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Interactions of dissolved CO₂ with Cadmium Isotopes in the Southern Ocean

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ABSTRACT

Here we report the first ever observations of a strong correlation in ocean surface waters of the dissolved $\delta^{114}\text{Cd}$ with dissolved CO₂. This is observed in the Southern Ocean along the 0°W meridian in both the Antarctic Circumpolar Current and the Weddell Gyre, as well as in the Weddell Sea proper, near the Antarctic Peninsula and in Drake Passage. This uniform trend in several surface water masses hints at a uniform biochemical mechanism within the Southern Ocean. One hypothesis for the underlying mechanism would be a role of Cd in the carbonic anhydrase function for conversion of bicarbonate ion [HCO₃⁻] into CO₂, the latter being required by RuBisCO (Ribulose-1,5-bisphosphate carboxylase/oxygenase) that only accepts CO₂. At low ambient [CO₂] the algae maintain growth by also operating a Carbon Concentrating Mechanism (CCM) for utilization of [HCO₃⁻] and its conversion to CO₂. For this the algae need more enzyme carbonic anhydrase that normally has Zn as its co-factor, but Cd may substitute for Zn and there also are Cd-specific carbonic anhydrases known for some phytoplankton species. Indeed in incubations of the local plankton communities it is shown that the phytoplankton have a very strong preferential uptake of CO₂, such that the uptake ratio {[CO₂]/[HCO₃⁻]} is much higher than the dissolved ratio {[CO₂]/[HCO₃⁻]} in ambient seawater. Therefore the here reported observations in the Southern Ocean are also expressed for $\delta^{114}\text{Cd}$ as function of the ratio {[CO₂]/[HCO₃⁻]} in ambient seawater. Future research of local phytoplankton in unperturbed natural waters of the Southern Ocean is recommended to be able to verify the hypothesis of a function of Cd in carbonic anhydrase in Antarctic phytoplankton.

Keywords:

Cadmium, Carbon dioxide, Southern Ocean, Isotopes

Three highlights:

- First observation of relation in seawater of Cadmium isotopic composition with CO₂.
- First observation of relation in seawater of concentrations of Cadmium and CO₂.
- Apparent role of Cd in metabolism of Antarctic phytoplankton deserves more research.

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1. Introduction

1.1. Cadmium and the biological cycle. Cadmium (Cd) was one of the first transition metal elements for which oceanographically consistent data was obtained (Boyle et al., 1976; Martin et al., 1976; Bruland et al., 1978; Bruland, 1980). Along vertical profiles at several locations in the oceans, a striking correlation between dissolved Cd and nutrient phosphate (PO_4) was reported. This was surprising as until then Cd was not known to be an element with relevance for biology. Just like PO_4 , the dissolved Cd is apparently removed from surface waters leading to very low concentrations in surface waters, and enriched in deep waters due to remineralization. Obviously Cd is a non-conservative chemical element in the oceans, i.e. its distribution is not only determined by circulation and mixing of ocean waters, but also by involvement in biological and/or chemical processes.

Phytoplankton, and in fact all other living organisms, comprise and hence require not only carbon (C) but also the nutrient elements N and P, as well as 6 trace nutrient elements, here given in order of their typical abundance in living cells:

$$\text{C} > \text{N} > \text{P} \gg \text{Fe} > \text{Zn} > \text{Mn} > \text{Cu} > \text{Ni} \gg \text{Co} \quad (1)$$

For the major nutrient elements and some, but not all, trace nutrient elements, this order also more or less reflects the abundances of the dissolved chemical elements in ambient seawater. Conversely, for the major nutrient elements the latter abundances have been used to derive the average stoichiometry of phytoplankton, notably the Redfield ratio of C:N:P (106:16:1 after Redfield et al., 1963) and significant variations thereof (e.g. Fanning, 1992; Anderson and Sarmiento, 1994; de Baar et al., 1997).

The apparent correlation of another trace element, in this case dissolved Cd, along vertical profiles with the biological cycle of soft tissue organic matter, would preferably be demonstrated versus the primary biological element carbon (C). Such a demonstration is not straightforward, however, as C is also strongly involved in the cycle of calcareous hard shells, and also affected by air/sea gas exchange of CO_2 . Thus property-property plots of Cd versus the tracer Dissolved Inorganic Carbon (DIC) are not very suitable. Resolution versus the dissolved nitrate (NO_3^-) tracer representing the secondary biological element nitrogen (N), would suffer from interference due to net reductive removal of dissolved nitrate within Oxygen Minimum Zones. Therefore the apparent interaction of Cd with the biological cycle has traditionally been quantified in plots versus the relatively minor nutrient phosphate, as the latter is virtually free of unwanted interferences (e.g. de Baar et al., 1994; Cullen, 2006; Baars et al., 2014; Xie et al., 2015; among many others).

Despite more than 40 years of research, the underlying removal mechanism of Cd from surface waters still is subject to debate. It may be (i) purposeful uptake for a role in a Cd-specific form of the enzyme carbonic anhydrase as reported for some diatom species of phytoplankton (Lane and Morel, 2000; Lane et al., 2005; Xu et al., 2008), or (ii) substituting for Zn in its well known function in carbonic anhydrase (Price and Morel, 1990; Lee et al., 1995; Lee and Morel, 1995; Xu et al., 2007), or (iii) non-specific biological uptake and homeostasis (Horner et al., 2013a) or (iv) adsorptive scavenging on the outside of plankton in surface waters. All four proposed mechanisms would lead to some Cd within or associated with biogenic particles to be removed from surface waters by vertical settling of biogenic debris into the deep ocean. Mineralization in deep waters would return Cd and PO_4 into seawater leading to higher concentrations. Thus, with respect to (i) and (ii) and the intracellular biochemistry of phytoplankton, Cd is envisioned to be mostly involved in the CO_2 metabolism rather than the phosphorus metabolism, but for ocean tracer approaches the opposite has thus far been applied by focusing on relations of Cd with PO_4 . Here we now aim

to unravel conceivable direct relations of dissolved Cd and its isotopic composition with components of the CO₂ system in seawater.

1.2. Cadmium Isotopes in Seawater. In 1984 Prof. Harry Elderfield suggested to the lead author (HdB) that a strong fractionation of stable isotopes of Cd in seawater might well support the first two mechanisms of a true biological function (this akin to the well-known ¹³C/¹²C biological fractionation), yet despite much effort the team was at the time not able to produce precise measurements of Cd isotopic compositions. However recently several laboratories have been able to produce accurate datasets of Cd isotopic composition for seawater collected during our expedition (Abouchami et al., 2011, 2014; Xue et al., 2013) and elsewhere (Gault-Ringold et al., 2012; Conway and John, 2015a,b; Xie et al., 2017). These breakthroughs are also based on efforts to improve reference standards and analytical methods as well as laboratory intercomparisons (Abouchami et al., 2010; Xue et al. 2012; Boyle et al., 2012; Conway et al., 2013).

Previously we have shown that the Cd isotope fractionation in the Southern Ocean (Geotraces section GIPY5) is controlled by biological uptake that imparts the $\delta^{114}\text{Cd}$ signature in the surface layer while that of deep waters is determined by the flux of regenerated isotopically-light Cd from sinking organic matter from the surface ocean and the degree of mixing of distinct water masses (Abouchami et al., 2011, 2014; Xue et al., 2013). Moreover, detailed assessment reveals fine structure within the 'HNLC trend', which may record differences in the biological fractionation factor (e.g. Abouchami et al., 2011, their Figure 4b; Xue et al., 2013, their Figure 5; Abouchami et al., 2014; their Figure 3a), different scenarios of closed and open system isotope fractionation, and/or distinct source water compositions. Surface waters of the Southern Ocean proper do comprise ample dissolved Cd, such that due to some removal by biological uptake, there develops a fractionation of the Cd isotopes that are left behind in the surface waters.

The SubAntarctic Zone (SAZ) is very different with very low Cd concentrations (one sample with Cd = 0.036 nM, Abouchami et al., 2011; 0.0072 nM < Cd < 0.15 nM, Gault-Ringold et al., 2012) such that in a seasonal study an about 50-fold depletion of Cd due to biological uptake was found; in essence all Cd is removed and hence virtually no Cd isotope fractionation discernible in the remaining seawater (Gault-Ringold et al., 2012). Recently Conway and John (2015a) reported a comprehensive section (Geotraces GA03) of $\delta^{114}\text{Cd}$ in the North Atlantic Ocean that also was interpreted to reflect fractionation due to *in situ* biological uptake of isotopically light Cd in the very surface ocean, in combination with mixing of deep water masses of both Antarctic and North Atlantic origin. Moreover for the western South Atlantic (part of our Geotraces section GA02) we reported $\delta^{114}\text{Cd}$ values that may be interpreted by either (i) sorption of Cd onto organic ligands, or (ii) an open system, steady state, fractionation model, in combination with mixing of intermediate and deep waters (Xie et al., 2017). The oligotrophic North East Pacific Ocean exhibits low Cd and high $\delta^{114}\text{Cd}$ in surface waters, whereas the locally very strong Oxygen Minimum Zone (OMZ) in the 600-2000m depth range was reported to affect the Cd geochemistry (Conway and John, 2015b).

These exciting new datasets have not only shed more light on the relation of Cd and $\delta^{114}\text{Cd}$ with the biological cycle, but also highlight the importance of the $\delta^{114}\text{Cd}$ signature of Antarctic source waters that beyond the Antarctic Ocean proper have a major imprint (AntArctic Bottom Water, AABW; AntArctic Intermediate Water, AAIW; and Subantarctic Mode Water, SAMW) on the $\delta^{114}\text{Cd}$ distribution in the entire Atlantic Ocean, if not the whole world ocean. Therefore the underlying mechanism of the biological fractionation of Cd isotopes within the Antarctic Ocean proper is of great significance for truly understanding the world ocean distributions of both Cd and $\delta^{114}\text{Cd}$.

Here we express the Cd isotopic composition in seawater relative to the international NIST SRM 3108 Cd isotope standard (std):

$$\delta^{114}\text{Cd} = \left\{ \left[\left(\frac{^{114}\text{Cd}}{^{110}\text{Cd}} \right)_{\text{sample}} / \left(\frac{^{114}\text{Cd}}{^{110}\text{Cd}} \right)_{\text{std}} \right] - 1 \right\} \times 1000 \quad (2)$$

This $\delta^{114}\text{Cd}$ notation is the notation of the forthcoming Geotraces 2017 International Data Product, yet please be aware that one original underlying dataset (Xue et al., 2013) has been reported in ϵ notation, where:

$$\delta^{114}\text{Cd} = (\epsilon^{114/110}\text{Cd}/10) \quad (3)$$

thus a simple factor 10 conversion factor. In fact the other underlying datasets (Abouchami et al., 2011, 2014) were reported in $\epsilon^{112/110}\text{Cd}$ that first was converted to $\epsilon^{114/110}\text{Cd}$ and then to $\delta^{114}\text{Cd}$. Similarly Xie et al. (2017) also report in the $\epsilon^{112/110}\text{Cd}$ notation but their data is not used here.

1.3. CO_2 System in Seawater. The Dissolved Inorganic Carbon (DIC) content of seawater encompasses an equilibrium of 4 different forms, specifically the chemical species of dissolved CO_2 , the carbonic acid, the bicarbonate ion and the carbonate ion:

$$\text{DIC} = [\text{CO}_2]_{\text{aqueous}} + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (4)$$

In seawater, the bicarbonate ion $[\text{HCO}_3^-]$ is dominant, at $\sim 2000 \mu\text{mol.kg}^{-1}$ representing $\sim 95\%$ of the DIC pool, followed by the carbonate ion $[\text{CO}_3^{2-}]$ at about $100 \mu\text{mol.kg}^{-1}$ representing $\sim 5\%$ and next the $[\text{CO}_2]_{\text{aqueous}}$ at about $10\text{-}20 \mu\text{mol.kg}^{-1}$ representing merely $\sim 1\%$ of the total DIC. Finally the chemical form $[\text{H}_2\text{CO}_3]$ i.e. the undissociated carbonic acid occurs in very low abundance ($\sim 0.02\text{-}0.04 \mu\text{mol.kg}^{-1}$) representing $\sim 0.002\%$ only. This carbonic acid $[\text{H}_2\text{CO}_3]$ cannot be analytically distinguished from the dissolved $[\text{CO}_2]_{\text{(aqueous)}}$ (Weiss, 1974), and in the current study is included in the dissolved $[\text{CO}_2]$ species:

$$[\text{CO}_2] = [\text{CO}_2]_{\text{aqueous}} + [\text{H}_2\text{CO}_3] \quad (5)$$

where the $[\text{H}_2\text{CO}_3]$ represents merely $\sim 0.2\%$ of the $[\text{CO}_2]$. Thus from here on we only consider 3 chemical species, the bicarbonate ion $[\text{HCO}_3^-]$, carbonate ion $[\text{CO}_3^{2-}]$ and dissolved $[\text{CO}_2]$, as follows:

$$\text{DIC} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (6)$$

For photosynthesis within the plant cell, the enzyme RuBisCO (Ribulose-1,5-bisphosphate carboxylase/oxygenase) only accepts CO_2 as the substrate, and hence algae prefer to take up the CO_2 chemical species from the ambient seawater (Neven et al., 2011). However in conditions of lower concentration of CO_2 , the algae can also take up HCO_3^- and within the cell convert this to CO_2 with the enzyme carbonic anhydrase, as required by RuBisCO, albeit at the expense of some of the accumulated solar energy (Figure 1). In general carbonic anhydrase has zinc (Zn) as its central atom, i.e. Zn is required for the algae to be able to assimilate and convert the HCO_3^- bicarbonate ion. However as mentioned above, Cd may substitute for Zn, and there also exist Cd-specific forms of carbonic anhydrase.

1.4. Geotraces. The Antarctic Ocean expedition ANT XXIV-3 in 2008 (International Polar Year) aboard RV Polarstern (Fahrbach et al., 2010, 2011) had an extensive Geotraces program (Geotraces section GIPY5; www.geotraces.org) aiming to measure, with state-of-the-art accuracy, a large number of trace elements and their isotopes, these in conjunction with the

tracers of major biological elements. This approach now enables new studies that seek to identify novel trends and relationships within this large suite of ocean chemical tracers.

1.5. This work. Here we report the first-ever observation in the oceans of correlations between previously measured and published data for the Cd isotopic composition in surface waters of the Southern Ocean (Abouchami et al., 2011, 2014; Xue et al., 2013) with here newly reported results for $[\text{CO}_2]$ as well as the concentration ratio $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ in ambient seawater. Furthermore this is illustrated by independent biological incubation experiments previously reported by Neven et al. (2011). Whilst these experiments do not inform directly about biological fractionation of the Cd isotopic composition the results are nevertheless useful as they enable calculation of the effective uptake ratio $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ by the local phytoplankton communities. Finally recommendations are given for future biological incubation experiments as required for firm validation of the hypothesis of the key mechanism of biological Cd isotope fractionation that may, or may not, cause the here reported correlations of the CO_2 system with the Cd isotopic composition of surface waters.

