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Non-Rayleigh control of upper-ocean Cd isotope fractionation in the western South Atlantic

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ABSTRACT

We present seawater Cd isotopic compositions in five depth profiles and a continuous surface water transect, from 50°S to the Equator, in the western South Atlantic, sampled during GEOTRACES cruise 74JC057 (GA02 section, Leg 3), and investigate the mechanisms governing Cd isotope cycling in the upper and deep ocean.

The depth profiles generally display high $\epsilon^{112/110}\text{Cd}$ at the surface and decrease with increasing depth toward values typical of Antarctic Bottom Water (AABW). However, at stations north of the Subantarctic Front, the decrease in $\epsilon^{112/110}\text{Cd}$ is interrupted by a shift to values intermediate between those of surface and bottom waters, which occurs at depths occupied by North Atlantic Deep Water (NADW). This pattern is associated with variations in Cd concentration from low surface values to a maximum at mid-depths and is attributed to preferential utilization of light Cd by phytoplankton in the surface ocean. Our new results show that in this region Cd-deficient waters do not display the extreme, highly fractionated $\epsilon^{112/110}\text{Cd}$ reported in some earlier studies from other oceanic regions. Instead, in the surface and subsurface southwest (SW) Atlantic, when [Cd] drops below 0.1 nmol kg⁻¹, $\epsilon^{112/110}\text{Cd}$ are relatively homogeneous and cluster around a value of +3.7, in agreement with the mean value of 3.8 ± 3.3 (2SD, $n = 164$) obtained from a statistical evaluation of the global ocean Cd isotope dataset. We suggest that Cd-deficient surface waters may acquire their Cd isotope signature via sorption of Cd onto organic ligands, colloids or bacterial/picoplankton extracellular functional groups. Alternatively, we show that an open system, steady-state model is in good accord with the observed Cd isotope systematics in the upper ocean north of the Southern Ocean. The distribution of $\epsilon^{112/110}\text{Cd}$ in intermediate and deep waters is consistent with the water mass distribution, with the north-south variations reflecting changes in the mixing proportion of NADW and either AABW or AAIW depending on the depth. Overall, the SW Atlantic Cd isotope dataset demonstrates that the large-scale ocean circulation exerts the primary control on $\epsilon^{112/110}\text{Cd}$ cycling in the global deep ocean.

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1. Introduction

The geochemistry of dissolved cadmium (Cd) in the global ocean has been extensively studied over the past 40 years. Early

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studies showed that the spatial distribution of Cd closely matches that of the macronutrient phosphate (PO₄), with low concentrations in surface waters and high concentrations at depth (Boyle et al., 1976; Bruland et al., 1978). The similar behavior of Cd and PO₄ has led to the suggestion that Cd may be a micronutrient for marine organisms, despite its known toxicity in the environment (Xu and Morel, 2013). Evidence for a biochemical function of Cd comes from the observed substitution of Cd for Zn in the metalloenzyme

carbonic anhydrase in cultures under Zn-limited conditions (Price and Morel, 1990) and, the report of cadmium-cofactored carbonic anhydrase (CdCA) in some marine diatoms (Cullen et al., 1999; Lane and Morel, 2000).

The first Cd isotope data obtained on phytoplankton cultures in Mediterranean waters featured Cd isotopic compositions indicative of a preferential incorporation of the light Cd isotopes into the cell (Lacan et al., 2006), a result supported by recent data on phytoplankton culture experiments (John and Conway, 2014). The fractionated Cd isotope signature seen in oceanic surface waters, in contrast to that of deep waters, provided strong support for a biologically-induced Cd isotope fractionation, with preferential uptake of light Cd in the surface ocean and release at depth during remineralization (e.g., Abouchami et al., 2011; Ripperger et al., 2007). Although the body of oceanic Cd isotope data has significantly increased recently, there remains some debate on the mechanisms governing stable Cd isotope fractionation. For example, deviations from a simple closed-system Rayleigh fractionation have been attributed to external eolian inputs of Cd along with microbial degradation and zooplankton repackaging within the mixed layer of the South China Sea (Yang et al., 2012, 2015). Also, the roles of cellular uptake of Cd, passive uptake, and involvement of CdCA are still unclear (Abouchami et al., 2014; Horner et al., 2013a, 2013b; Morel, 2013).

Regardless of the mechanisms causing surface Cd isotope fractionation, deep waters below 1000 m in the Pacific and Southern Oceans appear to be relatively homogeneous with $\epsilon^{112/110}\text{Cd}$ value of around +1 (Abouchami et al., 2014; Conway and John, 2015b; Ripperger et al., 2007; Xue et al., 2013), while northern-sourced waters in the Atlantic, at $\epsilon^{112/110}\text{Cd} \approx +2$, are heavier by one epsilon-unit (Boyle et al., 2012; Conway and John, 2015a; Xue et al., 2012).

In general, the global ocean Cd isotope dataset has been modeled in terms of closed-system Rayleigh fractionation (Abouchami et al., 2011, 2014; Xue et al., 2013) with some exceptions, such as in surface waters off New Zealand (Gault-Ringold et al., 2012). Possible explanations for the contrasting behavior of Cd isotopic fractionation in various oceanic regimes include: (1) a dependency on the local biogeochemical conditions (nutrient and trace metal availability – e.g., Cd, Zn, Fe), marine ecosystem communities and their nutrient requirements (Abouchami et al., 2011, 2014; Gault-Ringold et al., 2012); and (2) a distinction between a closed-system Rayleigh fractionation model in High Nutrient Low Chlorophyll (HNLC) regions versus a steady-state open system in non-HNLC regions (Xue et al., 2013).

In this study, we present the first seawater Cd isotope data in the western South Atlantic. In total, 82 seawater samples were collected from 5 stations and 15 tow-Fish sites during the GEOTRACES GA02 Leg 3 South Atlantic transect on board of the RRS James Cook (74JC057) from Punta Arenas (Chile) to Las Palmas (Canary Islands, Spain) (March to April 2011) (Fig. 1). The distributions of chemical and physical parameters, identifying major water masses along the deep Atlantic western boundary, were described in previous studies (Dulaquais et al., 2014; Rijkenberg et al., 2014; Xie et al., 2015). Our new results indicate a homogeneous $\epsilon^{112/110}\text{Cd}$ signature in low-Cd, upper South Atlantic waters ($[\text{Cd}] < 0.1 \text{ nmol kg}^{-1}$) of about +3.7 that cannot be easily reconciled with a closed-system Rayleigh fractionation. By exploring alternative models in the framework of the global Cd isotope dataset published, we show that under Cd supply-limited conditions the upper ocean stable Cd isotope fractionation might be governed by sorption of Cd onto organic ligands, colloids or extracellular functional groups and could be accounted for by a steady-state model.

Fig. 1. Location of the five stations (circles) and fifteen tow-Fish sampling sites (crosses) along GEOTRACES GA02 Leg 3 in the southwest Atlantic analyzed for Cd isotopes. The same color-coding for the stations is maintained throughout the manuscript and figures. Color contours are plotted for sea surface salinity. Also shown on the map are the locations of stations PS71-249 (open square; Xue et al., 2013) and PS71-104 (grey square; Abouchami et al., 2014) in the Southern Ocean. Oceanic fronts are drawn after Orsi et al. (1995). This map is created using Ocean Data View (ODV; Schlitzer, 2014). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Methods

2.1. Water sampling

Five Cd isotope depth profiles are presented for stations 2, 6, 12, 17, and 18, for which Cd concentrations were reported by Xie et al. (2015). The samples were collected using the PRISTINE ultraclean sampling system of NIOZ (Rijkenberg et al., 2015), and subsequently filtered on board in a Class-100 clean container through 0.2 μm Sartobran 300 cartridges (Middag et al., 2011) into high-density polyethylene (HDPE) bottles cleaned prior use with hot (60 °C) 6N HCl.

In addition, we present Cd isotope and concentration data on 15 surface water samples (5–10 m) collected continuously from 49°S to 3°S using a tow-FISH system and filtered (to 0.2 μm) into 10 L hot-acid-cleaned HDPE canisters. All samples were acidified on board to pH ~ 2 with ultra-clean concentrated HCl (Seastar Baseline, 12 N) immediately after filtration. Samples were then double-bagged in clean containers and shipped to the home laboratory.

