted seawater

357   CO_2 in summer compared to the open Southern Ocean, suggesting variations in pCO_2

358   cannot provide a mechanism to explain the observed seawater Cd/PO_4^{3-} (Álvarez et

359   al., 2002; Bakker et al., 1997; Gibson and Trull, 1999; Hoppema et al., 2000;

360   Takahashi et al., 2002). Hence, the most likely explanation for the lower utilisation of

361   Cd is that the higher micronutrient conditions in coastal waters influences CA activity,

362   Cd requirements or uptake mechanisms. It has been postulated that the non-linear

363   relationship between Cd and PO_4^{3-} is a result of two different fractionation

364   relationships between Cd and PO_4^{3-} in Fe replete and deficient conditions (Cullen et

365   al., 2003). Under high Fe conditions, Cd/P uptake into cellular material is reduced,

366   possibly due to a competing Fe-Cd cellular transporter (Armbrust, 2004; Cullen,

367   2006). Furthermore, the substitution of Zn into the Cd-CA structure influences the

368   enzyme activity, such that CA activity and Cd requirements vary with Zn

369   concentrations in the ambient medium (Park et al., 2007; Xu et al., 2008).

370

371   In Fe and Zn deficient regions (e.g. Subantarctic Zone), uptake of Cd with respect to P

372   follows a simple trend given by Equation 6 with a constant fractionation factor, α_{Cd-P}

373   = 3.5. In Fe and Zn replete conditions of the CCSZ (e.g. Table 5) uptake of Cd

374   follows a trend with a lower fractionation factor (α_{Cd-P} = 2; Figure 6). Phytoplankton

375   grown under such conditions have lower Cd requirements (Cullen, 2006), which could

376   provide a mechanism behind the lower value of α_{Cd-P} in coastal waters. Further,

377   competitive interaction between metals (Sunda and Huntsman, 1998) or biologically

378   produced ligands (Lee et al., 1996) can modulate uptake of Cd. For example,

379   production of metal-binding polypeptides, phytochelatins, is activated in cultured

380   diatoms under high internal and external Cd concentrations (Lee et al., 1996).

381   Increased production of phytochelatins under higher micronutrient conditions could

382   explain the reduction in uptake of Cd in coastal zones.

383

384   *4.2   Seasonal variability and population structure*

385

386   Our data show some scatter about the linear relationship between Cd and PO_4^{3-} in

387   Ryder Bay (Figure 6), which reflects seasonal variations in seawater Cd/PO_4^{3-} due to

388   changes in diatom species composition and environmental conditions. Such

389   population related variations may also influence large scale global cycling of macro-

390   and micronutrients in seawater given the predictable geographical variation in

391   plankton types and sizes.

392

393   Surface Cd/PO_4^{3-} of Ryder Bay has an initial background of ~ 0.4-0.5 nmol/µmol

394   (Figure 5). Although this estimate is based on approximate concentrations measured

395   using standard addition, it agrees well with other Antarctic coastal regions, e.g.

396   Deception Island ~ 0.6; Palmer Station 0.3-0.35; (Sañudo-Wilhelmy et al., 2002).

397   These values are also similar to the upper estimates of Cd/PO_4^{3-} for UCDW, 0.35-0.5

398   nmol/µmol (Löscher et al., 1998). This is consistent with coastal Antarctic seawater

399   being influenced by high Cd/PO_4^{3-} waters from upwelling UCDW (Meredith et al.,

400   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

426　　analyses indicate there is a shift away from large centrics in the early summer towards

427　　smaller diatom species in the later bloom (Annett, pers. com.). In other words, these

428　　results show that a switch does not have to be between phytoplankton divisions during

429　　the　　bloom　　(e.g　　diatoms　　to　　flagellates)　　in　　order　　to

430　　influence the seawater Cd/PO_4^{3-} ratio but may be between phytoplankton genera

431　　within a division.

432　　The variation in Cd requirements with respect to macronutrients with population and

433　　size structure in seawater may also influence the "global relationship" between Cd

434　　and PO_4^{3-}. For example, high nutrient upwelling zones favour the growth of

435　　microplankton (in particular diatoms) with high Cd requirements. Temperate open

436　　ocean regions favour the growth of other larger phytoplankton. Conversely, tropical

437　　oligotrophic gyres favour the growth of picoplankton and autotrophic bacteria with

438　　lower Cd requirements. Further, there is an effective microbial loop in these regions

439　　that results in more rapid regeneration, which may mask the effect of biological

440　　fractionation (Alvain et al., 2005; Follows et al., 2007).