2. Hydrography and the High Nutrient Low Chlorophyll condition

The expedition ANT-XXIV/3 from 6 February to 16 April 2008 worked along consecutive sections at the Zero Meridian, across the Weddell Sea and across the Drake Passage (Figure 2). The region is characterized by the eastward flowing Antarctic Circumpolar Current (ACC) entering from the Pacific region at $\sim 70^\circ\text{W}$ through Drake Passage, across the Atlantic sector and beyond 20°E towards the Indian Ocean sector.

In the region of the Zero Meridian, the northern boundary of the ACC is at the SubAntarctic Front (SAF) situated at $\sim 45^\circ\text{S}$, beyond which is the SubAntarctic Zone (SAZ). The SAF is the northern boundary of the Southern Ocean. Going southwards in the Polar Frontal Zone (PFZ), the Polar Front (PF) is situated at $\sim 50^\circ\text{S}$. The PF is also known as the Antarctic Polar Front (APF, e.g. Baars et al., 2014). The PF is a more rapidly flowing jet-stream within the ACC akin but larger than the Gulfstream or the Kuroshio Current in the North Atlantic and North Pacific, respectively. The PF is defined as the surface expression of the 2°C isotherm, whereby all waters south of the PF have lower surface temperatures. The PF is the site where, once the seasonal sea-ice cover has disappeared, in austral spring and summer the extra supply of dissolved Fe permits major blooms of large, heavily silicified diatoms that effectively remove all dissolved silicate from the surface waters (de Baar et al., 1995). The PF is the northern boundary of the Antarctic Ocean.

South of the PF is the AntArctic Zone (AAZ) extending until the Southern Boundary of the ACC (SB-ACC) encountered at $\sim 56^\circ\text{S}$ during the expedition. Southwards of $\sim 56^\circ\text{S}$ is the Weddell Gyre, towards and under the extended continental ice sheet of Antarctica at $\sim 69.8^\circ\text{S}$, and by latitude extending from the east-side ($\sim 51^\circ\text{W}$) of the Antarctic Peninsula to about 30°E . Within the Weddell Gyre a major phytoplankton bloom was observed during the preceding Polarstern cruise (ANTXXIV/2) where on the occupation of the Zero Meridian during 17-28 January 2008 very high turbidity and low pCO_2 was found with maximum turbidity and pCO_2 reduction at about 63.5°S . This bloom was also visible in satellite observations of the Chlorophyll *a* distribution in January, but in the subsequent February-March period of our cruise this bloom had largely disappeared (Rutgers van der Loeff et al., 2011; their Figure 7). However the signal of a strong summer minimum of major nutrients did remain in the $62\text{--}67^\circ\text{S}$ region (Figure 3).

Due to upwelling of Circumpolar Deep Water (CDW) in the Weddell Gyre and the AAZ there is a general northwards flow of surface waters in which towards the PF the major and trace nutrients steadily decrease due to biological uptake. More abruptly at the PF the seawater is almost completely stripped of the nutrient silicate by intensive diatom blooms in

spring and summer (Figure 3). Beyond the PF in the PFZ the other nutrients phosphate and nitrate steadily decrease northwards to very low oligotrophic concentration at and beyond the SAF into the SAZ (Figure 3). Overall only the surface waters south of the PF in the Antarctic Ocean proper ($>50^{\circ}\text{S}$) show the truly High Nutrient Low Chlorophyll (HNLC) condition of ample abundance of all 3 major nutrient Si, P and N (Table 1), but generally low phytoplankton Chlorophyll *a*. This HNLC condition is mostly due to a combination of iron limitation and light limitation (de Baar et al., 2005). Moreover, co-limitation and/or interactions have also been reported in the Ross Sea for Co (vitamin-B12) interacting with Fe (Bertrand et al., 2007, 2011) and in the Weddell Sea and Gyre (Figure 2) for the apparent Mn/P uptake ratio as function of ambient dissolved Fe (Middag et al., 2013).

3. Materials and methods

3.1. Cadmium isotopes by Max Planck Institute

Surface seawater samples were collected during the Geotraces ANT XXIV/3 expedition (Figure 2) on board the RV Polarstern (February 10 to April 16, 2008, austral late summer–early autumn, Cape Town, South Africa-Punta Arenas, Chile). Along the Zero Meridian, 12 surface water samples were collected underway at 12 positions at high spatial resolution between 41°S and 61°S , between two and five meters depth, during underway sampling using an IFISH torpedo sampler with an all-Teflon pump. Each sample was given its own consecutive station number, and position and time of sampling were recorded. In addition, 7 upper water samples were collected using the ultraclean Titan Frame equipped with 24 internal-teflon-coated GO-FLO (General Oceanics) samplers (de Baar et al., 2008). All samples were filtered on board in a class 100 clean room environment through $0.2\ \mu\text{m}$ filter capsules (Sartobran-300, Sartorius) under slight nitrogen pressure and collected into acid-cleaned Nalgene high density polyethylene (HDPE) bottles and canisters. Samples were acidified onboard to $\text{pH}=2$ with 12 N HCl (Baseline, Seastar). Small aliquots of the filtered seawater were analyzed colorimetrically with an auto-analyzer on shipboard for the major nutrients phosphate, silicate and nitrate (van Heuven et al., 2011a).

On return, the samples were analyzed as described in detail by Abouchami et al. (2011, 2014). Briefly upon addition of ^{106}Cd - ^{108}Cd double spike after Schmitt et al. (2009a), samples were processed first over a BioRad AG1-X8 anion exchange resin, then dried down and converted in bromide form and next passed over a secondary AG1-X8 anion exchange resin column. Measurements of Cd isotopic compositions were performed by Thermal Ionization Mass Spectrometry, with methods after Schmitt et al. (2009a,b). By subsequent calculations this yields both the total Cd concentration and the $\epsilon^{112/110}\text{Cd}$ isotopic composition. International Cd isotope reference materials were used that confirmed the accuracy of the measurements (Abouchami et al., 2012). The original reported $\epsilon^{112/110}\text{Cd}$ dataset (Abouchami et al., 2011; see also Abouchami et al. 2014) has for the purpose of the current article been converted to $\delta^{114}\text{Cd}$ (Table 2), this also for compatibility with the dataset originally in $\epsilon^{114/110}\text{Cd}$ units of Imperial College.

3.2. Cadmium isotopes by Imperial College

Along the Zero Meridian, 13 surface samples were collected underway at 13 positions in the Weddell Gyre (Figure 2) between two and five meters depth using the IFISH torpedo sampler with an all-teflon pump. Station number, position and time of sampling were recorded. Moreover at one station (245) in the northern Drake Passage another surface sample was collected with the IFISH torpedo. In addition we report here the 4 uppermost samples of hydrocasts at station 163 along the Zero Meridian, station 198 in the Weddell Sea, station 216 near the Antarctic Peninsula, and station 249 in the northern Drake Passage. After collection, the samples were immediately filtered using $0.2\ \mu\text{m}$ nominal size cutoff filter cartridges into

pre-cleaned bottles and acidified to about pH 2. Small aliquots of the filtered seawater were analyzed on shipboard for the major nutrients phosphate, silicate and nitrate.

On return the samples were analyzed as described in detail by Xue et al. (2013). Briefly upon addition of ^{111}Cd - ^{113}Cd double spike, a three-stage column chemistry was employed for separation and purification of the Cd. The isotopic analyses were carried out using a Nu Plasma HR MC-ICP-MS, with data being processed offline to calculate both the total Cd concentration and the $\epsilon^{114/110}\text{Cd}$ that here is converted to $\delta^{114}\text{Cd}$ (Table 2). Analyses of international Cd isotope reference materials showed excellent agreement with consensus values (Abouchami et al., 2012).

3.3. Dissolved CO_2 in surface waters

Continuous surface water pCO_2 measurements are obtained by a system permanently installed aboard Polarstern. This system draws its water from the ship's sea water supply, where sensors also continuously measure salinity S and temperature T . A steady flow of this water is led through an 'equilibrator' vessel, filling it almost halfway before flowing out of it into the ship's drain. The air in the headspace of this equilibrator takes on the pCO_2 value of the seawater. The air of this headspace is circulated through a LiCor 7000 infrared gas analyzer. Sensors data for vapour, pressure and temperature was used for regular minor corrections. Four calibration gasses (pCO_2 at 0, 175, 350 and 700 μatm) are available for hourly recalibration of the gas analyzer. Atmospheric air is measured every hour. The dissolved $[\text{CO}_2]$ is proportional to the measured pCO_2 by Henry's law:

$$[\text{CO}_2] = K' \text{pCO}_2 \quad (\text{Eq. 7})$$

where K' is the solubility as function of temperature T and salinity S . Using the measured pCO_2 , T , and S the dissolved $[\text{CO}_2]$ is calculated, yielding 9395 data values along the Zero Meridian. Selections of these dissolved $[\text{CO}_2]$ values at the same place and time as the Cd isotope surface water samples, are directly compared with the $\delta^{114}\text{Cd}$ data and the Cd concentration data in the below Results section 4.1.

3.4. Dissolved CO_2 system including major nutrients

Samples collected in vertical profiles with the Titan sampling frame, were analyzed for Alkalinity as described by Van Heuven et al. (2011b) using VINDTA 3C instrumentation of Marianda, Kiel, Germany. Briefly, measurements of DIC were performed using the coulometric method (Johnson et al., 1993). Determinations of Alkalinity were performed by an acid titration following the standard settings of the VINDTA after Mintrop et al. (2000). In order to set the measurement accuracy, Certified Reference Material (CRM, see Dickson 2001) was analyzed at least three times per day. Measurements of dissolved nutrients (silicate, nitrate and phosphate) were performed colorimetrically and on board with an auto-analyzer. Accuracy of all three nutrient determinations is considered to be better than 0.25% as confirmed by calibration versus reference samples, and versus a preliminary batch of a novel international reference material for nutrients in seawater (Aoyama et al., 2010; Van Heuven et al., 2011a).

3.5. Calculations of the $[\text{HCO}_3^-]$ concentration

The $[\text{HCO}_3^-]$ concentration is needed in order to be able to compare the $\delta^{114}\text{Cd}$ and Cd concentration with the $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ ratio in ambient seawater, see below Results section 4.3. Here one needs a second variable of the seawater CO_2 system at exactly the same place of the overall 37 samples (Table 2). For (total) alkalinity, synthetic values $A_{\text{T}}^{\text{synth}}$ were obtained

from a multivariate relationship between measured Alkalinity of vertical profiles of the ANT-XXIV/3 cruise and latitude, longitude, salinity, temperature and depth as follows:

$$A_{T^{synth}} = 316.8 - 0.948*lat - 0.085*lon + 56.81*sal - 0.041*depth - 1.66*temp \quad (8)$$

where (n=1866) and rmse: = 8.9 $\mu\text{mol.kg}^{-1}$. The coefficients of this relationship were derived from the GLODAPv2 dataproduct (Key et al., 2015; Olsen et al., 2016; this dataproduct includes the chemical profile data collected during ANT-XXIV/3), from all Alkalinity data available in the geospatial domain [65°W-5°E, 70°S-35°S; depth<50m]. The uncertainty of $A_{T^{synth}}$ (i.e., $\pm 8.9 \mu\text{mol/kg}$) translates to only a minor error in calculated $[\text{HCO}_3^-]$ of $\pm 4.3 \mu\text{mol/kg}$. Comparison for the top-of-profile samples of $A_{T^{synth}}$ to measured Alkalinity shows good agreement. For consistency of the 26 underway samples with the 11 bottle samples, subsequent calculations are performed using $A_{T^{synth}}$ for all 37 samples. From the combined dataset of $p\text{CO}_2$, $A_{T^{synth}}$, T, S, silicate and phosphate, the $[\text{HCO}_3^-]$ ion was calculated using CO2SYS for Matlab (van Heuven et al., 2011b).

3.5. Inorganic carbon uptake by phytoplankton

The contribution of direct HCO_3^- uptake and direct CO_2 uptake was determined in independent plankton community incubation experiments by Neven et al. (2011). Large diatoms were the dominant species in most of the plankton communities that were sampled along the Zero Meridian, in the Weddell Sea and in Drake Passage. Briefly the isotope disequilibrium technique makes use of the relatively slow inorganic equilibration of dissolved DIC system species. The HCO_3^- uptake requires a Carbon Concentrating Mechanism (CCM), that either involves uptake across the cell wall or an external carbonic anhydrase enzyme (eCA) on the outside of the cell wall. By a special inhibition step the gross HCO_3^- uptake can be divided into these two CCM mechanisms (Neven et al., 2011; their Table 3), but these are here considered together as overall HCO_3^- uptake. Next the uptake ratio $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ is calculated for comparison with the concentration ratio $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ in the incubator seawater as calculated after Van Heuven et al. (2011b) from the initial DIC and Alkalinity (see above 3.4.) at the thermostat-controlled constant 2°C temperature of the incubator seawater (Table 3).

4. Results

4.1. Dissolved CO_2 and Cd isotopes

The $\delta^{114}\text{Cd}$ values of surface waters along the Zero Meridian transect are shown in Figure 4a. Notice here the agreement for the data of two laboratories, obtained using very different analytical methods. This confirms the overall accuracy of the datasets of both laboratories. The underway dissolved $[\text{CO}_2]$ in surface waters is shown in Figure 4b for all data, and in Figure 4c for selected data only at the same station positions as the Cd isotope samples. When now plotting the $\delta^{114}\text{Cd}$ as function of the dissolved $[\text{CO}_2]$ a striking inverse correlation is found (Figure 5) with linear regression:

$$\delta^{114}\text{Cd} = -0.0771 [\text{CO}_2] + 2.2221 \quad (9)$$

with $R^2 = 0.85$ (n=32) $p < 0.0001$

When $[\text{CO}_2]$ becomes lower the $\delta^{114}\text{Cd}$ becomes higher, i.e. the ratio $^{114}/^{110}\text{Cd}$ is higher. This may be explained by considering that at lower available $[\text{CO}_2]$ the phytoplankton cells need to take up relatively more $[\text{HCO}_3^-]$ to sustain growth, and this requires more carbonic anhydrase to convert the $[\text{HCO}_3^-]$ to CO_2 suitable for use by RuBisCo. Thus, more Cd is taken up, whereby

the light isotope ^{110}Cd is taken up preferentially, such that ^{114}Cd is left behind and the $\delta^{114}\text{Cd}$ of the ambient seawater increases.