2.2. Analytical methods

The chemical separation of Cd was performed in a Class-100 clean laboratory at the Max Planck Institute for Chemistry in Mainz, Germany. All acids used were either ultra pure acids from SEASTAR™ BASELINE or sub-boiling distilled using a Savillex DST-1000 PFA still.

The analytical methods for Cd-rich samples (up to one-liter water volume) follow those previously described by Abouchami et al. (2011) (see Supplementary Material). For low-Cd ($< 0.1 \text{ nmol kg}^{-1}$) and larger water volumes (up to 10 liters), a new analytical protocol was developed for the first-step chemical separation of Cd and summarized in the flow chart (Fig. 2) and fully described in Supplementary Material. The Cd isotope measurements were performed by Thermal Ionization Mass Spectrometry (TIMS) on a ThermoFisher Triton, running in static multi-collection mode (see

Fig. 2. A schematic flow chart of the chemical procedure developed for extraction of low-level Cd from large seawater volumes.

Supplementary Material), and the reproducibility of the standard NIST SRM-3108 is reported in Table S1. Cd isotopic compositions are expressed as $\epsilon^{112/110}\text{Cd}$, which is the deviation in parts per ten thousands of the $^{112}\text{Cd}/^{110}\text{Cd}$ ratio relative to that of the NIST SRM-3108 Cd:

$$\epsilon^{112/110}\text{Cd} = \left(\frac{(^{112}\text{Cd}/^{110}\text{Cd})_{\text{sample}}}{(^{112}\text{Cd}/^{110}\text{Cd})_{\text{NIST}}} - 1 \right) \times 10^4$$

The SAFe D1 seawater reference material was analyzed for intercalibration purposes and yielded $[\text{Cd}]$ of $1008 \pm 3 \text{ pmol kg}^{-1}$ and $\epsilon^{112/110}\text{Cd}$ of 1.55 ± 0.13 (weighted average, $n = 3$, 2σ) (see Table S2). These values agree with the GEOTRACES $[\text{Cd}]$ consensus value of $991 \pm 31 \text{ pmol kg}^{-1}$ (www.geotraces.org) and the Cd isotopic compositions reported in previous studies (1.30 ± 0.09 , $n = 5$, Conway et al., 2013; 1.63 ± 0.14 , $n = 4$, Xue et al., 2012).

3. Results

3.1. Surface transect

Cadmium concentrations and $\epsilon^{112/110}\text{Cd}$ values for the tow-Fish samples are reported in Table S3. The Cd concentrations range from 0.1 pmol kg^{-1} to 81 pmol kg^{-1} . In general, tow-Fish samples south of 40°S have much higher $[\text{Cd}]$ (40 to 800 fold) than those collected north of this latitude (Fig. 3). Geographically, latitude 40°S corresponds to the location of the sub-tropical front (Fig. 1), which separates the Southern Ocean surface waters rich in nutrients nitrate and phosphate, from the nutrient-poor subtropical waters.

Despite significant differences in surface water $[\text{Cd}]$, $\epsilon^{112/110}\text{Cd}$ values along the GA02 Leg 3 surface transect show little variation and vary around $\epsilon^{112/110}\text{Cd} = 3.7 \pm 1.1$ (2SD, $n = 13$) (grey shading in Fig. 3). This value is relatively uniform, and contrasts markedly with the $\epsilon^{112/110}\text{Cd}$ of up to +20 that have been reported in low-Cd (picomolar) surface waters from other oceanic regions (North Atlantic and North Pacific) (Conway and John, 2015a; John and Conway, 2014; Ripperger et al., 2007).

3.2. Depth profiles

The $\epsilon^{112/110}\text{Cd}$ vertical profiles from stations 2, 6, 12, 17, and 18 (Table S2) are shown in Fig. 4. All five profiles display similar

Fig. 3. Tow-Fish surface seawater Cd concentrations (left y-axis) and isotopic compositions (right y-axis) along the GEOTRACES GA02 Leg 3 transect from 50°S to the equator. Grey shading highlights the mean surface water $\epsilon^{112/110}\text{Cd}$ value of 3.7 ± 1.1 (2SD) along this transect. Blue arrows and shadings indicate oceanic fronts and frontal zones: SAF – Subantarctic front; STF – subtropical front; ST-SEF – subtropical-subequatorial front; SAZ – Subantarctic zone; STZ – subtropical zone; TZ – tropical zone. Inset shows a close-up of Cd concentrations in the range of 0–5 pmol kg^{-1} along the same transect. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$\epsilon^{112/110}\text{Cd}$ distributions in the top 1000 m, with high $\epsilon^{112/110}\text{Cd}$ surface values that decrease with increasing depth. This pattern is antithetic to that observed in the $[\text{Cd}]$ profiles that have low concentrations at the surface, increasing to maximum values at intermediate depths (Fig. 4; Xie et al., 2015).

There are clear differences in the vertical distributions of $\epsilon^{112/110}\text{Cd}$ at station 2 (Fig. 4) located in the Southern Ocean vs. those at stations north of the Subantarctic Front (SAF; Fig. 1). In particular, $\epsilon^{112/110}\text{Cd}$ in the top 50 m is highest (+5.4) at station 2 while it ranges between +1.7 and +3.0 at the northern stations. Below 50 m, $\epsilon^{112/110}\text{Cd}$ decreases rapidly toward a value of $\sim +1.2$ and remains uniform at depths greater than 1000 m. Such a vertical distribution is very similar to that reported in GEOTRACES Section GPY5 in the South Atlantic (PS71-104, Abouchami et al., 2014; PS71-249, Xue et al., 2013) (see Figure S1). Stations PS71-249 and PS71-104 lie directly along the Antarctic Circumpolar Current (ACC) up-stream and down-stream of station 2 (this study), respectively (Fig. 1). Cadmium isotope depth profiles from these two stations ($\sim 68^\circ$ in longitude or $\sim 4600 \text{ km}$ apart) are within analytical error of the station 2 profile below $\sim 300 \text{ m}$ (Figure S1), regardless of the differences in the timing of sampling and analytical methods, as also reported for the Cd concentration profiles (Xie et al., 2015). This is in contrast to the variability seen in (sub)surface waters where a difference of up to 2ε-units is observed between station 2 and the tow-Fish samples collected nearby (see Tables S2, S3). Such a fine-scale Cd isotope variability is associated with changes in salinity, temperature, fluorescence and nutrients (Figure S2), demonstrating the short-term response of Cd isotopes to local physical, chemical and biological conditions. We note that similar short-length scale and seasonal Cd isotope variability have been reported in the Subantarctic Pacific (Gault-Ringold et al., 2012).

The profiles at the northern stations (6, 12, 17, 18) are different to that at station 2. A decreasing trend of $\epsilon^{112/110}\text{Cd}$ with depth is interrupted by excursions to higher $\epsilon^{112/110}\text{Cd}$, coinciding with the depth layer occupied by NADW. The southward flowing NADW is identified northwards at stations 17 and 18, between 1500 and 4000 m, with $\epsilon^{112/110}\text{Cd}$ values of about +2.1, a value typical of NADW measured in the northwest Atlantic (Boyle et al., 2012; Conway and John, 2015a). Below the depth corresponding to

Fig. 4. (a) Cd concentration profiles from Xie et al. (2015) and (b) Cd isotope depth profiles of stations 2 (blue), 6 (red), 12 (green), 17 (purple), and 18 (orange). The blue and orange dashed lines indicate the $\epsilon^{112/110}\text{Cd}$ endmember values for NADW and AABW, respectively. The grey shadings from top to bottom highlight the depth ranges occupied by AAIW, NADW, and AABW. Depth range of Upper Circumpolar Deep Water (UCDW) is indicated between AAIW and NADW. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

NADW, $\epsilon^{112/110}\text{Cd}$ decreases to around +1.2, including in the deepest parts of southernmost station 2, consistent with the presence of AABW (Abouchami et al., 2014; Xue et al., 2013).