441

442　　*4.3　Implications for glacial-interglacial reconstructions*

443

444　　We have shown the non-linear relationship between Cd and PO_4^{3-} in seawater can be

445　　explained by a combination of 1) water mass mixing; 2) differential biological

446　　fractionation due to variation in micronutrient concentration, and 3) changes in

447　　phytoplankton community structure. These processes are likely to change on glacial-

448　　interglacial timescales, due to shifts in deep water formation processes and

449　　atmospheric inputs, resulting in long-term changes in the Cd/PO_4^{3-} ratio of Southern

450　　Ocean seawater.

451

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

501

502

503 We present a time series of Cd and macronutrient data from a coastal site adjacent to

504 the West Antarctic Peninsula, which shows that Cd is taken up during periods of high

505 biological productivity despite nearshore, micronutrient replete conditions. These

506 Antarctic coastal waters show high Cd/PO_4^{3-} and can impact the preformed nutrient

507 content of seawater in the open Southern Ocean through deep water formation and

508 mixing with water masses originating further north. We have demonstrated that the

509 non-linear relationship between Cd and PO_4^{3-} in seawater can be explained by a

510 combination of 1) water mass mixing; 2) differential biological fractionation due to

511 variation in micronutrient concentration, and 3) changes in phytoplankton community

512 structure, which can vary within a season. These processes are likely to change on

513 glacial-interglacial timescales, due to shifts in deep water formation processes and

514 atmospheric inputs, resulting in long-term changes in the Cd/PO_4^{3-} ratio of Southern

515 Ocean seawater. An understanding these shifts in the preformed Cd/PO_4^{3-} ratio of

516 seawater, and changes in biological fractionation in Southern Ocean surface waters,

517 could resolve discrepancies between benthic foraminiferal Cd/Ca records and other

518 paleonutrient proxies.

530

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723

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

731

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

734

735 Figure 3: External reproducibility of 1 ppb Alfa Zürich standard and in-house standard
736 ("Ryder06") using A) ^{110}Cd/^{111}Cd and B) ^{110}Cd/^{114}Cd. Error bars show internal precision
737 ($\pm1.3\%$).

738

739 Figure 4: Comparison of methods for the analysis of dissolved Cd in seawater samples of
740 using two different isotope ratios for isotope dilution ($\pm1\sigma$).

741

742

743 Figure 5: Pigment and nutrient concentrations from 15 m collected at the RaTS site from
744 2005-2006. A) Total chlorophyll *a* concentrations (grey square; B) size fractionated chl *a*
745 (data courtesy of BAS); macronutrient concentrations C) nitrate (white triangles), D) silicic
746 acid (black squares) and E) phosphate (white diamonds); micronutrient concentrations F)
747 cadmium (measured by standard addition (SA; grey dots) and isotope dilution (ID; black
748 circles) and G) Cd/PO$_4$$^{3-}$. (grey circles). N and P measurements carried out by Weston, UEA,
749 and Carson, Edinburgh. All errors bars show $\pm2\sigma$.

750

751

752

753 Figure 6: Fractionation of dissolved Cd and PO$_4$$^{3-}$ or DIP in Southern Ocean waters.
754 Upwelling CDW (cyan dashed line) is formed from a mixture of NADW and AABW.
755 Endmember compositions shown in the large cyan circles (de Baar and al, 1994; Elderfield
756 and Rickaby, 2000; Frew, 1995; Westerlund and Ohman, 1991). The mixing of these water
757 masses can be observed in measurements of Cd and P measurements in Subantarctic Zone
758 Waters (SAW, black circles), Polar Front regions (PF, red circles) and Antarctic Zone Waters
759 (AAW, green circles). In open water regions (e.g. Subantarctic Zone, black circles),
760 fractionation of Cd with respect to P follows a simple fractionation trend given by Equation 6
761 with a constant fractionation factor, $\alpha_{Cd-P} = 3.5$. In coastal conditions in the (CCSW e.g. this
762 study, dark blue circles and the Princess Elizabeth Trough, PET, yellow circles) there is 1)
763 stock of Cd, Cd$_{xs}$, that is not utilised (Equation 7), and 2) a lower fractionation factor, $\alpha_{Cd-P} =$
764 2.0. Utilisation and decay of nutrients follow trajectories given by the grey arrows. Note that
765 the Cd/PO$_4$$^{3-}$ of upwelling waters will depend on the depth of mixing due to the deeper
766 regeneration cycle of Cd.