Otherwise please notice that one sample at station 101 in the SubAntarctic Zone is an obvious outlier and its data was excluded from the above linear regression. This sample was collected in the SAZ outside the Southern Ocean and both P and Si are depleted, i.e. oligotrophic, but still some nitrate is present (Figure 3). As such this sample is very different from the generally HNLC conditions seen at most other stations. The dissolved Cd concentration is also very low at 0.036 nM, typical for most open ocean oligotrophic surface waters. As a result the small total amount of Cd available in the sample led to a relatively large error bar for the measured $\delta^{114}\text{Cd}$ Cd (Figure 4a). Given both the exceptional hydrography, and the poor precision of the $\delta^{114}\text{Cd}$ data, it is not unjustified to further ignore this sample.

On the other hand the data obtained at the station 198 in the Weddell Sea, the station 216 in the Weddell Sea near the Antarctic Peninsula, and the stations 245 and 249 in the northern Drake Passage are nicely consistent with the data and regression line of the Zero Meridian. This suggests that the above relationship (Equation 9) is robust.

As a matter of fact the suggestion of more uptake of Cd at low ambient $[\text{CO}_2]$ condition is indeed evident, by the lower dissolved Cd concentration left behind in the seawater (Figure 6). Here again is a strong linear regression:

$$[\text{Cd}][\text{nmol.kg}^{-1}] = 0.0575 [\text{CO}_2][\mu\text{mol.kg}^{-1}] - 0.83 \quad (10)$$

with $R^2=0.78$ ($n=32$) $p<0.0001$

Notably, these results are well consistent with previous studies reporting more Cd uptake at lower seawater pCO_2 values (Cullen et al., 1999; Cullen and Sherrell, 2005).

4.2. The $\text{CO}_2/\text{HCO}_3^-$ uptake ratio of phytoplankton communities

The independent shipboard experiments on the relative uptake of $[\text{CO}_2]$ and $[\text{HCO}_3^-]$ may shed some light on what the phytoplankton community is doing here (Neven et al., 2011). From the 13 experiments (Neven et al., 2011, their Table 3) the uptake ratio $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ was calculated. For these 13 stations the concentrations of $[\text{CO}_2]$ and $[\text{HCO}_3^-]$ were derived by CO2SYS (Van Heuven et al., 2011b) (see above 3.5.) and next the initial ratio $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ in seawater was calculated (Table 3). The plot of the uptake ratio shows a strong linear relationship with the ratio in ambient seawater for 10 of the 13 experiments, the 3 others (stations 161, 191, 216) are distinct outliers (Figure 7). When, for the time being, ignoring these outliers the following linear regression is found:

$$\text{Uptake ratio} = 2327.7 \text{ Seawater Ratio} - 30.7 \quad (11)$$

with $R^2=0.95$ ($n=10$)

Considering the 3 ignored outliers from stations 161, 191, 216 we do not really have an explanation for the anomalous behavior. Nevertheless a best-fit line can be drawn through these 3 outliers, and this indicates an about 83-fold enhancement of the uptake ratio versus the ambient seawater ratio (Figure 7). In addition, notice that the cluster of stations 104, 125, 150, 167, 178, 198 together with outliers 161, 191, 216 provide similar results with fairly low uptake ratio:

$\{[\text{CO}_2]/[\text{HCO}_3^-]\} < 1.0$ as compared to higher uptake ratios $2.0 < \{[\text{CO}_2]/[\text{HCO}_3^-]\} < 6.0$ seen for the cluster of stations 113, 186, 193, 204. Anyway at all 13 stations the uptake ratio is always higher than the ambient seawater ratio.

The high value 2327.7 found for the slope of the regression line (Eq. 11) demonstrates that the phytoplankton is very keen to preferentially assimilate $[\text{CO}_2]$ instead of $[\text{HCO}_3^-]$. Plant physiologists are well aware of this observation (Neven et al., 2011) which shows how

effectively plant cells can discriminate. Similar discrimination and hence isotope fractionation is also known for the $^{13}\text{C}/^{12}\text{C}$ stable isotope ratio of the CO_2 system, and in fact several other bio-essential elements (Eq. 1) and their stable isotopes.

We note however, that these shipboard phytoplankton community experiments did not include any measurement of the $\delta^{114}\text{Cd}$ value. Hence, whilst these experiments provide some insight into the mechanisms at play in carbon assimilation and the important role of carbonic anhydrase, they do not provide direct evidence to constrain the cause of the $\delta^{114}\text{Cd}$ signal. This implies that any debate on these experiments and their outcome (Figure 7, Eq. 11) would not affect the factual observations made for $\delta^{114}\text{Cd}$ versus the dissolved CO_2 system (Figures 5, 6, 8, 9 with Equations 9, 10, 12, 13, respectively).

4.3. Cd isotopes and the ambient $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ ratio

Given the observation in the phytoplankton community experiments that the cells are responding to the ambient $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ ratio in seawater, it is likely that their need to produce more carbonic anhydrase and hence uptake more Cd for that purpose is also dependent on the seawater $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ ratio. Therefore, we have plotted $\delta^{114}\text{Cd}$ as a function of $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ in seawater (Figure 8) and found the following relationship:

$$\delta^{114}\text{Cd} = -184.4 \{[\text{CO}_2]/[\text{HCO}_3^-]\}_{\text{seawater}} + 2.51 \quad (12)$$

with $R^2=0.83$ ($n=32$) $p<0.0001$

The correlation coefficient (R^2) is not significantly different from the above regression (Eq. 9) versus $[\text{CO}_2]$ in seawater, yet Figure 8 and relationship (Eq. 12) are deemed to better represent the presumed underlying mechanisms.

Similarly it is reckoned that for the uptake of Cd and resulting decrease in the dissolved Cd concentration of seawater, the relationship versus $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ in seawater (Figure 9) is more suitable, with the regression:

$$[\text{Cd}][\text{nmol.kg}^{-1}] = 143.1 \{[\text{CO}_2]/[\text{HCO}_3^-]\}_{\text{seawater}} - 1.10 \quad (13)$$

with $R^2=0.82$ ($n=32$) $p<0.0001$

Notably this relationship (Eq. 13) provides a somewhat better correlation coefficient ($R^2=0.82$) for the data compared to the above relationship (Eq. 10) versus only $[\text{CO}_2]$ in seawater ($R^2=0.78$).

5. Discussion

5.1. The facts

The observations on the basis of accurate analyses of real seawater samples collected in the real Southern Ocean are a fact and somehow the result of the processes that are at play in these polar surface waters. We find a close relationship between the $\delta^{114}\text{Cd}$ in seawater and the $[\text{CO}_2]$ concentration as well as versus the concentration ratio $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ of seawater. Given this finding it is important to identify the key processes that are responsible for the Cd isotope fractionation and the observed distribution of $\delta^{114}\text{Cd}$ in the Southern Ocean.

In general, two different types of processes, namely (i) equilibrium isotope effects and (ii) kinetic isotope effects, may in general cause isotope fractionation (Kendall and Caldwell, 1998). Equilibrium effects are thereby associated with processes whereby the forward and reverse reactions tend to have similar or identical reaction rates. Conversely, in kinetic isotope effects the forward and reverse reaction rates are not identical. Biological processes are generally uni-directional and are hence typically associated with kinetic isotope fractionation. Organisms thereby preferentially use the lighter isotopic species as these move

or react faster, resulting in significant fractionations between the substrate (heavier) and the biologically mediated product (lighter). This is confirmed and well understood for $\delta^{13/12}\text{C}$, for $\delta^{15/14}\text{N}$, and likely also true for other, but less well studied, stable isotope systems of bio-essential chemical elements. Conversely when a significant isotope fractionation is observed, such as here for $\delta^{114}\text{Cd}$, this is seen as strong evidence for uptake by biota and subsequent biochemical reactions and functioning within the cell.

5.2. Is there a role for Cd in the enzymatic function of carbonic anhydrase ?

Given (i) the previously reported existence of a specific Cd-based form of carbonic anhydrase (Lane et al., 2000, 2005; Xu et al., 2008) found in some phytoplankton species, and (ii) the many experimental studies that have shown that Cd can substitute for Zn in ideally Zn-based carbonic anhydrase (Price and Morel, 1990, and many others), the most attractive, if not also most straightforward, explanation is that Cd can play a role in the functioning of carbonic anhydrase. Indeed our studies thus far of Cd isotope distributions in surface waters and deep waters of the Southern Ocean (Abouchami et al., 2011; Xue et al., 2013; Abouchami et al., 2014) point toward a biological mechanism of Cd isotope fractionation within the Southern Ocean. However, other processes such as large scale ocean circulation, variable fractionation conditions (closed versus open system), and distinct isotopic compositions of source waters, have also been mentioned by these authors.

The existence of external carbonic anhydrase (eCA) that is attached to the outside of plankton cells (Neven et al., 2011) to affect the conversion of HCO_3^- to CO_2 , may also play a role. In this case, the incorporation of Cd in this eCA would perhaps be more of an equilibrium process, which would be associated with a distinct, lesser, fractionation, compared to that for true uptake into the cell.

Nevertheless, the exact nature of the biological mechanism of Cd isotope fractionation in the Southern Ocean is yet to be proven. Also the convincing evidence for a new specific Cd-based ζ -form carbonic anhydrase (Lane et al., 2005; Xu et al., 2008; see also Bertini et al., 2007; Sigel et al., 2013) is for a temperate ocean diatom species *Thalassiosira weissflogii*, whereas a specific Cd-based carbonic anhydrase has yet to be discovered for an Antarctic phytoplankton species, notably a large bloom-forming diatom. Obviously more research is needed before firm conclusions can be drawn on what are the most dominant mechanism(s) of Cd isotope fractionation in the Southern Ocean.

5.3. Adsorptive scavenging

Several trace elements in the oceans show a vertical and interoceanic distribution akin to the major nutrient elements Si, P and N. Indeed the major nutrients all display correlations (of variable quality) with the bio-essential trace elements Co, Ni, Cu, Zn. Such correlated behavior is generally not seen for bio-essential Mn and Fe of which their distributions are dominated by redox processes. However relationships between Mn and P have been found in upper waters of the Southern Ocean, with dependence on the concentration of Fe (Middag et al., 2011a, 2013). Moreover, a number of abiotic trace elements, e.g. Ag and many others, also show nutrient-type distributions. For all these trace elements, including Cd, the process of adsorptive scavenging on settling biogenic debris has been invoked as an explanation for the nutrient-type distribution. Such adsorption on the outside of settling particles is deemed to involve only one or at most a few chemical reactions, and presumably dominated by equilibrium isotope fractionation. As such, adsorption is unlikely to cause a major isotopic fractionation.

Nevertheless outside of the Southern Ocean, in the South Atlantic part of the Atlantic GEOTRACES GA02 section, the surface and subsurface waters do not show strongly fractionated Cd isotope signatures, suggesting a locally more modest role of biological Cd uptake with regards to ensuing isotope fractionation (Xie et al., 2017; see also Gault-Ringold

et al., 2012). If so, then other processes, such as adsorption, may become relatively more significant, whereby fine colloids < 0.2 micron have been suggested to play an important role (Xie et al., 2017). Such fine colloids would pass through the filtration system, and end up in the dissolved fraction. An alternative explanation is also provided by Xie et al. (2017), namely an open system, steady state, fractionation model. Otherwise, the deep waters of the Southwest Atlantic Ocean appear to be dominated by mixing of waters from the North Atlantic and Southern Ocean, respectively, whereby biological fractionation in such source waters has been suggested (Xie et al., 2017).

Given the now well-charted strong isotopic signature of Cd isotopes in the Southern Ocean (Abouchami et al., 2011; Xue et al., 2013; Abouchami et al., 2014) it is here understood that adsorptive scavenging cannot solely be responsible, such that true biological/biochemical processes are more likely to be dominant within the Southern Ocean.

5.4. Homeostasis

Next to the here suggested Cd isotope fractionation due to the role of Cd in carbonic anhydrase, an alternative concept for a biological mechanism, namely that of non-specific uptake and homeostasis, has been proposed to explain the Cd isotope distributions in the world oceans (Horner et al., 2013).

One first consideration is that our study and the underlying Cd isotope measurements (Abouchami et al., 2011; Xue et al., 2013; Abouchami et al., 2014) are all focused on the Southern Ocean, which differs considerably from the other, temperate and tropical oceans. Firstly the HNLC condition of the Southern Ocean are seen not only for major nutrients Si, N and P (Figure 2) but also for bio-essential Co, Ni, Cu, Zn and indeed Cd as well (Table 1). In contrast the temperate and tropical ocean is oligotrophic for the major nutrients as well as Co, Zn and Cd, and to lesser extent for Ni and Cu (Table 1, North Atlantic and North Pacific). Next, the biological cycling of chemical elements in the Southern Ocean, including C and Cd, is dominated by two major bloom-forming groups or species: on the one hand several species of often very large and heavily silicified diatoms, on the other hand the species *Phaeocystis antarctica*, the latter very common in parts of the Ross Sea but also elsewhere in the Southern Ocean.

The investigation of Horner et al. (2013) differs from our study in that the former is based on experiments rather than ocean observations, and experiments (admittedly including the carbon uptake experiments of Neven et al. 2011, which are however, completely independent of the here reported $\delta^{114}\text{Cd}$ versus CO_2 relations) always have the inherent risk of artefacts. Indeed there has been some debate about the relevance of these experiments (Morel, 2013; Horner et al., 2013b). Secondly, the species used by Horner et al. (2013), a transgenic construct of *Escherichia coli* with coding sequences of the non-polar diatom *Thalassiosira weissflogii*, is not representative of the bloom-forming phytoplankton species in the Southern Ocean. Similarly the growth medium is not representative of the HNLC conditions found in natural seawater of the Southern Ocean. Due to these differences and the caveat of experimental artifacts, it is not feasible to compare the findings of Horner et al. (2013) with the observations here reported for the Southern Ocean. Nevertheless the concept of homeostasis remains to be an option to be considered.

5.5. Speciation and organic complexation of Cd versus Zn in the Southern Ocean

There is ample dissolved Zn on the order of $\sim 3\text{nM}$ in surface waters of the Southern Ocean, as well as ample dissolved Cd, on the order of 0.4-0.6 nM, in comparison to the oligotrophic oceans (Table 1). Nevertheless, one realizes these concentrations of Zn in Antarctic surface waters are almost tenfold higher than the Cd concentrations. Hence, there should be no need for Cd to substitute for Zn in carbonic anhydrase, and thus there would only remain the functionality of Cd in specific Cd-carbonic-anhydrase in perhaps some or several bloom-

forming species of diatoms. Whether or not some of the Antarctic phytoplankton species, notably the bloom-forming diatoms, would have the specific Cd-carbonic-anhydrase, i.e. require Cd as bio-essential element, has yet to be investigated and is not known at present.