Overall, dissolved $\epsilon^{112/110}\text{Cd}$ in the western South Atlantic exhibits a strong contrast between surface and deep waters. The highest $\epsilon^{112/110}\text{Cd}$ values are found in the euphotic zone and vary from +5.4 in the ACC (station 2) to +3.0 north of the ACC. The lowest values of around +1.2 are found at depths occupied by AABW. The general decrease in $\epsilon^{112/110}\text{Cd}$ with increasing depth closely matches the increase in Cd concentrations (Xie et al., 2015). The resulting co-variation between Cd concentration and $\epsilon^{112/110}\text{Cd}$ is in general similar to that previously reported in seawater from the Pacific (Conway and John, 2015b; Janssen et al., 2017; Ripperger et al., 2007), the North Atlantic (Boyle et al., 2012; Conway and John, 2015a; John and Conway, 2014) and the Southern Ocean (Abouchami et al., 2014; Xue et al., 2013).

4. The upper ocean water column

4.1. What governs the Cd isotopic fractionation in the upper ocean?

In this section, we focus our discussion on the Cd isotope systematics in the upper 1000 m in the western South Atlantic, and consider the global seawater Cd isotope dataset available to date.

First, $\epsilon^{112/110}\text{Cd}$ increases as Cd becomes more depleted towards the surface. A closed-system Rayleigh fractionation model has generally been used to explain the relationship between dissolved $\epsilon^{112/110}\text{Cd}$ and Cd concentrations in the upper ocean (Abouchami et al., 2011; Ripperger et al., 2007). This is due to the well-defined linear trends in plots of $\epsilon^{112/110}\text{Cd}$ versus $\ln([\text{Cd}])$, consistent with a simple Rayleigh relationship. In the Rayleigh

model, light Cd isotopes are progressively “distilled” out of the dissolved pool via phytoplankton Cd uptake within the euphotic zone, driving the $\epsilon^{112/110}\text{Cd}$ of ambient seawater toward more positive, heavier values. The extent of Cd isotope fractionation due to Cd uptake is expressed in the fractionation factor (α) determined from the slope of the regression line in an $\epsilon^{112/110}\text{Cd}$ vs. $\ln([\text{Cd}])$ space. Abouchami et al. (2011) showed that different biogeochemical provinces in the Southern Ocean can be identified by distinct $\alpha^{112/110}\text{Cd}$ of ~ 1.0002 and 1.0001 , for the ratio $^{112}\text{Cd}/^{110}\text{Cd}$, in the ACC and Weddell Gyre, respectively.

Similarly, our western South Atlantic dataset defines two arrays in Figure S3 suggesting differences in fractionation factors delimiting the stations in the Southern Ocean from those north of the Subantarctic Front (SAF). While the intermediate and sub-surface waters (<1000 m) at station 2 (49°S), which is located in the ACC westward of the Zero Meridian, fall along a Rayleigh line consistent with a fractionation factor of $\alpha^{112/110}\text{Cd} \sim 1.0002$, those at stations further north display a shallower slope with $\alpha^{112/110}\text{Cd} \sim 1.0001$. Several factors could cause a change in fractionation factor as discussed by Abouchami et al. (2011, 2014) and these ultimately reflect the physical, chemical and biological processes of the local water column. These include changing ecologies across the SAF (Abouchami et al., 2011) as well as the availability and interaction of trace metals, in particular Zn, Mn, Fe which can variably affect Cd uptake (Sunda, 2012; Sunda and Huntsman, 2000). Our knowledge of the influence of community structures on Cd isotope fractionation factors so far relies only on two culture experiments (Lacan et al., 2006; John and Conway, 2014) and additional experimental data are urgently needed to better understand the factors controlling Cd isotope fractionation in different nutrient regimes. Close examination of

Fig. 5. Cd isotope systematics in the western South Atlantic (a) and the global ocean (b). Color circles for profile samples, and open circles for tow-Fish seawater samples (this study). Grey diamonds – North Atlantic (Boyle et al., 2012; Conway and John, 2015a; John and Conway, 2014); Open triangles – North (Conway and John, 2015b; Ripperger et al., 2007) and South Pacific (New Zealand – Gault-Ringold et al., 2012, South China Sea and Philippine Sea – Yang et al., 2012, 2014); open squares – Southern Ocean (Abouchami et al., 2011, 2014; Xue et al., 2013). Red dashed line schematically highlights the evolution of seawater $\epsilon^{112/110}\text{Cd}$ toward low Cd concentrations. Error bars (2σ) are shown. Inset in (a) shows a zoom-out version of the same plot.

the trace metals dataset available (analysts R. Middag, H. de Baar, K. Bruland; Mawji et al., 2015) show no systematic variations between either Zn, or Mn concentrations and $\epsilon^{112/110}\text{Cd}$ along the surface water transect. Clearly, a change in the behavior of Cd isotopes occurs at extremely low Cd in the GA02 Leg 3 waters, with a break-down of the Rayleigh relationship at a nominal threshold dissolved [Cd] of 0.1 nmol kg^{-1} (Fig. 5). This observation indicates that the closed-system Rayleigh fractionation model may not be adequate for describing the Cd isotope systematics of South Atlantic Cd-deficient surface and subsurface waters. These waters generally have $\epsilon^{112/110}\text{Cd}$ varying between +2 and +5, albeit within error, and are an order of magnitude lower than values predicted by a closed-system Rayleigh fractionation with $\alpha^{112/110}\text{Cd}$ of 1.0002.

The relatively homogeneous $\epsilon^{112/110}\text{Cd}$ signature of the upper South Atlantic waters is also at odds with the available global oceanic Cd isotope dataset that indicates a larger variability and generally much higher $\epsilon^{112/110}\text{Cd}$ values in the upper ocean (see Fig. 5b). Our data compilation shows, however, that only 8% of the

Fig. 6. Histogram of global dissolved $\epsilon^{112/110}\text{Cd}$ in surface and subsurface waters with $\text{Cd} < 0.1 \text{ nmol kg}^{-1}$. Data is compiled from the North Atlantic (Conway and John, 2015a; John and Conway, 2014; Ripperger et al., 2007), eastern South Atlantic (Abouchami et al., 2011, 2014), western South Atlantic (this study), North Pacific (Conway and John, 2015b; Ripperger et al., 2007), South Pacific (Gault-Ringold et al., 2012), South China and West Philippine Seas (Yang et al., 2012, 2015), and the Arctic Ocean (Ripperger et al., 2007).

global waters with $[\text{Cd}] < 0.1 \text{ nmol kg}^{-1}$ ($n = 179$) have $\epsilon^{112/110}\text{Cd}$ greater than 10. This is best illustrated by the histogram distribution of $\epsilon^{112/110}\text{Cd}$ shown in Fig. 6. The remainder, and majority of the low-Cd surface waters (including our dataset), yields an average $\epsilon^{112/110}\text{Cd}$ value of 3.8 ± 3.3 (2SD, $n = 164$) highlighted by the red line in Fig. 5. The greater variability observed at $[\text{Cd}] < 0.004 \text{ nmol kg}^{-1}$ (equivalent to $\sim 0.4 \text{ ng kg}^{-1}$) in Fig. 5b might partly reflect some analytical limitations at low-level Cd, which should be evaluated by an inter-laboratory comparison of common low-level and high-level Cd samples. In the following, we have chosen to exclude the extreme, high- $\epsilon^{112/110}\text{Cd}$ surface samples (14 out of 179) in Fig. 5b and focus our discussion on the origin(s) of the apparent relatively uniform $\epsilon^{112/110}\text{Cd}$ signature of global surface and subsurface waters by considering alternative models to the closed-system Rayleigh fractionation model.

4.2. Organic ligand control of Cd-deficient surface water isotopic composition

It is important to bear in mind that all the seawater samples analyzed for Cd isotopes in this, and other studies thus far, were filtered onboard to $0.2 \mu\text{m}$ to remove particulate Cd. Therefore, any particulate matter, colloids or organic ligands (e.g. exudates, polymer gels, phytochelatin) smaller than $0.2 \mu\text{m}$ are bound to be present in our samples. Cadmium bound to such organic detritus or organic ligands would then be released back into the seawater upon sample acidification. In the following, we will refer to the “dissolved pool” as the inorganically-complexed Cd in solution, while the “bound” Cd is that associated with organic detritus or organic ligands; both of these would pass $0.2 \mu\text{m}$ filtration and are technically in a “dissolvable” state.