767

768

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

769 *Certified seawater reference material for trace metals, National Research Council Canada
770 Table 1: Cd analysis of reference seawater standards. Errors are ±2σ.

771
772

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)

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

775
776

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

777 Table 3: Analytical parameters of ICP-MS analysis

778
779

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

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

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784 % signal = (counts from interference at mass peak)/(total counts at mass peak) x 100.

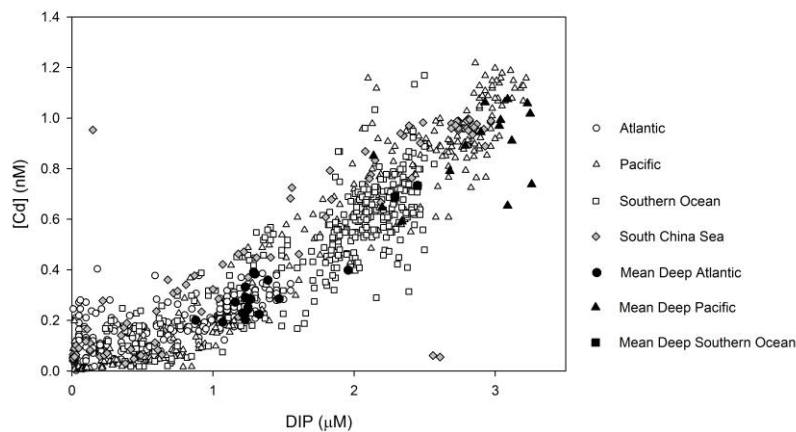785
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Region	[Fe] (nM)	[Zn] (nM)	Reference
Palmer Station, WAP	4-6	4-5	(Sañudo-Wilhelmy et al., 2002)
King George Island, South Georgia		> 40	(Prendez and Carrasco, 2003; Prendez et al., 1996)
Weddell Sea	1-6	3-5	(Westerlund and Ohman, 1991)
Terra Nova 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
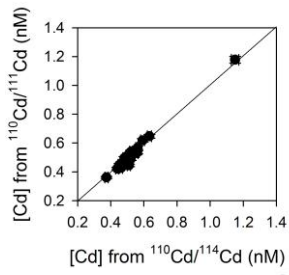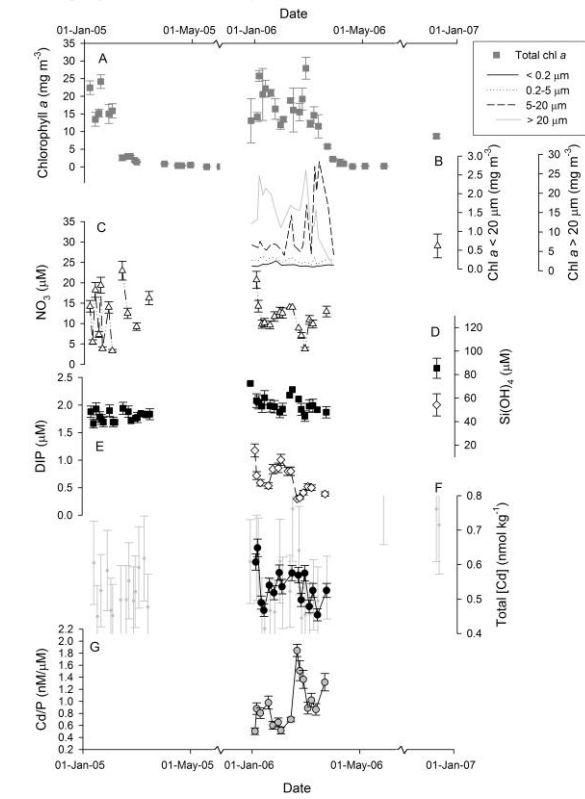795 Antarctica.
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