However, several experimental studies have shown that under conditions of low available Zn, phytoplankton may use Cd as a substitute in carbonic anhydrase. There are some caveats, as most of these experiments have been done with an overdose of EDTA, an organic metal-complexant in the seawater medium, and this is known to grossly distort the chemical speciation of trace elements, i.e. of Zn and Cd (Gerringa et al., 2000; Bruland et al., 2014). A key distortion is the interference with the natural organic entities that are known to form strong organic complexes with trace elements, i.e. here Zn and Cd. For both Zn and Cd it is thereby well known from measurements in the oligotrophic open ocean that these are strongly bound by organic complexes (Donat and Bruland, 1990; Bruland, 1989, 1992; Ellwood and van den Berg, 2000; Jakuba et al. (2008). This is also the case in the subAntarctic waters off New Zealand (Ellwood, 2004).

However the Antarctic Ocean features unique conditions, as it is a High Nutrient Low Chlorophyll (HNLC) ocean not only for the major nutrients, but also for Zn and Cd and some other bio-essential trace metal elements (Table 1). During the same 2008 expedition as here reported, the organic complexation of Zn was investigated by Baars and Croot (2011), and the organic complexation of Cd by Baars et al. (2014). Along the Zero Meridian, in the Antarctic Zone (AAZ) and in the Weddell Gyre, the concentration of organic Zn-binding ligands was found to be on the order of ~ 2 nM, but due to the overall very high total dissolved seawater Zn content, there was an 'excess' of free dissolved Zn (defined as Zn') of about 0.1 to 1 nM (Baars and Croot, 2011, their Figure 5, middle graph). For Cd in surface waters along the Zero Meridian, Baars et al. (2014, their Table 3) found a Cd-binding ligand concentration of 0.8 nM, such that some 45-75% of the dissolved Cd would be bound to this ligand, still leaving an 'excess' of free dissolved Cd (defined as Cd') of 0.14 to 0.45 nM.

Thus the Antarctic Ocean is unique indeed because not only are the total dissolved Zn and Cd in ample supply in surface waters, but also when subtracting the organic-bound fraction, there still remains ample 'free' Zn and Cd available in seawater. Unfortunately we do as yet not know whether or not the organic bound fraction is also readily available for uptake by phytoplankton. This obviously would depend on the kinetic rate of exchange for Zn and Cd with the dissolved organic ligands. If the dissociation rate is fast, then the organic fraction would be available, but if dissociation is slow then it would not be available. In the first case the total dissolved Zn and Cd would be available for phytoplankton uptake at a Zn/Cd concentration ratio of ~ 10 . In the second case the concentration ratio of free Zn' to free Cd' would be in the range of $0.2 < \{[Zn']/[Cd']\} < 7$ or thereabout. This is always lower than the concentration ratio of ~ 10 defined by total dissolved Zn and Cd, and perhaps at the lower end of the range at 0.2 it would be preferable for phytoplankton to utilize Cd instead of Zn for carbonic anhydrase. However, more investigations are required before any firm conclusion can be drawn.

Zn and Cd are in the same Group 12 (formerly Group IIB) of the Periodic Table (IUPAC, 2016) and hence have similarities in their chemical properties. Therefore one may also hypothesize that phytoplankton cannot very well differentiate between Zn and Cd during uptake. Therefore while needing Zn for several well-known biochemical functions, notably in Carbonic Anhydrase, even when there is plenty dissolved Zn available, Cd fractionation might occur if Cd is 'mistakenly' taken up along with Zn (Horner et al., 2013).

5.6. Interactions with major nutrients

The general upwelling of deep waters that are relatively rich in most (but not all) of the 9 bio-essential chemical elements (Eq. 1) supports summer blooms of phytoplankton that partially remove the same 9 elements from the surface waters. For the major nutrients (N, P, Si) in the

Antarctic Ocean there remains an ample surplus throughout the year. There also remains a high background concentration of DIC but the $[CO_2]$ component decreases significantly during blooms. The other extreme of the 9 bio-essential elements is Fe as this is seriously depleted and thus limits phytoplankton growth. Given the interaction of Cd with the biological cycle, one may also look for relations of $\delta^{114}Cd$ with the major nutrients in surface waters. For the same $\delta^{114}Cd$ dataset these relationships are listed in Table 4, on the basis of regression plots.

Not surprisingly, $\delta^{114}Cd$ also shows strong relationships with the major nutrients phosphate and (nitrate+nitrite) with correlation coefficients R^2 of 0.84 and 0.80, respectively, as growth requires uptake of all nutrients. These coefficients are comparable with those of the relations of $\delta^{114}Cd$ versus $[CO_2]$ or $\{[CO_2]/[HCO_3^-]\}$, as defined by equations (9) and (12) with $R^2=0.85$ and $R^2=0.83$, respectively. However the relations of $\delta^{114}Cd$ versus either phosphate or (nitrate+nitrite) are otherwise quite meaningless, simply because for Cd notably as an analog of Zn, there is no biochemical role in either the assimilation of phosphate and/or nitrate, or the intracellular biochemistry of either phosphorus and nitrogen. Indeed Twining and Baines (2013) in an excellent review state: "To date, the only confirmed use of Cd in phytoplankton is as a substitute for Zn in carbonic anhydrase in diatoms". Therefore Cd, as analog of Zn, is deemed to be quite suitable both for the assimilation of $[HCO_3^-]$, for example by external Carbonic Anhydrase (Neven et al., 2011), and for internal conversion by Carbonic Anhydrase of $[HCO_3^-]$ to $[CO_2]$ (Figure 1).

This being stated, plots of Cd and $\delta^{114}Cd$ versus phosphate or nitrate can still be very useful. For example, in the Oxygen Minimum Zone (OMZ) of the North East Pacific Ocean an impact on Cd geochemistry versus phosphate was reported (Conway and John, 2015b). Here it also would be interesting to look for nitrate deficits versus phosphate due to nitrate reduction, as an indicator of the reductive intensity of OMZ conditions (e.g. Broecker and Peng, 1982; their Figure 3-16).

5.7. Interactions with other trace elements

Previously the uptake of Cd by plankton has been related not only to the availability and uptake of Zn, as well as substitutions for Co, but ambient availability of Mn and Fe may also play a role (Sunda and Huntsman, 2000; Timmermans et al., 2001; Cullen et al., 2003; Cullen and Sherrell, 2005; Cullen, 2006; Xu et al., 2007; Saito and Goepfert, 2008). This is in fact not surprising, as phytoplankton can, to some extent, adapt to variable external conditions by adjusting their elemental composition (stoichiometry) of not only the major (C, Si, P, N) but also trace constituents (Fe, Zn, Mn, Cu, Ni, Co). For example the uptake ratio N/P at the Antarctic Polar Front was found to vary considerably, likely due to more or less availability of dissolved Fe (de Baar et al., 1997). This was later on confirmed by N/P measurements in the >20 micron size class phytoplankton in the EIFEX *in situ* Fe fertilization experiment (Hoffmann et al., 2006; their Figure 6). More recently, the apparent uptake ratio Mn/P in the Antarctic Ocean was also found to be dependent on the ambient dissolved Fe concentration (Middag et al., 2011a, 2013). Thus, while the here reported correlation (Eq. 12) between $\delta^{114}Cd$ and the concentration ratio $\{[CO_2]/[HCO_3^-]\}$ in ambient seawater is very strong ($R^2=0.83$), some caution is advisable due to the possible role of the other bio-essential trace elements, notably Fe and Mn that occur in very low, suboptimal, concentrations in the Antarctic Ocean (Figure 10). On the one hand, the maxima and minima versus latitude of dissolved Mn in surface waters are somewhat akin to those of Cd. On the other hand, the distribution of Fe is quite uniform and does not appear to mimic either Cd or Mn. In this context, it is also noteworthy that collection of the seawater samples was preceded by an atmospheric dust input event at about 55°S, which may be responsible for the elevated concentrations of both Mn and Fe at 55°S. Overall, it is very likely that the difference of our significant correlations (with $R^2=0.85$ or $R^2=0.83$; Equations 9 and 12) to a perfect ($R^2>0.99$) correlation is, at least partly, due to the variable abundances of other dissolved metals,

variations of their organic complexation, most notably for Fe (Thuroczy et al., 2011) the resulting more or less limiting dissolved free metal concentrations, and the biochemical roles of Fe and Mn, as well as of Zn and Co in these polar surface waters.

6. Summary, recommendations and closing remarks

Ambient surface waters in the Atlantic sector of the Southern Ocean show a strong correlation between $\delta^{114}\text{Cd}$ and the concentration of $[\text{CO}_2]$ as well as the concentration ratio $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ in ambient seawater. Strong correlations also exist between the concentration of Cd and $[\text{CO}_2]$ as well as $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ in seawater.

The significant trends of $\delta^{114}\text{Cd}$ both in surface waters and in deep waters (Abouchami et al., 2011, 2014; Xue et al., 2013) of the Southern Ocean, appear to be mostly due to biological fractionation and hence biological uptake of Cd by plankton from surface waters.

The strong relationship in surface waters of $\delta^{114}\text{Cd}$ with the concentration of $[\text{CO}_2]$ as well as the concentration ratio $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ can be ascribed to the role of Cd in carbonic anhydrase, as the most simple and hence preferable working hypothesis for future research.

Recommendations Future research would ideally include carefully designed shipboard incubation experiments of the local Antarctic phytoplankton community in unperturbed natural Antarctic seawater (without addition of EDTA or other artificial complexants), accompanied by (i) sampling and measurements of $\delta^{114}\text{Cd}$ in the medium and in the collected plankton, (ii) assessments of carbonic anhydrase and its activity, (iii) control and measurements of the CO_2 system, (iv) studies of the concentrations and organic speciation of Cd and Zn in the medium, and (v) study of the intracellular localization of Cd and its isotopic composition and this in relation with cellular functions. Moreover parallel measurements of other bio-essential and locally potentially bio-limiting trace elements, e.g. Fe, Mn, but also Co, and their organic complexation, are recommended. Similarly in the home laboratory, incubation experiments with a single large Antarctic bloom-forming diatom species, in unperturbed natural seawater collected in the Antarctic, are conceivable.

Closing remarks The Southern Ocean, comprising some 20% of the world oceans, is very different from the mostly oligotrophic temperate and tropical oceans. South of the SubAntarctic Front (SAF) the entire Southern Ocean has ample high nitrate and phosphate in the surface waters. South of the Antarctic Polar Front (APF) the Antarctic Ocean proper has ample of all 3 major nutrients nitrate, phosphate and silicate in surface waters (HNLC condition), as well as similarly high concentrations of trace nutrients Co, Ni, Cu, Zn, and trace element Cd as well (Table 1). As such our findings in surface waters of the Southern Ocean, and its major component the Antarctic Ocean, are not necessarily valid for the local biogeochemistry in the other oceans, and vice versa. This being stated one realizes that the local biogeochemical processes that are at play in the Southern Ocean do imprint on the water masses AntArctic Bottom Water (AABW), AntArctic Intermediate Water (AAIW) and Subantarctic Mode Water (SAMW) that are outflowing into the other oceans, and hence do affect the distribution of $\delta^{114}\text{Cd}$ in the global ocean.

Finally given the myriad interactions and co-limitations conceivable for all 9 bio-essential elements (Eq. 1), and these also with Cd and $\delta^{114}\text{Cd}$, and the roles of light limitation and of ocean water mass mixing, here the authors are very much aware that we are only, and here literally, scratching the surface of the dynamic complexity of the true inner workings of the awesome Southern Ocean.

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HdB organized the Geotraces component and several research grants for the expedition, was involved in shipboard sampling, and wrote the article with involvement and contributions by all authors. SvH did the shipboard sampling and measurements of the CO₂ system and afterwards the further CO₂-System calculations to determine [CO₂] and [HCO₃⁻]. JvO did the shipboard measurements of the major nutrients. RM collected the Cd isotopes samples and produced the data of Mn. WA and SG produced the Cd isotope data of MPI. Similarly ZX and MR produced the Cd isotope data of Imperial College.

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Tables

#		Major Inorganic Species	Concentration Unit	North Atlantic Ocean		Antarctic Ocean		North Pacific Ocean	
				surface	deep	surface	deep	surface	deep
6	C	HCO ₃ ⁻	[μmol.kg ⁻¹]	2050	2200	2210-2220	2240-2260	2000	~2350
7	N	NO ₃ ⁻	[μmol.kg ⁻¹]	<1	25	25-30	30-38	<1	45
14	Si	H ₄ SiO ₄	[μmol.kg ⁻¹]	<1	40	35-63	83-129	<1	170
15	P	HPO ₄ ⁻	[μmol.kg ⁻¹]	<0.1	1.2-1.5	1.6-1.9	2.26-2.35	<0.1	2.5-3.3
25	Mn	Mn ²⁺	[nmol.kg ⁻¹]	0.2-3.0	0.1-0.15	0.04-0.5	~0.1	~1-2	~0.2
26	Fe	Fe(OH) ²⁺	[nmol.kg ⁻¹]	0.2-2.0	0.6	0.02-0.1	0.4	0.05	0.6
27	Co	Co ²⁺	[pmol.kg ⁻¹]	30	60	20-85	~60	10-50	50-250
28	Ni	Ni ²⁺	[nmol.kg ⁻¹]	2	4	5.5-6.5	5.5-7.0	2.1	11
29	Cu	CuCO ₃ ⁰	[nmol.kg ⁻¹]	1±0.5	1.3-2.2	1-2	2-4	<0.5	5
30	Zn	Zn ²⁺	[nmol.kg ⁻¹]	0.1	2	2.5-3.1	6.2-7.8	0.07	9
48	Cd	CdCl ₂ ⁰	[nmol.kg ⁻¹]	10	300	0.15-0.65	0.77-0.86	1.4	1100

Table 1.

Comparison of the Antarctic Ocean HNLC condition with the temperate/tropical oligotrophic Atlantic and Pacific Oceans. Concentrations in seawater of the 9 chemical elements that are **essential for all life in bold print** as well as 2 chemical elements that play a role in specific taxonomic groups, i.e. Si that is essential for the important group of diatoms, and Cd that has or can have a function in carbonic anhydrase, see main text. Each element symbol preceded by its atomic number #. Major dissolved inorganic species, i.e. here not taking into account the strong organic complexation for several trace elements as discussed for Cd and Zn in the main text. Given concentrations are typical values, real concentrations vary around these as function of depth and geographic location. Please notice that the Antarctic Ocean has HNLC conditions not only for N, Si and P but also for Co, Ni, Cu, Zn and Cd, see main text. Data sources are as follows:

DIC Atlantic is at Bermuda Atlantic Time Series Station (BATS) of GEOTRACES cruise GA02-64PE321 aboard RV Pelagia, station 21 (31°45.92'N, 64°04.95'W at 13 June 2010) after Rijkenberg et al. (2015) and available at (www.geotraces.org). DIC Antarctic: van Heuven et al. 2011a; DIC Pacific is from RV Melville cruise 318M2004 along WOCE line PO2, station 119 (30.00 °N, 159.70 °W at 4 August 2004) is available in GLODAP-2 via CCHDO. (<https://cchdo.ucsd.edu/cruise/318M200406>).