Here we consider the possibility that organic-bound Cd is responsible for the “leveling off” of $\epsilon^{112/110}\text{Cd}$ at very low Cd concentrations seen in Fig. 5. In this case, it is conceivable that at higher concentrations of Cd, the inorganically-complexed Cd imparts its signature to the dissolved pool, while at very low concen-

trations, the predominance of the $<0.2 \mu\text{m}$ “bound” Cd ($\sim 70\%$) (e.g., Bruland, 1992) determines the dissolved $\epsilon^{112/110}\text{Cd}$. Since Cd adsorption (Wasylenzi et al., 2014), partitioning into calcite (Horner et al., 2011), ion-exchange (Schmitt et al., 2009) and ab initio calculations (J. Yang et al., 2015) all suggest that the solid phase favors the light isotopes of Cd, one would expect such “bound” Cd to lie at lower $\epsilon^{112/110}\text{Cd}$ than that of the dissolved Cd. In effect, the data would fall below the Rayleigh line in plots such as Figure S3 at very low Cd concentrations, and this is what is actually observed.

Thus, one explanation we propose here for the homogeneity of $\epsilon^{112/110}\text{Cd}$ in Cd-deficient surface waters is that Cd isotope fractionation is chemically rather than biologically driven. In principle, any organic detritus phases, colloids or organic ligands might be binding Cd at low levels. The adsorption and binding mechanisms are likely to differ among them, but the net effects will probably be similar, vis-à-vis preferential binding of the lighter isotopes of Cd. Below, we will consider Cd bound onto bacteria/picoplankton surface extracellular functional groups as an example.

Surfaces of bacteria and photosynthetic picoplankton (e.g. cyanobacteria) retain abundant reactive ligands that can deprotonate at seawater pH, thus providing reactive “sites” to bind metal cations such as Pb, Cu, Zn and Cd (Cox et al., 1999; Fein et al., 1997). The binding behavior of numerous trace metals is relatively similar and only affected by the presence of Fe (Hao et al., 2016). These reactive ligands include, but are not limited to, carboxyl, hydroxyl, phosphoryl, and amino groups.

Early culture experiments showed that the accumulation of Cd and other toxic metals on dead phytoplankton cells is comparable to that on living cells (Fisher et al., 1984), suggesting that metal cations are initially adsorbed onto cell surfaces prior to assimilation/incorporation (Gélbert et al., 2007; González-Dávila, 1995). For example, preferential adsorption of heavy Zn isotopes onto diatom surfaces was observed in experiments (Gélbert et al., 2006; John et al., 2007). This is in contrast to Cd isotopes where the light isotope seems to be preferentially incorporated (John and Conway, 2014; Lacan et al., 2006).

The adsorption process can be described using simple surface complexation equilibria; an equilibrium is generally established within 2 to 4 hours after trace metal addition in culture experiments (González-Dávila, 1995), independently of the bacteria/picoplankton species involved (Borrok et al., 2004; Yee and Fein, 2001). The Cd-ligand complexes on bacteria surfaces are fairly stable, with stability constants ranging from $10^{3.4}$ to $10^{5.4}$ (Fein et al., 1997). The average adsorbed Cd concentration in cyanobacteria cultures is reported to be equivalent to $\sim 8 \text{ nmol Cd L}^{-1}$ at seawater pH (Liu et al., 2015). Although it is an order of magnitude smaller than those reported for various bacteria (e.g., Borrok et al., 2004; Kenney and Fein, 2011), there is no doubt that surfaces of picoplankton and bacteria have the ability to adsorb considerable amounts of cations like Cd.

In the Subantarctic Southern Ocean, Cd is shown to strongly bound to natural organic ligands (1–2.5 nM) with a conditional stability constant $\log K_L$ of ~ 10 (Baars et al., 2014; Ellwood, 2004). Using the equations of Ellwood (2004) and Ellwood and Van den Berg (2000), we derive the fraction of inorganic Cd relative to total Cd (Cd'/Cd_T) measured (Fig. 7). Here, Cd' refers to the sum of all inorganically complexed Cd (mainly chloro-complexes) and free Cd^{2+} ions. At total Cd $<0.1 \text{ nmol kg}^{-1}$ and ligand concentration of 1 nM, Cd'/Cd_T remains $<10\%$ through a wide range of total [Cd]. Only above a threshold of 0.1 nmol kg^{-1} is there a significant increase in $[\text{Cd}']$. Interestingly, the distribution of Cd'/Cd_T against total Cd (Fig. 7) is a mirror image of the global $\epsilon^{112/110}\text{Cd}$ distribution shown in Fig. 8a. This finding provides strong support for an important role of ligand-bound Cd in setting the Cd isotope

Fig. 7. Relative proportion of inorganic Cd concentrations ($[\text{Cd}']$), assuming a conditional stability constant $\log(K_{\text{CdL}})$ of 10. The $[\text{Cd}']$ at equilibrium is calculated following equations detailed in Ellwood (2004) and Ellwood and van den Berg (2000). Three different scenarios are shown with ligand concentrations of 2 nM (blue), 1 nM (black) and 0.5 nM (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

composition of Cd-deficient surface waters; this is further demonstrated below.

Here, we consider seawater at the base of the thermocline along GA02 ($[Cd] \sim 0.5 \text{ nmol kg}^{-1}$, $\varepsilon^{112/110}Cd \sim +2$) being constantly upwelled and fed to the surface ocean. At ligand concentration of 1 nM, Cd/Cd_T in these waters is $\sim 15\%$ (Fig. 7), which yields $[Cd']$ of 75 pmol kg^{-1} . This $[Cd']$ is the starting concentration for the Rayleigh fractionation process. With respect to the Cd_L fraction, it is reasonable to assume that there is no isotope fractionation between Cd_L and total Cd at equilibrium, so that Cd_L has an $\varepsilon^{112/110}Cd$ of $+2$. This is different to the isotopic fractionation between Cd_L and Cd' , in which bound-Cd tends to have lighter $\varepsilon^{112/110}Cd$ than dissolved Cd, as detailed in the aforementioned discussion. On the other hand, this assumption leads to $\varepsilon^{112/110}Cd' \sim +2$ at $[Cd_T]$ of 0.5 nmol kg^{-1} based on mass balance. Assuming an $\alpha^{112/110}Cd$ of 1.0002, a decrease in $[Cd_T]$ from 0.5 nmol kg^{-1} to 1 pmol kg^{-1} would result in an $\varepsilon^{112/110}Cd_T$ of $+15$ in ambient seawater. However, when starting the Rayleigh curve at 75 pmol kg^{-1} , surface water would have a much lower $\varepsilon^{112/110}Cd'$ of $+10$. Knowing the isotopic compositions of Cd' and Cd_L , mass balance calculation determines an $\varepsilon^{112/110}Cd_T$ of $+3.2$ at $[Cd_T]$ of 1 pmol kg^{-1} , a value consistent with what we observed in low-Cd waters. When Cd' is utilized and removed from the surface ocean, $[Cd']$ decreases; meanwhile, Cd_L ($\varepsilon^{112/110}Cd = +2$) continuously dissociates, freeing up Cd' and keeping $\log K_L$ conserved. Effectively, the ligand-bound Cd, making up $>85\%$ of the total Cd, adds $\varepsilon^{112/110}Cd$ of $+2$ at all times to the Rayleigh system; this process buffers $\varepsilon^{112/110}Cd_T$ to low, relatively uniform values. Such a process is visually illustrated in Figure S4 with varying $\alpha^{112/110}Cd$. Mathematically, the Cd isotopic composition of the dissolvable pool is a weighted mean of the bound $\varepsilon^{112/110}Cd_L$ and the inorganically-free $\varepsilon^{112/110}Cd'$.

These results show that adsorption processes provide a viable explanation for both the large range in dissolved Cd concentrations (0.0001 to $0.01 \text{ nmol kg}^{-1}$) in surface and subsurface waters filtered at $0.2 \mu\text{m}$ (Fig. 5) and the deviation of $\varepsilon^{112/110}Cd$ from a model Rayleigh fractionation line. It will be important in future studies to fully assess the role of organic ligand Cd complexation by examining the effect of different pore-size on dissolved Cd isotope composition, as has been done for Fe isotopes (Fitzsimmons et al., 2015).