P Atlantic BATS site, see above DIC; P Antarctic: Baars et al. (2014); P Pacific see above DIC.

N Atlantic BATS site, see above DIC; N in Antarctic: de Baar et al., 1997; N Pacific see above DIC.

Si Atlantic BATS site, see above DIC; Si Antarctic: Zhao et al 2014; Si Pacific see above DIC.

Mn Atlantic: Middag et al., 2015b; Mn Antarctic: Middag et al., 2011b, 2012, 2013; Mn Pacific: Resing et al. 2015.

Fe Atlantic: Rijkenberg et al. 2014; Fe Antarctic: Klunder et al., 2011, 2014 and Gerringa et al., 2015; Fe Pacific: Martin et al., 1989.

Co Atlantic: Middag et al., 2015b, Noble et al., 2012. Co Antarctic: Saito et al., 2010; Co Pacific: Hawco et al., 2016, values >50 pM in O₂ minimum zone.

Ni Atlantic: Middag et al. 2015b; Ni Antarctic: Cameron and Vance 2014; Ni Pacific: Bruland 1980

Cu Atlantic: Middag et al., 2015b; Cu Antarctic: Bown et al., 2016; Cu Pacific: Bruland, 1980

Zn Atlantic: Middag et al., 2015b; Zn Antarctic: Zhao et al. (2014); Zn Pacific: Bruland, 1989.

Cd Atlantic: Middag et al. (2015b); Cd Antarctic: this work and Baars et al. (2014); Cd Pacific: Bruland, 1980.

Cruise	region	date	time	station	cast	bottle number	Latitude	Longitude	Depth m	Cd nM	ε114/110Cd	2sd of ε	δ114Cd	laboratory for δ114Cd and Cd
ANT24-3	Sub-Antarctic	13/02/08	6:52:00 PM	101	2	24	-42,3388	8,9935	10,0	0,036	6,58	2,22	0,658	MPI
ANT24-3	ACC	16/02/08	3:58:00 AM	103	1	24	-45,9995	5,8812	10,0	0,155	9,83	0,63	0,983	MPI
ANT24-3	PFZ	17/02/08	1:48:00 AM	104	2	23	-47,6718	4,2893	14,5	0,260	7,89	0,40	0,789	MPI
ANT24-3	PFZ	17/02/08	1:48:00 AM	104	2	23	-47,6718	4,2893	14,5	0,255	7,69	0,81	0,769	MPI
ANT24-3	PFZ	17/02/08	6:45:00 PM	105	fish	fish	-48,0417	3,8150		0,249	8,78	0,40	0,878	MPI
ANT24-3	PFZ	18/02/08	10:28:00 PM	107	3	23	-50,2622	1,4325	10,0	0,388	6,27	0,44	0,627	MPI
ANT24-3	PFZ	19/02/08	1:20:00 PM	109	fish	fish	-51,6573	0,0045		0,415	5,95	0,38	0,595	MPI
ANT24-3	AAZ	19/02/08	8:40:00 PM	111	fish	fish	-52,1667	-0,5333		0,513	5,23	0,22	0,523	MPI
ANT24-3	AAZ	20/02/08	11:17:00 AM	113	1	24	-53,0000	0,0067	9,9	0,554	4,98	0,50	0,498	MPI
ANT24-3	AAZ	20/02/08	10:35:00 PM	114	fish	fish	-53,1833	0,0003		0,527	4,98	0,24	0,498	MPI
ANT24-3	AAZ	21/02/08	11:13:00 AM	117	fish	fish	-54,3167	0,0183		0,620	4,34	0,30	0,434	MPI
ANT24-3	SB ACC	21/02/08	11:33:00 PM	120	fish	fish	-55,2300	-0,0017		0,525	4,70	0,28	0,470	MPI
ANT24-3	Weddell Gyre	22/02/08	7:25:00 PM	123	fish	fish	-56,3000	0,0002		0,509	4,36	0,24	0,436	MPI
ANT24-3	Weddell Gyre	23/02/08	10:13:00 AM	126	fish	fish	-57,2083	-0,0002		0,525	4,14	0,24	0,414	MPI
ANT24-3	Weddell Gyre	24/02/08	1:16:00 AM	129	fish	fish	-58,2000	-0,0002		0,459	4,66	0,28	0,466	MPI
ANT24-3	Weddell Gyre	24/02/08	5:23:00 PM	133	fish	fish	-59,0000	0,0003		0,431	4,72	0,32	0,472	MPI
ANT24-3	Weddell Gyre	26/02/08	6:05:00 AM	136	fish	fish	-60,2333	-0,0003		0,392	4,90	0,24	0,490	MPI
ANT24-3	Weddell Gyre	26/02/08	6:36:00 PM	138	1	24	-61,0007	-0,0073	24,8	0,334	6,58	0,54	0,658	MPI
ANT24-3	Weddell Gyre	26/02/08	7:55:00 PM	139	fish	fish	-61,1500	0,0000		0,314	5,19	0,44	0,519	MPI
ANT24-3	Weddell Gyre	27/02/08	11:46:00 AM	142	fish	fish	-62,5227	0,0000		0,270	6,76	0,50	0,676	Imperial
ANT24-3	Weddell Gyre	28/02/08	2:17:00 AM	145	fish	fish	-63,2463	0,0003		0,257	7,31	0,50	0,731	Imperial
ANT24-3	Weddell Gyre	29/02/08	11:23:00 PM	148	fish	fish	-64,2090	0,0124		0,247	7,38	0,50	0,738	Imperial
ANT24-3	Weddell Gyre	29/02/08	12:50:00 PM	151	fish	fish	-65,2382	0,0001		0,378	5,39	0,50	0,539	Imperial
ANT24-3	Weddell Gyre	29/02/08	9:02:00 PM	153	fish	fish	-66,0012	0,7296		0,373	6,34	0,50	0,634	Imperial
ANT24-3	Weddell Gyre	07/03/08	2:39:00 PM	156	fish	fish	-66,5220	0,0077		0,382	5,76	0,50	0,576	Imperial
ANT24-3	Weddell Gyre	08/03/08	3:49:00 PM	160	fish	fish	-66,0345	-0,0727		0,263	7,48	0,68	0,748	Imperial
ANT24-3	Weddell Gyre	09/03/08	11:00:00 AM	162	fish	fish	-66,5637	-0,0001		0,386	5,66	0,50	0,566	Imperial
ANT24-3	Weddell Gyre	09/03/08	5:01:00 PM	163	1	24	-67,0007	0,0020	8,8	0,460	5,85	0,32	0,585	Imperial
ANT24-3	Weddell Gyre	09/03/08	5:21:00 PM	164	fish	fish	-67,0190	-0,0051		0,434	4,75	0,70	0,475	Imperial
ANT24-3	Weddell Gyre	10/03/08	12:55:00 AM	166	fish	fish	-67,5812	0,0001		0,461	4,54	0,70	0,454	Imperial
ANT24-3	Weddell Gyre	10/03/08	9:30:00 AM	168	fish	fish	-68,2887	-0,0001		0,413	4,83	0,71	0,483	Imperial
ANT24-3	Weddell Gyre	10/03/08	3:18:00 PM	170	fish	fish	-68,6531	0,0001		0,384	4,99	0,70	0,499	Imperial
ANT24-3	Weddell Gyre	10/03/08	7:46:00 PM	172	fish	fish	-68,9582	0,0001		0,390	5,00	0,50	0,500	Imperial
ANT24-3	Weddell Sea	21/03/08	8:09:00 AM	198	2	23	-65,6141	-36,3982	25,3	0,549	4,04	0,63	0,404	Imperial
ANT24-3	Weddell Sea	27/03/08	10:53:00 PM	216	4	22	-63,6991	-50,8446	24,5	0,645	4,65	0,82	0,465	Imperial
ANT24-3	Drake Passage	09/04/08	9:46:00 PM	245	fish	fish	-56,8850	-62,5210		0,374	6,81	0,82	0,681	Imperial
ANT24-3	Drake Passage	10/04/08	10:28:00 PM	249	3	24	-56,1190	-63,7570	8,5	0,400	6,68	0,63	0,668	Imperial

station	Salinity	Temperature °C	PO4 μmol/L	Silicate μmol/L	NO3+NO2 μmol/L	NO2 μmol/L	NO3 μmol/L	ATSynth μmol/kg	fCO2 μatm	HCO3- μmol/kg	CO32- μmol/kg	CO2 μmol/kg	[[CO2]]/[HCO3-]]
	INPUT	INPUT	INPUT	INPUT	INPUT	INPUT	INPUT	INPUT	INPUT	OUTPUT	OUTPUT	OUTPUT	
101	34,02	10,99	1,04	0,49	14,35	0,19	14,16	2267,0	369,27	1916,2	140,4	15,75	0,00822
103	33,75	7,84	1,21	0,88	17,11	0,16	16,95	2265,2	351,91	1940,3	129,4	16,71	0,00861
104	33,73	6,74	1,35	1,86	19,50	0,27	19,23	2269,5	365,39	1967,5	120,0	18,19	0,00925
104	33,73	6,74	1,35	1,86	19,50	0,27	19,23	2269,5	365,39	1967,5	120,0	18,19	0,00925
105	33,71	6,28	1,40	1,89	20,12	0,27	19,85	2270,4	362,23	1968,0	120,1	18,15	0,00922
107	33,76	3,18	1,51	12,31	23,41	0,32	23,09	2282,9	367,91	2013,1	106,6	20,62	0,01024
109	33,70	2,70	1,56	15,68	24,36	0,33	24,03	2283,3	366,29	2017,7	104,8	20,93	0,01037
111	33,69	2,30	1,69	23,27	25,60	0,35	25,26	2285,3	384,20	2033,5	99,2	22,34	0,01099
113	33,79	1,27	1,73	35,26	26,04	0,33	25,71	2291,8	378,91	2044,2	97,3	22,80	0,01115
114	33,76	1,42	1,80	34,31	26,80	0,34	26,46	2291,2	381,80	2044,4	96,9	22,90	0,01120
117	33,82	0,98	1,84	44,32	27,29	0,30	26,99	2296,0	381,12	2051,2	96,0	23,19	0,01131
120	33,78	0,81	1,80	50,26	26,36	0,27	26,09	2295,5	373,13	2048,8	96,8	22,90	0,01118
123	33,96	0,67	1,84	63,77	26,67	0,25	26,42	2306,0	373,92	2058,6	96,9	23,09	0,01122
126	34,08	0,64	1,87	64,78	27,31	0,28	27,04	2312,9	376,56	2064,8	97,2	23,22	0,01124
129	34,03	0,34	1,84	67,09	26,41	0,26	26,15	2311,8	377,76	2067,7	95,6	23,57	0,01140
133	33,98	0,19	1,84	62,69	26,23	0,31	25,92	2310,4	372,94	2065,6	95,9	23,40	0,01133
136	33,91	0,11	1,76	62,13	25,22	0,21	25,01	2306,5	347,00	2048,1	101,3	21,76	0,01062
138	33,91	0,19	1,63	57,04	22,94	0,17	22,77	2306,7	329,16	2036,7	106,0	20,58	0,01010
139	33,91	0,40	1,69	57,62	23,49	0,16	23,33	2307,3	329,93	2036,9	106,2	20,57	0,01010
142	33,95	0,44	1,69	57,76	23,69	0,16	23,53	2309,6	322,71	2032,1	109,0	19,99	0,00984
145	33,91	0,59	1,61	53,83	23,31	0,16	23,15	2308,2	321,81	2030,4	109,2	19,92	0,00981
148	33,94	0,60	1,60	46,87	22,91	0,15	22,76	2308,4	327,55	2045,3	103,3	21,10	0,01032
151	33,95	-0,24	1,62	62,49	25,35	0,22	25,14	2314,3	329,63	2048,4	104,3	21,05	0,01027
153	33,85	-0,21	1,61	61,97	25,74	0,23	25,52	2309,7	323,90	2040,9	105,5	20,65	0,01012
156	33,80	-0,76	1,64	59,23	25,45	0,21	25,25	2308,7	324,59	2046,7	102,7	21,17	0,01034
160	34,09	-0,41	1,63	58,70	25,68	0,27	25,41	2321,7	319,19	2048,6	107,2	20,49	0,01000
162	33,84	-0,76	1,67	58,26	25,53	0,21	25,32	2312,1	325,77	2049,7	102,9	21,23	0,01036
163	33,97	-0,75	1,71	62,60	26,38	0,23	26,15	2316,5	336,37	2059,2	100,9	21,89	0,01063
164	33,94	-0,73	1,77	65,49	27,00	0,23	26,77	2316,7	336,19	2059,1	100,9	21,87	0,01062
166	33,93	-0,76	1,84	67,56	27,50	0,25	27,25	2316,5	341,80	2062,7	99,4	22,27	0,01080
168	33,97	-0,74	1,78	62,87	26,68	0,28	26,40	2319,3	336,02	2061,6	101,0	21,91	0,01063
170	33,93	-0,78	1,74	60,58	25,94	0,27	25,67	2316,5	328,25	2054,9	102,5	21,42	0,01042
172	33,92	-1,02	1,75	60,50	25,93	0,27	25,66	2318,3	330,42	2060,0	101,2	21,76	0,01056
198	34,16	-1,45	1,88	73,33	27,85	0,26	27,59	2326,1	354,56	2082,8	95,1	23,65	0,01135
216	34,14	-1,85	2,05	73,04	28,92	0,12	28,80	2322,8	373,58	2094,5	89,0	25,40	0,01213
245								2287,3	362,67	1991,6	117,3	18,84	0,00946
249	33,87	4,56	1,66	5,23	24,14	0,27	23,87	2286,7	365,10	2000,2	113,4	19,46	0,00973

For CO2 system calculations the INPUT data and OUTPUT data is given in the column headers
 *)245 For CO2 system calculations the missing data of hydrography is filled in from nearby station 249

Table 2. Dataset for section 4.1. (Figures 5, 6 and Equation 9, 10) and section 4.3. (Figures 8, 9 and Equations 12, 13). Also for section 5.6 and its Table 4. The CO2SYS calculations also yield values of the carbonate ion [CO₃²⁻] that are also listed here but not further used.

station	CO2 uptake % Neven Table 3	HCO3- uptake % Neven Table 3	eCA uptake % Neven Table 3	Sum uptake HCO3-+eCA %	Uptake Ratio $\{[CO_2]/[HCO_3-]\}$	Uptake Ratio $\{[CO_2]/[HCO_3-]\}$ outliers deleted	Uptake Ratio $\{[CO_2]/[HCO_3-]\}$ outliers
104	3,18	96,82	0,00	96,82	0,0328	0,0328	
113	67,87	0,00	32,13	32,13	2,1124	2,1124	
125	4,79	92,85	2,36	95,21	0,0503	0,0503	
150	30,72	69,28	0,00	69,28	0,4434	0,4434	
161	31,85	47,05	21,10	68,15	0,4674		0,4674
167	21,47	76,52	2,01	78,53	0,2734	0,2734	
178	19,56	76,04	4,40	80,44	0,2432	0,2432	
186	67,87	0,00	32,13	32,13	2,1124	2,1124	
191	26,26	73,74	0,00	73,74	0,3561		0,3561
193	75,87	24,13	0,00	24,13	3,1442	3,1442	
198	7,95	88,97	3,08	92,05	0,0864	0,0864	
204	84,33	11,37	4,30	15,67	5,3816	5,3816	
216	29,85	48,96	21,19	70,15	0,4255		0,4255

station	INPUT Salinity	INPUT In situ Temperature °C	INPUT Alkalinity µmol/kg	INPUT DIC µmol/kg	INPUT Silicate	INPUT PO4	OUTPUT IST pH	OUTPUT In situ Temp pCO2 µatm	OUTPUT In situ Temp fCO2 µatm	OUTPUT In situ Temp [HCO3-] µmol/kg	OUTPUT In situ Temp [CO3-] µmol/kg	OUTPUT In situ Temp [CO2] µmol/kg
104	33,73	6,50	2276,7	2133,9	5,67	1,42	8,02	423,68	421,97	2005,10	107,82	21,01
113	33,79	1,20	2293,8	2162,9	35,55	1,75	8,06	370,03	368,43	2041,50	99,09	22,27
125	34,09	0,49	2320,9	2186,4	63,82	1,81	8,08	359,81	358,24	2063,10	101,11	22,22
150	34,03	-0,20	2323,2	2181,1	64,95	1,70	8,11	330,85	329,39	2054,80	105,27	20,99
161	34,33	-1,70	2328,2	2217,9	62,68	2,09	8,04	390,93	389,17	2104,40	87,23	26,28
167	34,03	-0,70	2320,3	2181,4	63,96	1,75	8,11	329,78	328,32	2056,80	103,21	21,34
178	34,02	-1,46	2315,7	2170,8	51,66	1,71	8,14	304,23	302,87	2044,10	106,37	20,29
186	33,94	-1,80	2311,1	2183,1	65,24	1,92	8,10	335,45	333,94	2063,90	96,50	22,69
191	34,28	-1,70	2342,4	2215,9	73,42	1,93	8,09	350,96	349,38	2096,00	96,29	23,60
193	34,46	-1,70	2351,9	2226,8	77,12	2,00	8,08	358,47	356,86	2107,10	95,63	24,08
198	34,17	-1,40	2331,4	2197,6	73,92	1,89	8,10	334,80	333,30	2075,20	100,19	22,26
204	34,23	-1,70	2351,9	2234,5	79,85	2,09	8,06	376,69	375,00	2117,70	91,48	25,34
216	34,10	-1,80	2322,7	2210,1	71,97	2,02	8,05	379,38	377,67	2096,20	88,31	25,64

station	OUTPUT 2 °C pH	OUTPUT 2 °C pCO2 µatm	OUTPUT 2 °C fCO2 µatm	OUTPUT 2 °C [HCO3-] µmol/kg	OUTPUT 2 °C [CO3-] µmol/kg	OUTPUT 2 °C [CO2] µmol/kg	Seawater Ratio $\{[CO_2]/[HCO_3-]\}$	Seawater Ratio $\{[CO_2]/[HCO_3-]\}$ no outliers	Seawater Ratio $\{[CO_2]/[HCO_3-]\}$ outliers
104	8,09	347,17	345,68	2007,40	106,24	20,28	0,01010	0,01010	
113	8,05	383,95	382,31	2041,00	99,44	22,42	0,01099	0,01099	
125	8,05	385,61	383,96	2062,20	101,71	22,48	0,01090	0,01090	
150	8,08	366,10	364,53	2053,60	106,12	21,35	0,01040	0,01040	
161	7,98	462,94	460,96	2102,40	88,51	26,95	0,01282		0,01282
167	8,07	373,41	371,81	2055,40	104,22	21,77	0,01059	0,01059	
178	8,08	356,86	355,33	2042,30	107,65	20,81	0,01019	0,01019	
186	8,04	399,54	397,83	2062,00	97,84	23,31	0,01130	0,01130	
191	8,03	416,02	414,24	2094,10	97,60	24,22	0,01157		0,01157
193	8,02	424,88	423,06	2105,10	96,94	24,71	0,01174	0,01174	
198	8,05	391,57	389,90	2073,40	101,41	22,81	0,01100	0,01100	
204	8,00	446,31	444,40	2115,70	92,77	25,99	0,01229	0,01229	
216	7,99	451,46	449,53	2094,20	89,62	26,31	0,01257		0,01257

Inserted 2186.4 as DIC for station 125. This is mean of 50m samples of neighbouring stations 124 and 127 (2181 and 2191 respectively)
 Inserted 2320.9 as ALK for station 125. This is mean of 50m samples of neighbouring stations 124 and 127 (2320 and 2322 respectively)

Table 3. Dataset for section 4.2. (Figure 7 and Equation 11).

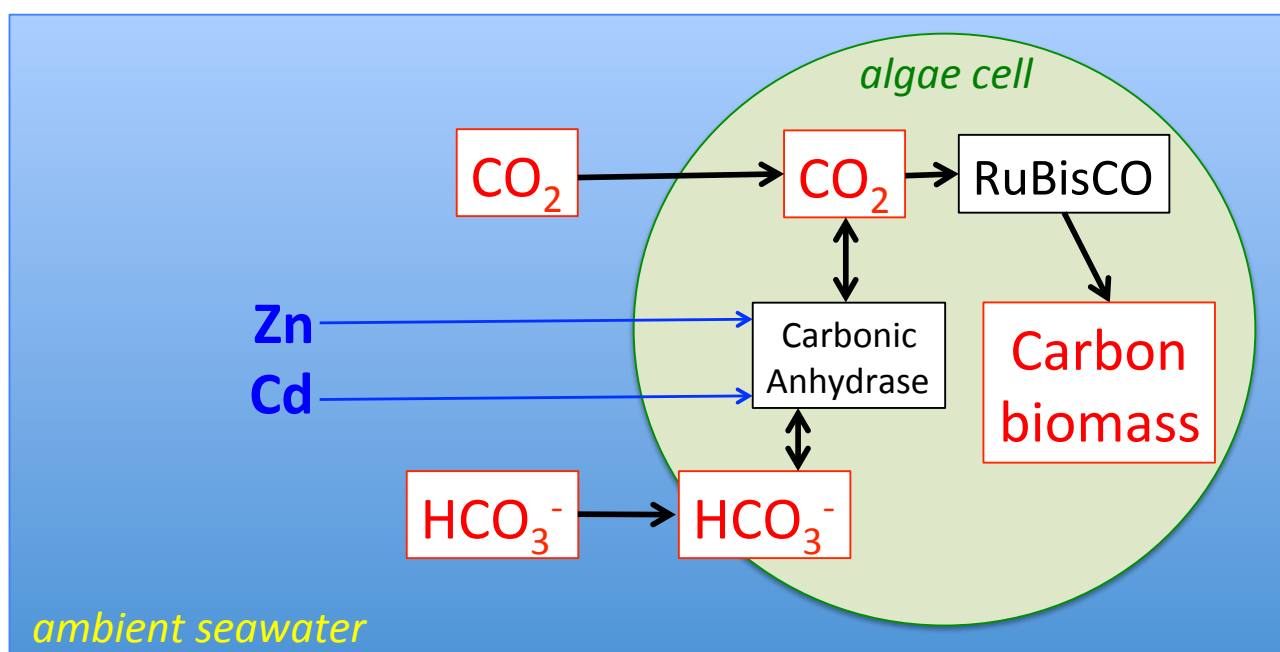
$\delta^{114}\text{Cd} = -0.797 [\text{PO}_4] + 1.915$	$R^2=0.84$	$n=32$
$\delta^{114}\text{Cd} = -0.049 \{[\text{NO}_3]+[\text{NO}_2]\} + 1.797$	$R^2 = 0.80$	$n=32$
$\delta^{114}\text{Cd} = -0.049 [\text{NO}_3] + 1.794$	$R^2 = 0.80$	$n=32$
$\delta^{114}\text{Cd} = -0.0041 [\text{SiO}_4] + 0.775$	$R^2 = 0.42$	$n=32$
$[\text{CO}_2] = 9.80 [\text{PO}_4] + 4.90$	$R^2 = 0.89$	$n=32$
$\{[\text{NO}_3] + [\text{NO}_2]\} = 14.8 [\text{PO}_4] + 0.018$	$R^2 = 0.87$	$n=32$
$[\text{NO}_3] = 14.12 [\text{PO}_4] + 0.981$	$R^2 = 0.83$	$n=32$

Table 4.

Equations of linear regressions of $\delta^{114}\text{Cd}$ in surface waters versus phosphate, nitrate+nitrite, nitrate, and silicate, respectively, with R^2 for $n=32$ samples. There is a small amount of nitrite in the order of $0.2 \mu\text{mol.kg}^{-1}$ in most surface samples and this should be taken together with the major concentration of nitrate in the $14\text{-}28 \mu\text{mol.kg}^{-1}$ range. However for only latter nitrate the regression is virtually identical.

Also listed are the similar equations for $[\text{CO}_2]$ versus phosphate and nitrate+nitrite versus phosphate and only nitrate versus phosphate, respectively, for the same $n=32$ samples. Here the relation of nitrate+nitrite with $R^2=0.87$ is better than for only nitrate versus phosphate with $R^2=0.83$. This supports our choice for using the sum nitrate+nitrite that is more relevant.

Figures



RuBisCO = Ribulose-1,5-bisphosphate carboxylase oxygenase

Figure 1. Illustration of the hypothesis for the physiological mechanism underlying the observed relationship of $\delta^{114}\text{Cd}$ and $[\text{CO}_2]$.

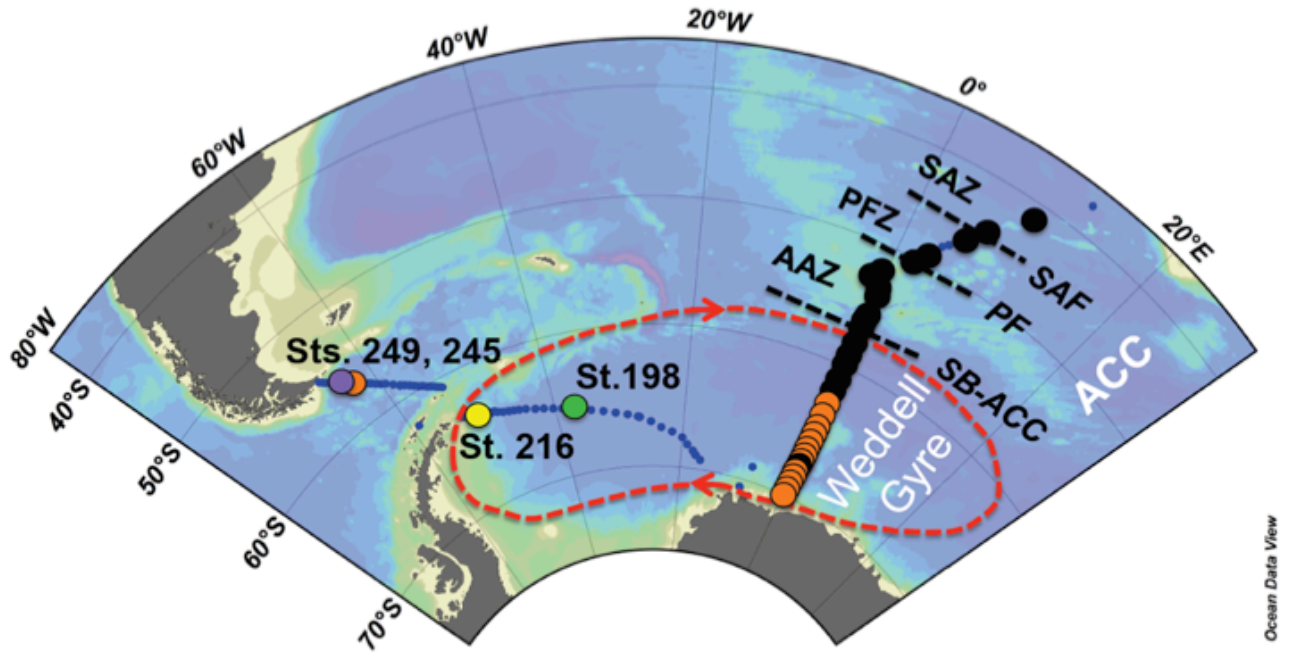


Figure 2. Chart of the sector of the Southern Ocean where observations were made. For hydrography see text section 2. Along or near the Zero Meridian the black dots are positions of surface water samples with $\delta^{114}\text{Cd}$ data by the Max Planck Institute. Orange dots are for $\delta^{114}\text{Cd}$ data by Imperial College. The data for station 198 (green) in the Weddell Sea, the station 216 (yellow) in the Weddell Sea near the Antarctic Peninsula, and the stations 245 (orange) and 249 (purple) in the northern part of the Antarctic Circumpolar Current (ACC) in the Drake Passage are also by Imperial College. Figure taken from original by Xue et al. (2013). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

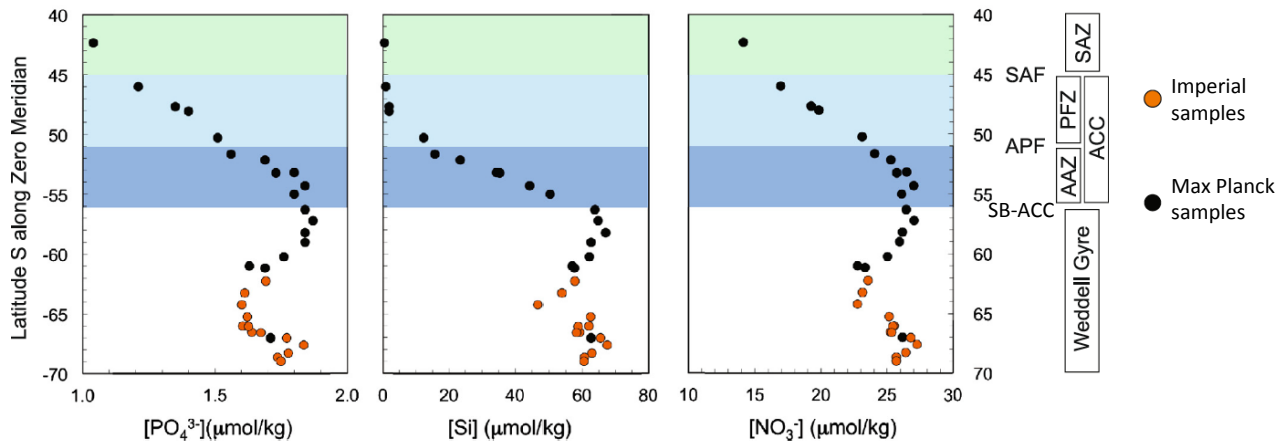


Figure 3. Dissolved nutrients phosphate, silicate and nitrate in surface waters along the Zero Meridian transect. Figure taken from original by Xue et al. (2013). (For interpretation of the references to color, the reader is referred to the web version of this article.)