4.3. An open system, steady-state model

The seawater Cd isotope systematics in the upper ocean can also be explained by an open system, steady-state two-box model with the water column subdivided into a surface layer and a deep layer (see Supplementary Material). At steady state, the mass fluxes of water and Cd into and out of the surface layer are in balance. The Cd inflow arises from upwelling (advective) or diapycnal mixing from below, while the outgoing flux is represented by sinking particles (with biologically-bound Cd) and, a combination of water outflow and downward mixing (Figure S5).

The atmospheric input of Cd to the upper ocean can be quantitatively assessed and is considered to be negligible. Applying an atmospheric Fe depositional flux rate of $0.02\text{--}0.2 \text{ g m}^{-2} \text{ yr}^{-1}$ (Mahowald et al., 2009) at our study site, and using a mean upper continental crustal Fe/Cd ratio of $2.88 \mu\text{g g}^{-1}$ (Taylor and McLennan, 1985) for the mineral dust, the eolian Cd depositional flux rate ranges from $60\text{--}600 \text{ ng m}^{-2} \text{ yr}^{-1}$. This value is relatively small compared to the upwelled Cd flux. An overall upwelling rate outside of major upwelling regions is estimated to be 1 myr^{-1} , if one assumes a mean oceanic depth of 4000 m and an oceanic overturning time of 4000 years. Along GA02 Leg 3, seawater at the base of the thermocline has a mean $[Cd]$ of $\sim 0.5 \text{ nmol kg}^{-1}$. Taking a seawater density of 1000 kg m^{-3} , the Cd upwelling flux rate is

approximately $60 \mu\text{g m}^{-2} \text{ yr}^{-1}$, which is 100- to 1000-fold higher than the atmospheric Cd depositional flux. This quantitative estimate is robust even if there are small variations in upwelling rate, $[Cd]$ at the base of thermocline, and seawater density.

Mathematically, the open-system model equations (see Supplementary Material) are the same as those for a simple batch-extraction model with continuous addition of Cd and assuming infinitesimal water mass mixing (see Abouchami et al., 2014); as Cd concentrations decrease in the surface layer box, residence times within the surface layer decrease accordingly. A similar open-system model has been mentioned in Ripperger et al. (2007) and Gault-Ringold et al. (2012). Although the open-system steady state model is an oversimplified 1D model of a multi-dimensional process and, as such, should be used with caution, it is arguably the simplest model for understanding what may govern surface layer Cd isotope systematics under some conditions.

The variation of the Cd isotopic composition in the surface layer as a function of surface Cd concentration, along with corresponding biomass $\varepsilon^{112/110}Cd$, can be calculated using $\varepsilon^{112/110}Cd$ and concentrations of different source waters as the starting composition. Fig. 8b illustrates the evolution of seawater (and particles) using this steady state model for the case of $\Delta = 2.5$ (i.e., $\alpha = 1.00025$), $\varepsilon_{DL} = 1.2$, and $Cd_{DL} = 0.8 \text{ nmol kg}^{-1}$. In reality, Δ (or α) varies depending on phytoplankton community structure and trace metal availability, and thus is not constant. Such a steady-state model appears to fit the observed global dissolved Cd dataset quite well (see blue solid and grey dotted lines in Fig. 8a). Here, the global dataset consists of samples from the top 500 m for the Pacific and top 1000 m for the rest of the oceans.

Gault-Ringold et al. (2012) presented a Cd isotope surface transect for the Subantarctic Southern Ocean south of New Zealand that looks remarkably similar to our own data (Fig. 8a), with $\varepsilon^{112/110}Cd$ leveling off at low Cd concentrations. This feature was explained by phytoplankton utilizing all the available Cd under supply limited-conditions, and thus resulting in no net Cd isotope fractionation. While it is true that under such circumstances the particle-incorporated (dead plankton) $\varepsilon^{112/110}Cd$ will be the same as that input into the surface layer, this will not be the case for the dissolved surface water pool (which was measured) that should, presumably and mathematically, still lie close to the Rayleigh model line.

Although these authors did examine an open-system model, they rejected it on the grounds that such a model could not explain the seasonal 50-fold change in Cd concentrations they observed. This argument is incorrect, however, since the surface layer concentrations depend simply on the amount of uptake/utilization in the surface layer alone, and are independent of the in-flux of Cd from below; mathematically, the in-flux has no bearing on $[Cd]$ and $\varepsilon^{112/110}Cd$ in the surface layer. Thus, a seasonal change of this magnitude seems entirely plausible and is no grounds for rejecting an open-system model per se. Overall, the agreement of the global and our own low-concentration dataset for $\varepsilon^{112/110}Cd$ seen in Fig. 8a with a simple open-system model suggests that this is a reasonable way of viewing surface layer Cd cycling in at least some parts of the global ocean.

5. The deeper water column

5.1. Water mass mixing control on $\varepsilon^{112/110}Cd$

Water mass mixing control on deep water Cd isotope compositions has been described previously (e.g. Abouchami et al., 2014), but is remarkably well illustrated here by the systematic Cd isotope variations with latitude along the deep water flow along the western boundary of the South Atlantic (Fig. 4a).

Table 1Cadmium concentrations, Cd isotopic compositions, and Cd/PO₄ ratios for endmember water masses in the deep Atlantic Ocean.

Water mass	Cd (nmol kg ⁻¹)	Cd/PO ₄ (nmol/μmol)	$\epsilon^{112/110}\text{Cd}$	Reference
AABW	0.78	0.344	1.23 ± 0.19 (2SD, $n = 22$)	Abouchami et al. (2014) Xue et al. (2012)
AAIW	0.65	0.315	2.24 ± 0.39 (2SD, $n = 13$)	Baars et al. (2014) This study
NADW	0.27	0.229	2.11 ± 0.52 (2SD, $n = 63$)	Boyle et al. (2012) Conway and John (2015a) Xue et al. (2012) Bruland and Franks (1983) Sakamoto-Arnold et al. (1987)

Fig. 9. Cross plot of $\epsilon^{112/110}\text{Cd}$ vs. $1/[\text{Cd}]$ illustrating water mass binary mixing. Color solid symbols – samples bathed by NADW; Color open symbols – samples bathed by AABW; Grey solid symbols – samples bathed by AAIW. Color boxes show endmember water masses AAIW (grey), NADW (blue) and AABW (orange). Black and grey lines are mixing lines between NADW ($\epsilon^{112/110}\text{Cd} = 2.11 \pm 0.52$; $\text{Cd} = 0.27 \text{ nmol kg}^{-1}$) and AABW ($\epsilon^{112/110}\text{Cd} = 1.23 \pm 0.19$; $\text{Cd} = 0.78 \text{ nmol kg}^{-1}$) and, NADW and AAIW ($\epsilon^{112/110}\text{Cd} = 2.24 \pm 0.39$; $0.65 \text{ nmol kg}^{-1}$), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The South Atlantic Cd dataset shows that major intermediate/deep water masses along the western boundary can be identified based upon distinctive $\epsilon^{112/110}\text{Cd}$ (Fig. 4). At station 2, “pure” AAIW and AABW have $\epsilon^{112/110}\text{Cd}$ of 2.19 ± 0.18 (2SD, $n = 2$) and 1.06 ± 0.08 (2SD, $n = 5$), respectively (Table S2), in agreement with values reported in previous studies from the Southern Ocean (AAIW $\epsilon^{112/110}\text{Cd} \sim 2.24$, AABW ~ 1.2 ; Table 1; Abouchami et al., 2014; Xue et al., 2013). The NADW endmember is characterized by $\epsilon^{112/110}\text{Cd}$ of ~ 2.11 , consistent with that reported elsewhere (Table 1; Boyle et al., 2012; Conway and John, 2015a), a heavy value compared to that of AABW, but similar to that of AAIW (Abouchami et al., 2014; this study). Fig. 4 shows that within the depth layer occupied by NADW, $\epsilon^{112/110}\text{Cd}$ values increase from south to north along our transect. We attribute the north–south gradient of $\epsilon^{112/110}\text{Cd}$ to changes in the admixing proportions of NADW and AABW with a strengthening influence of NADW northward and concomitant decrease of that of AABW. These trends are entirely consistent with the salinity section with latitude (see Xie et al., 2015 and Fig. 4 here).