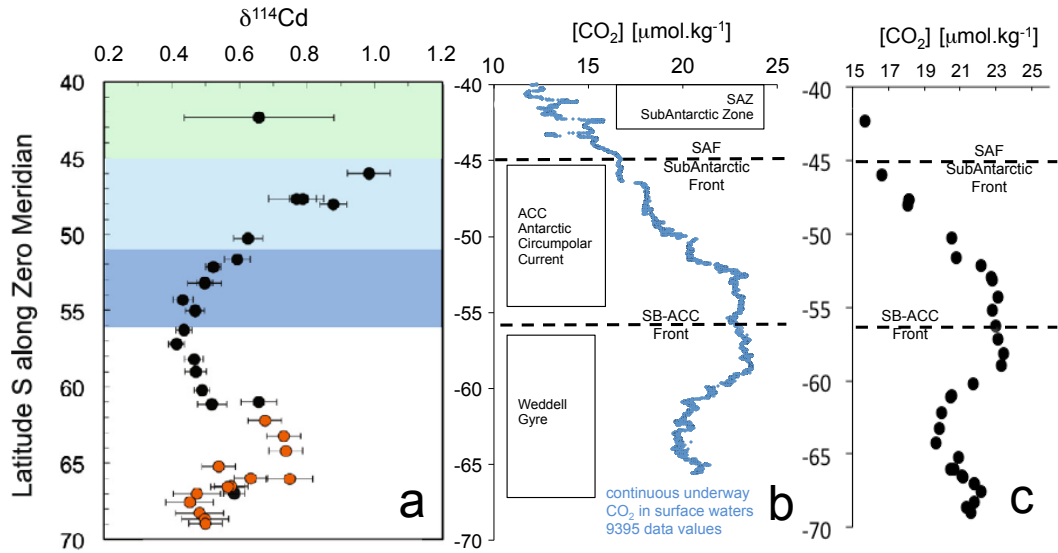


Figure 4.

- a) $\delta^{114}\text{Cd}$ in surface waters along the Zero Meridian transect. Black dots are for Max Planck Institute data, orange dots for Imperial College results. Figure taken from Xue et al. (2013).
- b) The 9395 data values of underway $[\text{CO}_2]$ in surface waters along the Zero Meridian transect. c) Selected underway $[\text{CO}_2]$ data for surface waters taken at the same time and position when the seawater for the $\delta^{114}\text{Cd}$ measurements was collected. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

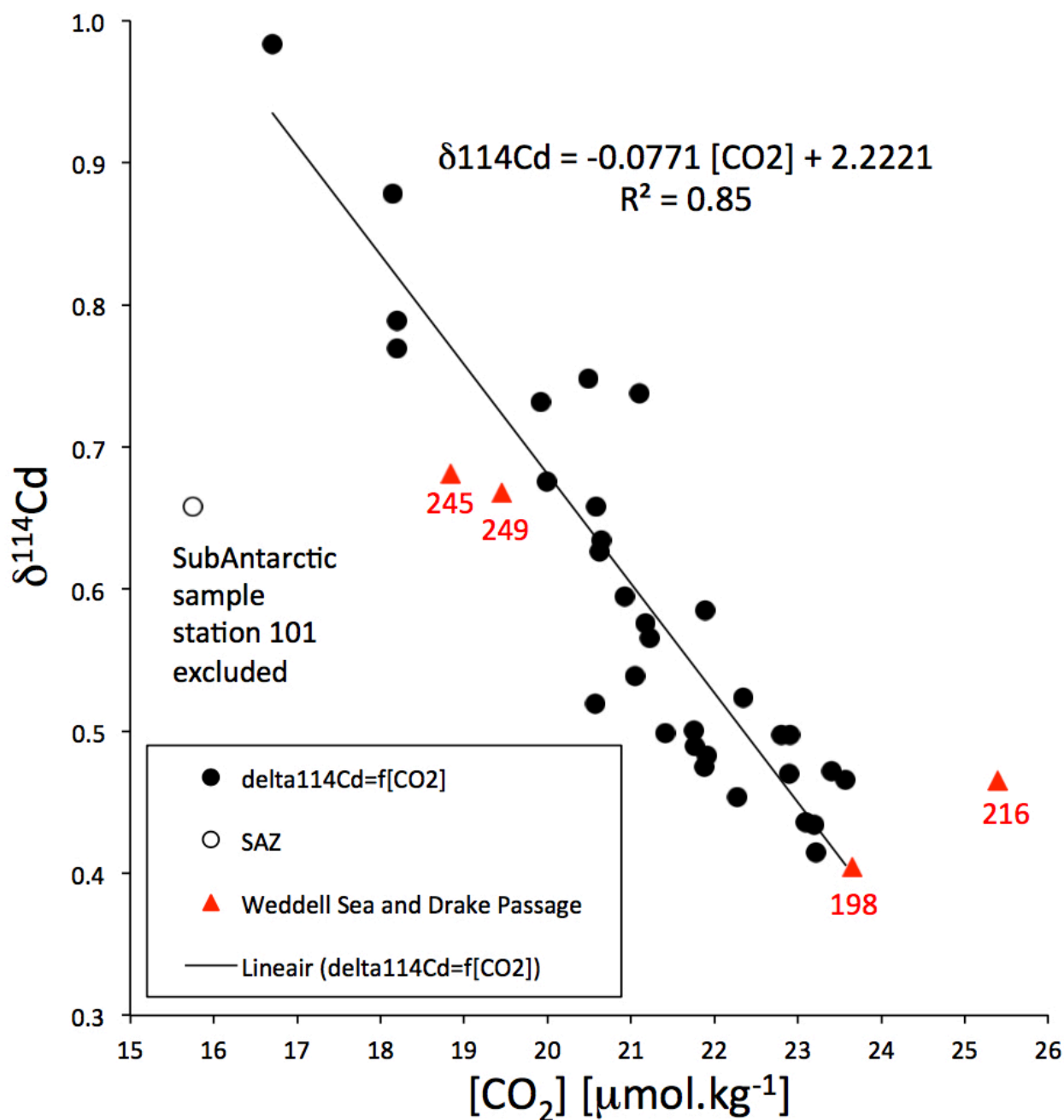


Figure 5. Relationship of $\delta^{114}\text{Cd}$ with dissolved $[\text{CO}_2]$ in surface waters along the Zero Meridian. The regression equation encompasses all data points (filled dots), excluding the SubAntarctic sample (open dot) from station 101, see main text. The red triangles represent the surface waters of stations 198, 216, 245, 249 see main text. These four results were not used in the linear regression. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

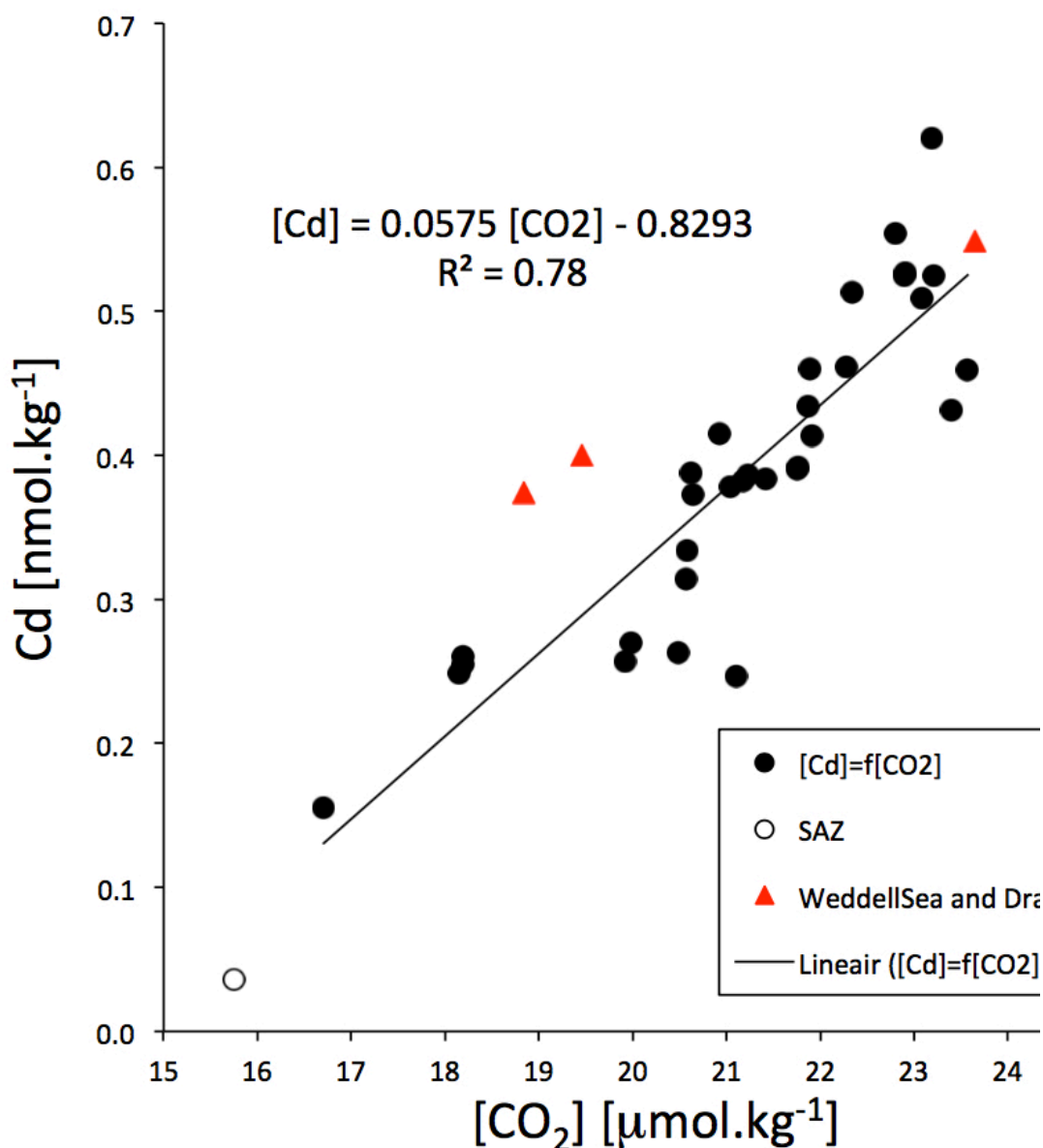


Figure 6. Relationship of dissolved Cd with dissolved [CO₂] in surface waters along the Zero Meridian. The Subantarctic station 101 is excluded from the linear regression. Otherwise station 101 extends the linear trend, and the stations 198, 216, 245, 249 in Weddell Sea and Drake Passage also follow the trend closely. When including these 5 extra stations the regression (not shown) would become $Cd = 0.0565[CO_2] - 0.8025$ with $R^2 = 0.81$ for $n = 37$ samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

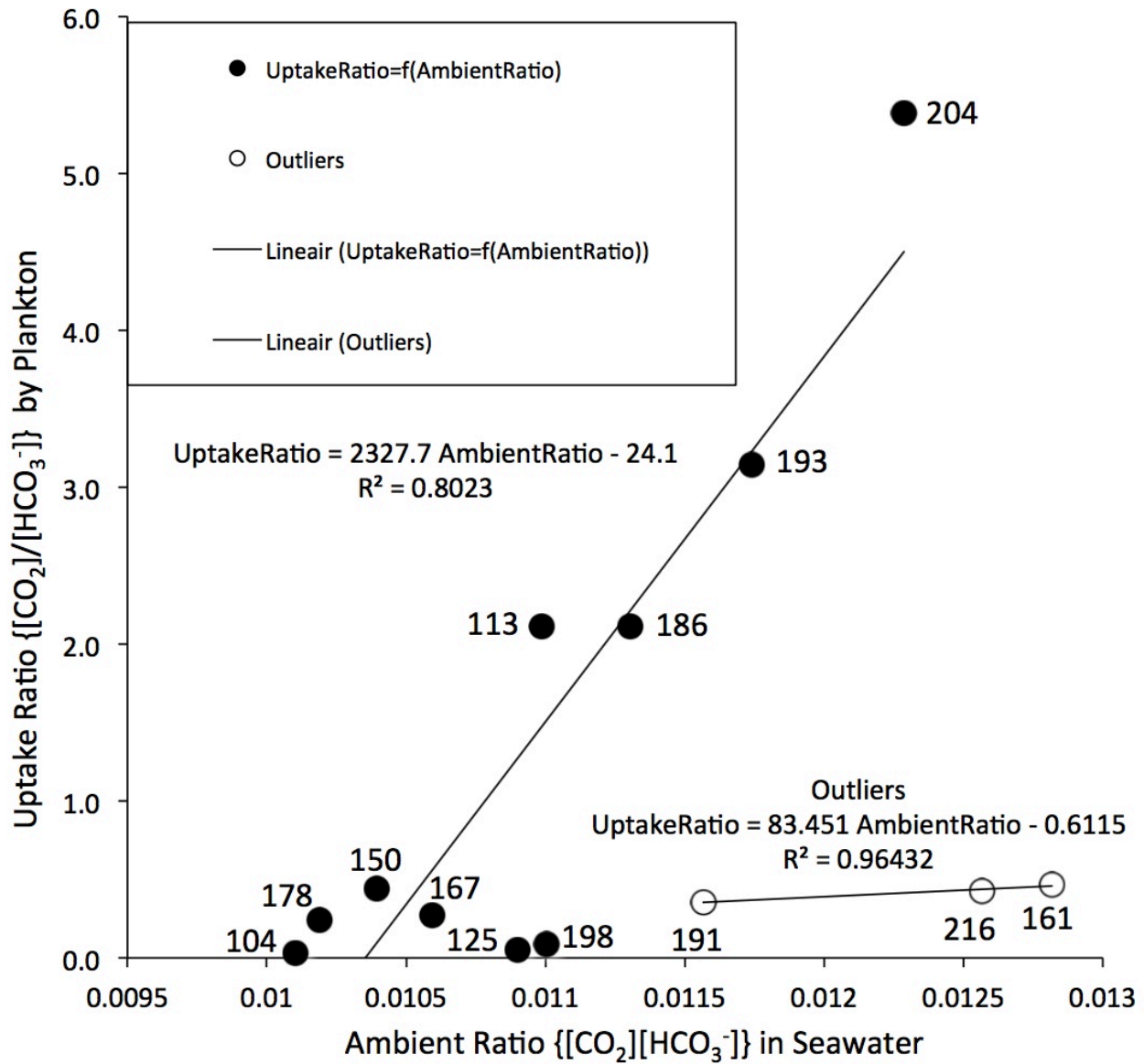


Figure 7. The uptake ratio $\{[CO_2]/[HCO_3^-]\}$ by the plankton community as measured in 13 shipboard incubation experiments as function of the concentration ratio $\{[CO_2]/[HCO_3^-]\}$ in ambient seawater. The data are for 13 experiments and each datapoint is labeled with the respective station number of the experiment. The regression slope of 2327.7 suggests a factor ~ 2300 preference for uptake of $[CO_2]$ versus uptake of $[HCO_3^-]$. The 3 obvious outliers from stations 161, 191, 216 were excluded from the main linear regression, yet in themselves also show a trend with slope of 83.5 implying the plankton still have an 83.5-fold preference for $[CO_2]$ over $[HCO_3^-]$. Otherwise please realize that the cluster of results from stations 104, 125, 150, 167, 178, 198 together with outliers 161, 191, 216 shows a similar and fairly low $\{[CO_2]/[HCO_3^-]\}$ uptake ratio of <1.0 , as compared to higher uptake ratio of $2.0 < \{[CO_2]/[HCO_3^-]\} < 6.0$ for the cluster of results from stations 113, 186, 193, 204.

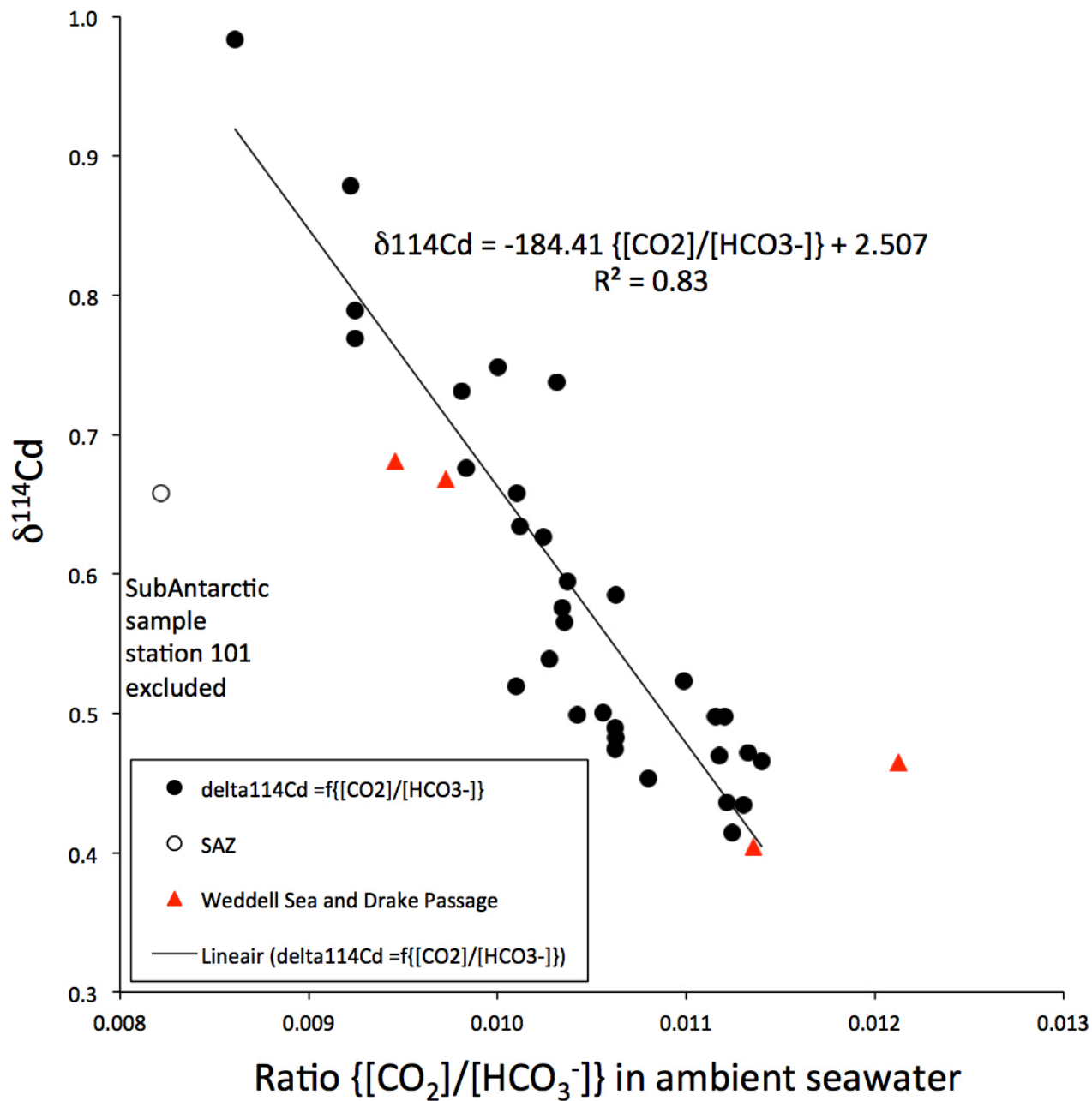


Figure 8. Relationship of $\delta^{114}\text{Cd}$ with the the concentration ratio $\{[\text{CO}_2]/[\text{HCO}_3^-]\}$ in surface waters along the Zero Meridian. The Subantarctic station 101 is excluded from the linear regression. (For the actual red color of the data points of 198, 216, 245 and 249 the reader is referred to the web version of this article.)

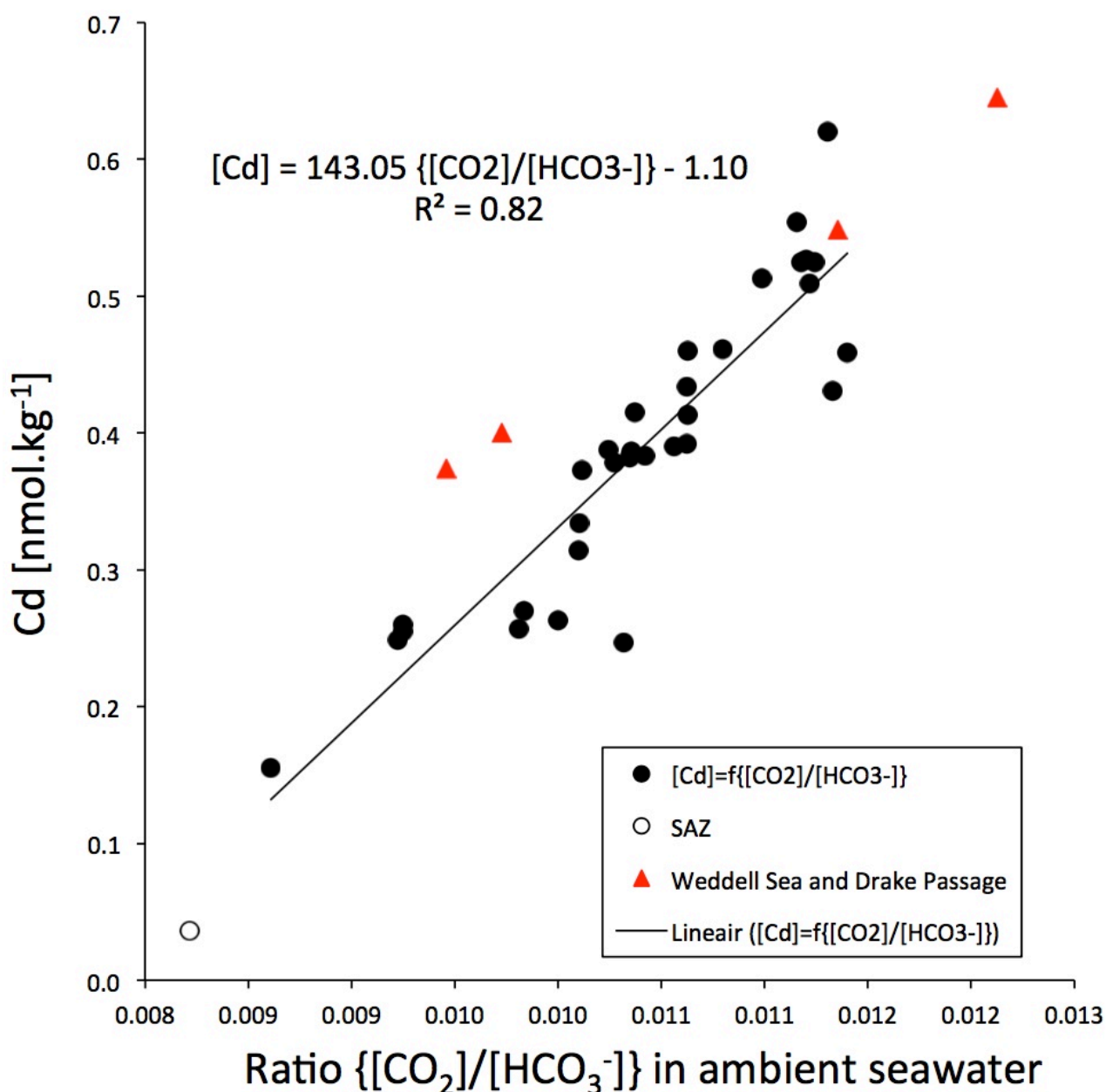


Figure 9. Relationship of dissolved Cd with the the concentration ratio {[CO₂]/[HCO₃⁻]} in surface waters along the Zero Meridian. The Subantarctic station 101 is excluded from the linear regression. Otherwise station 101 extends the linear trend, and the stations 198, 216, 245, 249 in Weddell Sea and Drake Passage also follow the trend closely. When including these 5 extra stations the regression (not shown) would become $Cd = 140.8 \{[CO_2]/[HCO_3^-]\} - 1.07$ with $R^2 = 0.84$ for $n = 37$ samples. (For the actual red color of the data points of 198, 216, 245 and 249 the reader is referred to the web version of this article.)

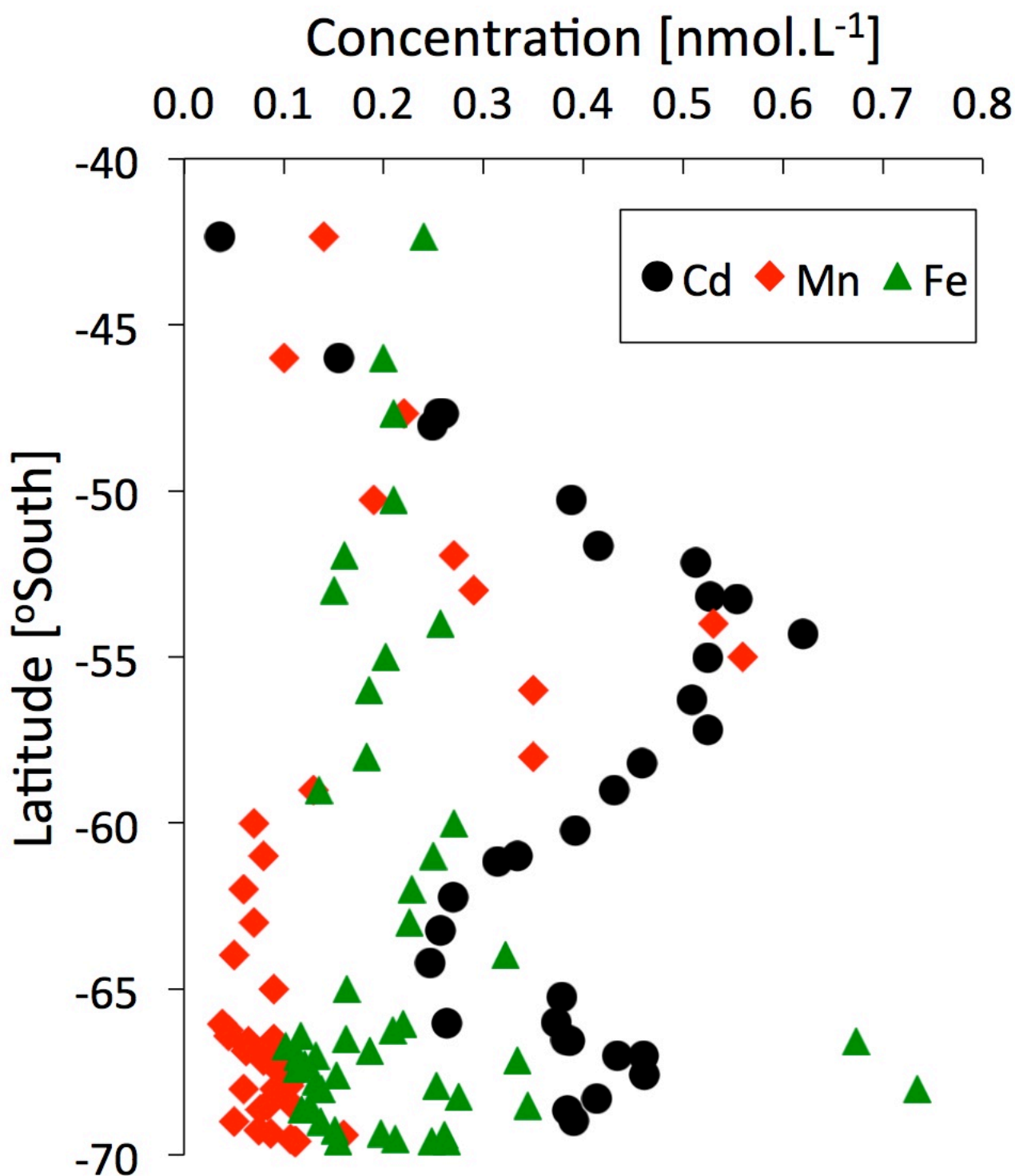


Figure 10. The concentrations of dissolved Cd, Mn and Fe in surface waters along the Zero Meridian as a function of latitude. The Cd data are from this work, the Mn data by Middag et al. (2011a) and Fe data from Klunder et al. (2011). On the one hand, the minima and maxima in the distribution of Mn are somewhat similar to those of Cd. On the other hand the distribution of Fe is quite uniform and does not appear to relate to either Cd or Mn. The lowest [Fe] is in the 60-65 °S region of the Weddell Gyre, where the preceding cruise encountered a major plankton bloom. Towards 70 °S, [Fe] is more elevated and noisy due to Fe supply from chunks of ice derived from the continental ice sheet. Otherwise, please note that an atmospheric dust input event occurred shortly before collection of the seawater samples at about 55°S. This may be partially responsible for the elevated concentrations of both Mn and Fe at 55°S, as also seen in dissolved Al (not shown here; see Middag et al., 2011b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)