In Fig. 9, our dataset is plotted in $\epsilon^{112/110}\text{Cd}$ vs. $1/[\text{Cd}]$ space and this defines two distinct arrays which can be modeled in terms of binary mixing between southern-sourced waters (AAIW or AABW) and northern-sourced water (NADW) (see Table 1). The equations for binary mixing are:

$$\text{Cd}_{\text{sample}} = \text{Cd}_{\text{NADW}} \cdot f + \text{Cd}_{\text{SSW}} \cdot (1 - f) \quad (1)$$

$$\epsilon_{\text{sample}} \cdot \text{Cd}_{\text{sample}}$$

$$= \epsilon_{\text{NADW}} \cdot \text{Cd}_{\text{NADW}} \cdot f + \epsilon_{\text{SSW}} \cdot \text{Cd}_{\text{SSW}} \cdot (1 - f) \quad (2)$$

where Cd and ϵ correspond to Cd concentration and $\epsilon^{112/110}\text{Cd}$ of the end-members, f represents the fraction of NADW, and SSW stands for southern-sourced water (AAIW or AABW).

Using (1) and (2) we can estimate the proportion of NADW and SSW contributing at any given location. Samples situated in NADW (color solid circles), AABW (color open circles), and AAIW (grey solid circles) fall along one of two mixing lines: between NADW and AABW (for deep waters) and NADW and AAIW (intermediate waters), with the exception of three intermediate and two deep samples (Fig. 9). The intermediate-depth samples are from station 2 (100 m), station 12 (640 m), and station 17 (500 m) and located at the upper limit of AAIW. Given the relatively shallow depths, the higher $\epsilon^{112/110}\text{Cd}$ in these samples may be a result of incomplete remineralization or vertical mixing with overlaying waters with heavy $\epsilon^{112/110}\text{Cd}$. Roshan and Wu (2015) recently demonstrated that regionally regenerated Cd in the upper 1000 m can account for >50% of the Cd measured in the North Atlantic. Two deep samples from station 18 (3000 m and 3500 m) do fall below the deep mixing line, however, and their lower $\epsilon^{112/110}\text{Cd}$ may possibly reflect an additional bottom source of Cd, either hydrothermal or Cd remobilized at the sediment–water interface. Nonetheless, the fact that the majority of the data closely follow the mixing lines between (i) NADW and AAIW and (ii) NADW and AABW, strongly indicates that $\epsilon^{112/110}\text{Cd}$ in the intermediate/deep ocean is quasi-conservative, highlighting its potential application in reconstructing paleo-circulation.

Fig. 9 shows that the proportion of Cd derived from NADW decreases from 80% at the northernmost stations 17 and 18 in the depth range 1500 to 4000 m, to ca. 50% at Station 6 (40°S) at 2000 m and only 12% at 3000 m. At the southernmost station 2 (49°S), about 28% of the Cd of Upper Circumpolar Deep Water (UCDW) is derived from NADW. These estimates agree relatively well with those at station PS71-104 (Abouchami et al., 2014) at a similar latitude downstream along the ACC (Fig. 1), and also with water mass transport budgets based on physical parameters (Talley, 2013). Below we discuss what determines the $\epsilon^{112/110}\text{Cd}$ of northern and southern end-member water masses in the Atlantic.

5.2. Origin of Atlantic deep and intermediate water Cd isotopic end-members

The Southern Ocean plays an important role in setting the pre-formed nutrient concentrations and isotopic compositions in the global ocean (e.g., Sarmiento et al., 2004). Vertical profiles of $[\text{Cd}]$ and $\epsilon^{112/110}\text{Cd}$ in the Southern Ocean seem to largely reflect relatively mild nutrient utilization at the surface and remineralization at depth (Abouchami et al., 2014; Xue et al., 2013). As a result, deep waters in this region (e.g., AABW or Weddell Gyre deep and bottom waters) have high Cd content and light $\epsilon^{112/110}\text{Cd}$ values.

These Cd-rich, low $\varepsilon^{112/110}\text{Cd}$ waters are delivered as AABW to all three major ocean basins (Atlantic, Indian, and Pacific). North of the APF, a portion of the upwelled Cd-rich water flows northward along the surface ocean. Strong biological utilization depletes lighter Cd (Abouchami et al., 2011), resulting in heavy $\varepsilon^{112/110}\text{Cd}$ in surface seawater that is later incorporated into AAIW and Subantarctic Mode Water (SAMW). The northward flowing AAIW and SAMW are considered as the major return path in the upper ocean for the southward outflow of NADW at depth (Talley, 2013), and thus the SAMW/AIW combination is a source of heavy Cd to the North Atlantic, as suggested by Abouchami et al. (2014).

Another potential source of heavy Cd delivery to the North Atlantic may be the Arctic Ocean. Ripperger et al. (2007) reported $\varepsilon^{112/110}\text{Cd}$ of 2.15 ± 0.07 ($n = 2$) for intermediate and deep waters in the Arctic Ocean within the Canadian Basin. In the high latitude North Atlantic, the $\varepsilon^{112/110}\text{Cd}$ of Labrador Sea Water (LSW) and Denmark Strait Overflow Water (DSOW) (Powell et al., 2011 unpublished) are found to be identical to those of deep Arctic waters. Because LSW and DSOW contribute to the formation of upper and lower NADW, respectively, the Arctic Ocean is a plausible source of heavy Cd for NADW. This heavy Cd isotopic signature in the Arctic Ocean intermediate and deep waters might derive from shallow waters entering the Arctic from the Pacific (sill depths <50 m) and from the Atlantic (sill depths <2600 m) (Skagseth et al., 2008), as these waters originate at depth with heavy $\varepsilon^{112/110}\text{Cd}$.

The distinctive Cd isotopic signatures of deep waters originating in the Southern Ocean and those in the high-latitude North Atlantic greatly influence the distribution of Cd isotopes along the deep Atlantic Basin. By contrast, Pacific intermediate and deep waters have homogeneous $\varepsilon^{112/110}\text{Cd}$, slightly heavier than those of AABW (Conway and John, 2015b; Janssen et al., 2017; Ripperger et al., 2007), probably due to the dominant influence of southern-sourced water in the Pacific basin (Talley, 2013). Because major Cd sources for NADW derive from AAIW/SAMW and the Arctic Ocean, changes in primary productivity along the APF and the relative proportion of AAIW/SAMW vs. Arctic waters exert a fundamental control on the Cd and $\varepsilon^{112/110}\text{Cd}$ compositions of NADW, the former of which was previously discussed by Abouchami et al. (2011). Ultimately, primary productivity in the surface ocean followed by net export production into deep waters determines the preformed Cd and $\varepsilon^{112/110}\text{Cd}$ values for the NADW and AABW end-members. The Atlantic Meridional Overturning Circulation, on the other hand, governs the water mass mixing and thus the distribution of both Cd and $\varepsilon^{112/110}\text{Cd}$ in the deep ocean.

6. Conclusions

We have presented Cd isotopic compositions from five stations and 15 tow-Fish surface waters from 50°S to the equator along GEOTRACES GA02 Leg 3. This transect crosses several major water mass domains along the western boundary of the South Atlantic.

Depth profiles of Cd isotopic compositions from the western South Atlantic exhibit high $\varepsilon^{112/110}\text{Cd}$ at the surface and low $\varepsilon^{112/110}\text{Cd}$ at depth; this is consistent with preferential biological uptake of light Cd in the surface ocean, and appears ubiquitous in the oceans, globally, from previous studies. Biological uptake and remineralization set the Cd isotope compositions of water masses; by contrast, mixing between the northern-sourced and southern-sourced waters is the main control on intermediate and deep water $\varepsilon^{112/110}\text{Cd}$ along the western boundary.

Our data for surface and subsurface dissolved $\varepsilon^{112/110}\text{Cd}$ in the Southwest Atlantic do not show evidence for extreme, high $\varepsilon^{112/110}\text{Cd}$ in samples having very low Cd concentrations. Together with a global ocean data compilation, surface and subsurface waters show a relatively uniform $\varepsilon^{112/110}\text{Cd}$ of 3.8 ± 3.3 (2SD, $n = 164$). We propose two models to explain the “flattening off” in

$\varepsilon^{112/110}\text{Cd}$ in surface waters as Cd concentrations decrease to low levels. The first is that Cd may be bound by organic detritus (e.g. bacterial/picoplankton extracellular functional groups), colloids or ligands which then pass the 0.2 μm filtration of the samples and, at very-low Cd concentrations, may dominate $\varepsilon^{112/110}\text{Cd}$ over that of the dissolved pool. This explanation warrants further investigation. There is a second alternative explanation for the relatively constant $\varepsilon^{112/110}\text{Cd}$ in low-Cd samples: we show that a simple open system, steady-state model for the surface mixed layer, fed with an in-flux of Cd from deeper waters, provides a good fit to the global surface water $\varepsilon^{112/110}\text{Cd}$ dataset in regions north of the Southern Ocean.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2017.04.024>.

References

- Abouchami, W., Galer, S.J.G., De Baar, H.J.W., Alderkamp, A.C., Middag, R., Laan, P., Feldmann, H., Andreae, M.O., 2011. Modulation of the Southern Ocean cadmium isotope signature by ocean circulation and primary productivity. *Earth Planet. Sci. Lett.* 305, 83–91.
- Abouchami, W., Galer, S.J.G., de Baar, H.J.W., Middag, R., Vance, D., Zhao, Y., Klunder, M., Mezger, K., Feldmann, H., Andreae, M.O., 2014. Biogeochemical cycling of cadmium isotopes in the Southern Ocean along the Zero Meridian. *Geochim. Cosmochim. Acta* 127, 348–367.
- Baars, O., Abouchami, W., Galer, S.J.G., Boye, M., Croot, P.L., 2014. Dissolved cadmium in the Southern Ocean: distribution, speciation, and relation to phosphate. *Limnol. Oceanogr.* 59, 385–399.
- Borrok, D., Fein, J.B., Kulpa, C.F., 2004. Proton and Cd adsorption onto natural bacterial consortia: testing universal adsorption behavior. *Geochim. Cosmochim. Acta* 68, 3231–3238.
- Boyle, E.A., John, S., Abouchami, W., Adkins, J.F., Echegoyen-Sanz, Y., Ellwood, M., Flegal, A.R., Fornace, K., Gallon, C., Galer, S., 2012. GEOTRACES IC1 (BATS) contamination-prone trace element isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration. *Limnol. Oceanogr., Methods* 10, 653–665.
- Boyle, E.A., Sclater, F., Edmond, J.M., 1976. On the marine geochemistry of cadmium. *Nature* 263, 42–44.
- Bruland, K.W., 1992. Complexation of cadmium by natural organic ligands in the central North Pacific. *Limnol. Oceanogr.* 37, 1008–1017.
- Bruland, K.W., Franks, R.P., 1983. Mn, Ni, Cu, Zn and Cd in the western North Atlantic. In: Boyle, E., Bruland, K.W., Burton, J.D., Goldberg, E.D. (Eds.), *Trace Metals in Sea Water*. Springer, pp. 395–414.
- Bruland, K.W., Knauer, G.A., Martin, J.N., 1978. Cadmium in northeast Pacific waters. *Limnol. Oceanogr.* 23, 61EM25.
- Conway, T.M., Rosenberg, A.D., Adkins, J.F., John, S.G., 2013. A new method for precise determination of iron, zinc and cadmium stable isotope ratios in seawater by double-spike mass spectrometry. *Anal. Chim. Acta* 793, 44–52.
- Conway, T.M., John, S.G., 2015a. Biogeochemical cycling of cadmium isotopes along a high-resolution section through the North Atlantic Ocean. *Geochim. Cosmochim. Acta* 148, 269–283.
- Conway, T.M., John, S.G., 2015b. The cycling of iron, zinc and cadmium in the North East Pacific Ocean – Insights from stable isotopes. *Geochim. Cosmochim. Acta* 164, 262–283.

- Cox, J.S., Smith, D.S., Warren, L.A., Ferris, F.G., 1999. Characterizing heterogeneous bacterial surface functional groups using discrete affinity spectra for proton binding. *Environ. Sci. Technol.* 33, 4514–4521.
- Cullen, J.T., Lane, T.W., Morel, F.M., Sherrell, R.M., 1999. Modulation of cadmium uptake in phytoplankton by seawater CO₂ concentration. *Nature* 402, 165–167.
- Dulaquais, G., Boye, M., Rijkenberg, M., Carton, X., 2014. Physical and remineralization processes govern the cobalt distribution in the deep western Atlantic Ocean. *Biogeosciences* 11, 1561–1580.
- Ellwood, M.J., 2004. Zinc and cadmium speciation in subantarctic waters East of New Zealand. *Mar. Chem.* 87, 37–58.
- Ellwood, M.J., Van den Berg, C.M., 2000. Zinc speciation in the northeastern Atlantic Ocean. *Mar. Chem.* 68, 295–306.
- Fein, J.B., Daughney, C.J., Yee, N., Davis, T.A., 1997. A chemical equilibrium model for metal adsorption onto bacterial surfaces. *Geochim. Cosmochim. Acta* 61, 3319–3328.
- Fisher, N.S., Bohe, M., Teyssie, J., 1984. Accumulation and toxicity of Cd, Zn, Ag, and Hg in four marine phytoplankters. *Mar. Ecol. Prog. Ser.* 18, 201–213.
- Fitzsimmons, J.N., Carrasco, G.G., Wu, J., Roshan, S., Hatta, M., Measures, C.I., Conway, T.M., John, S.G., Boyle, E.A., 2015. Partitioning of dissolved iron and iron isotopes into soluble and colloidal phases along the GA03 GEOTRACES North Atlantic Transect. *Deep-Sea Res., Part 2, Top. Stud. Oceanogr.* 116, 130–151.
- Gault-Ringold, M., Adu, T., Stirling, C.H., Frew, R.D., Hunter, K.A., 2012. Anomalous biogeochemical behavior of cadmium in subantarctic surface waters: mechanistic constraints from cadmium isotopes. *Earth Planet. Sci. Lett.* 341–344, 94–103.
- Gélalbert, A., Pokrovsky, O., Schott, J., Boudou, A., Feurtet-Mazel, A., 2007. Cadmium and lead interaction with diatom surfaces: a combined thermodynamic and kinetic approach. *Geochim. Cosmochim. Acta* 71, 3698–3716.
- Gélalbert, A., Pokrovsky, O., Viers, J., Schott, J., Boudou, A., Feurtet-Mazel, A., 2006. Interaction between zinc and freshwater and marine diatom species: surface complexation and Zn isotope fractionation. *Geochim. Cosmochim. Acta* 70, 839–857.
- González-Dávila, M., 1995. The role of phytoplankton cells on the control of heavy metal concentration in seawater. *Mar. Chem.* 48, 215–236.
- Hao, L., Guo, Y., Byrne, J.M., Zeitvogel, F., Schmid, G., Ingino, P., Li, J., Neu, T.R., Swanner, E.D., Kappler, A., 2016. Binding of heavy metal ions in aggregates of microbial cells, EPS and biogenic iron minerals measured in-situ using metal- and glycoconjugates-specific fluorophores. *Geochim. Cosmochim. Acta* 180, 66–96.
- Horner, T.J., Lee, R.B., Henderson, G.M., Rickaby, R.E., 2013a. Reply to Morel: cadmium as a micronutrient and macrotoxin in the oceans. *Proc. Natl. Acad. Sci.* 110, E1878.
- Horner, T.J., Lee, R.B.Y., Henderson, G.M., Rickaby, R.E.M., 2013b. Nonspecific uptake and homeostasis drive the oceanic cadmium cycle. *Proc. Natl. Acad. Sci.* 110, 2500–2505.
- Horner, T.J., Rickaby, R.E., Henderson, G.M., 2011. Isotopic fractionation of cadmium into calcite. *Earth Planet. Sci. Lett.* 312, 243–253.
- Janssen, D.J., Abouchami, W., Galer, S.J.G., Cullen, J.T., 2017. Fine-scale spatial and interannual cadmium isotope variability in the subarctic northeast Pacific. *Earth Planet. Sci. Lett.* submitted for publication. <http://dx.doi.org/10.1016/j.epsl.2017.04.048>.
- John, S.G., Conway, T.M., 2014. A role for scavenging in the marine biogeochemical cycling of zinc and zinc isotopes. *Earth Planet. Sci. Lett.* 394, 159–167.
- John, S.G., Geis, R.W., Saito, M.A., Boyle, E.A., 2007. Zinc isotope fractionation during high-affinity and low-affinity zinc transport by the marine diatom *Thalassiosira oceanica*. *Limnol. Oceanogr.* 52, 2710–2714.
- Kenney, J.P., Fein, J.B., 2011. Cell wall reactivity of acidophilic and alkaliphilic bacteria determined by potentiometric titrations and Cd adsorption experiments. *Environ. Sci. Technol.* 45, 4446–4452.
- Lacan, F., Francois, R., Ji, Y., Sherrell, R.M., 2006. Cadmium isotopic composition in the ocean. *Geochim. Cosmochim. Acta* 70, 5104–5118.
- Lane, T.W., Morel, F.M., 2000. A biological function for cadmium in marine diatoms. *Proc. Natl. Acad. Sci.* 97, 4627–4631.
- Liu, Y., Alessi, D., Owttrim, G., Petrash, D., Mloszewska, A., Lalonde, S., Martinez, R., Zhou, Q., Konhauser, K., 2015. Cell surface reactivity of *Synechococcus* sp. PCC 7002: implications for metal sorption from seawater. *Geochim. Cosmochim. Acta* 169, 30–44.
- Mahowald, N.M., Engelstaedter, S., Luo, C., Sealy, A., Artaxo, P., Benitez-Nelson, C., Bonnet, S., Chen, Y., Chuang, P.Y., Cohen, D.D., 2009. Atmospheric iron deposition: global distribution, variability, and human perturbations. *Annu. Rev. Mar. Sci.* 1, 245–278.
- Mawji, E., Bakker, K., de Baar, H., Gerringa, L., Gonzales, S., Klunder, M., Laan, P., Rijkenberg, M., Salt, L., van Aken, H., 2015. The GEOTRACES Intermediate Data Product 2014.
- Middag, R., Van Slooten, C., De Baar, H., Laan, P., 2011. Dissolved aluminium in the Southern Ocean. *Deep-Sea Res., Part 2, Top. Stud. Oceanogr.* 58, 2647–2660.
- Morel, F.M., 2013. The oceanic cadmium cycle: biological mistake or utilization? *Proc. Natl. Acad. Sci.* 110, E1877.
- Orsi, A.H., Whitworth, I.I., Nowlin Jr., W.D., 1995. On the meridional extent and fronts of the Antarctic Circumpolar Current. *Deep-Sea Res., Part 1, Oceanogr. Res. Pap.* 42, 641–673.
- Price, N., Morel, F., 1990. Cadmium and cobalt substitution for zinc in a marine diatom. *Nature* 344, 658–660.
- Rijkenberg, M.J., de Baar, H.J., Bakker, K., Gerringa, L.J., Keijzer, E., Laan, M., Laan, P., Middag, R., Ober, S., van Ooijen, J., 2015. “PRISTINE”, a new high volume sampler for ultraclean sampling of trace metals and isotopes. *Mar. Chem.* 177, 501–509.
- Rijkenberg, M.J., Middag, R., Laan, P., Gerringa, L.J., van Aken, H.M., Schoemann, V., de Jong, J.T., de Baar, H.J., 2014. The distribution of dissolved iron in the West Atlantic Ocean. *PLoS ONE* 9, e101323.
- Ripperger, S., Rehkämper, M., Porcelli, D., Halliday, A., 2007. Cadmium isotope fractionation in seawater – a signature of biological activity. *Earth Planet. Sci. Lett.* 261, 670–684.
- Roshan, S., Wu, J., 2015. Cadmium regeneration within the North Atlantic. *Glob. Biogeochem. Cycles* 29, 2082–2094.
- Sakamoto-Arnold, C.M., Hanson, A.K., Huizenga, D.L., Kester, D.R., 1987. Spatial and temporal variability of cadmium in Gulf Stream warm-core rings and associated waters. *J. Marine Res.* 45, 201–230.
- Sarmiento, J.L., Gruber, N., Brzezinski, M.A., Dunne, J.P., 2004. High-latitude controls of thermocline nutrients and low latitude biological productivity. *Nature* 427, 56–60.
- Schlitzer, R., 2014. Ocean data view. <http://odv.awi.de>.
- Schmitt, A.-D., Galer, S.J.G., Abouchami, W., 2009. High-precision cadmium stable isotope measurements by double spike thermal ionisation mass spectrometry. *J. Anal. At. Spectrom.* 24, 1079–1088.
- Skagseth, Ø., Furevik, T., Ingvaldsen, R., Loeng, H., Mork, K.A., Orvik, K.A., Ozhigin, V., 2008. Volume and heat transports to the Arctic Ocean via the Norwegian and Barents Seas. In: Dickson, R.R., Meincke, J., Rhines, P. (Eds.), *Arctic-Subarctic Ocean Fluxes: Defining the Role of the Northern Seas in Climate*. Springer, Netherlands, Dordrecht, pp. 45–64.
- Sunda, W., 2012. Feedback interactions between trace metal nutrients and phytoplankton in the ocean. *Front. Microbiol.* 3, 204.
- Sunda, W.G., Huntsman, S.A., 2000. Effect of Zn, Mn, and Fe on Cd accumulation in phytoplankton: Implications for oceanic Cd cycling. *Limnol. Oceanogr.* 45, 1501–1516.
- Talley, L.D., 2013. Closure of the global overturning circulation through the Indian, Pacific, and Southern Oceans: schematics and transports. *Oceanography* 26, 80–97.
- Taylor, S.R., McLennan, S.M., 1985. *The Continental Crust: Its Composition and Evolution*.
- Wasylenko, L.E., Swihart, J.W., Romaniello, S.J., 2014. Cadmium isotope fractionation during adsorption to Mn oxyhydroxide at low and high ionic strength. *Geochim. Cosmochim. Acta* 140, 212–226.
- Xie, R.C., Galer, S.J.G., Abouchami, W., Rijkenberg, M.J.A., De Jong, J., de Baar, H.J.W., Andreea, M.O., 2015. The cadmium-phosphate relationship in the western South Atlantic – the importance of mode and intermediate waters on the global systematics. *Mar. Chem.* 177 (Part 1), 110–123.
- Xu, Y., Morel, F.M., 2013. Cadmium in Marine Phytoplankton, Cadmium: From Toxicity to Essentiality. Springer, pp. 509–528.
- Xue, Z., Rehkämper, M., Horner, T.J., Abouchami, W., Middag, R., van de Flied, T., de Baar, H.J.W., 2013. Cadmium isotope variations in the Southern Ocean. *Earth Planet. Sci. Lett.* 382, 161–172.
- Xue, Z., Rehkämper, M., Schönbachler, M., Statham, P., Coles, B., 2012. A new methodology for precise cadmium isotope analyses of seawater. *Anal. Bioanal. Chem.* 402, 883–893.
- Yang, J., Li, Y., Liu, S., Tian, H., Chen, C., Liu, J., Shi, Y., 2015. Theoretical calculations of Cd isotope fractionation in hydrothermal fluids. *Chem. Geol.* 391, 74–82.
- Yang, S.-C., Lee, D.-C., Ho, T.-Y., 2012. The isotopic composition of cadmium in the water column of the South China Sea. *Geochim. Cosmochim. Acta* 98, 66–78.
- Yang, S.-C., Lee, D.-C., Ho, T.-Y., Wen, L.-S., Yang, H.-H., 2014. The isotopic composition of dissolved cadmium in the water column of the West Philippine Sea. *Front. Marine Sci.* 1, 61.
- Yang, S.-C., Lee, D.-C., Ho, T.-Y., 2015. Cd isotopic composition in the suspended and sinking particles of the surface water of the South China Sea: the effects of biotic activities. *Earth Planet. Sci. Lett.* 428, 63–72.
- Yee, N., Fein, J., 2001. Cd adsorption onto bacterial surfaces: a universal adsorption edge? *Geochim. Cosmochim. Acta* 65, 2037–2042.