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High-resolution Cd isotope systematics in multiple zones of the Southern Ocean from the Antarctic Circumnavigation Expedition

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Highlights:

- High-resolution Cd and $\delta^{114}\text{Cd}$ profiles from multiple zones and sectors of the Southern Ocean
- $\delta^{114}\text{Cd}$ fractionation factors show slight variations across different Southern Ocean zones ($\alpha = 0.99942$ to 0.99965)
- Natural Fe fertilization of surface waters off the Balleny Islands reduces phytoplankton demand for Cd
- The first complete picture of Cd and $\delta^{114}\text{Cd}$ cycling in the Pacific Ocean

Keywords:

trace metals; biogeochemistry; Antarctic Circumnavigation Expedition (ACE); Southern Ocean; Cd isotopes

Abstract

The Southern Ocean plays a major role in determining the global distribution of trace metals such as cadmium (Cd). Here, we present 17 high-depth-resolution profiles of dissolved Cd and its stable isotope composition ($\delta^{114}\text{Cd}$) over the top 1000 m of the Pacific and Atlantic sectors of the Southern Ocean, collected during the Antarctic Circumnavigation Expedition. Our dataset reinforces the view that Cd and its isotopes are dominated by shallow biological cycling in this region. A close examination of variations in Cd cycling across the different zones of the Southern Ocean reveals how the interplay between uptake and regeneration, seasonal mixing, and upwelling controls both Cd and $\delta^{114}\text{Cd}$ in this region. The only deviations from these systematics are due to the influence of local processes such as continental influence or Fe-fertilisation, close to the Mertz Glacier and the Balleny Islands, respectively. Deep convection during winter incorporates the Southern Ocean Cd isotope signatures into Subantarctic Mode Water and Antarctic Intermediate Water during water mass formation. Incorporating published data, we present the first complete picture of how Cd is cycled through the entire Pacific Ocean, revealing the manner in which the Southern Ocean controls the global cycling of Cd and $\delta^{114}\text{Cd}$; analogous to Si or Zn, we propose that Southern Ocean processes, in combination with global ocean circulation, cause a division into two separate Cd regimes, a Cd-depleted surface ocean above a Cd-rich deep ocean loop. Therefore, the relationship between Cd and PO_4 on a global scale is largely a result of these processes in the Southern Ocean, rather than a local correlation between the two elements.

1. Introduction

In the global ocean, the trace element cadmium (Cd) exhibits a spatial distribution similar to the major nutrients phosphate (PO_4) and nitrate (NO_3), suggesting a possible nutrient role for Cd for marine life (e.g. Bruland, 1980). Despite Cd's known toxicity for phytoplankton at high concentrations (Brand et al., 1986), there is clear evidence that Cd relieves zinc (Zn) limitation, and acts as a micronutrient in phytoplankton, substituting for Zn in the enzyme carbonic anhydrase (Lane and Morel, 2000; Lane et al., 2005). Cd uptake is also closely linked to availability of other trace metal micronutrients like iron (Fe) and Zn (e.g. Sunda and Huntsman, 2000; Cullen, 2006), suggesting common uptake pathways. Other studies, on the other hand, have suggested that Cd uptake may be accidental (Horner et al., 2013). Though the exact biological function of Cd in phytoplankton remains unclear, the nutrient-type distribution of dissolved Cd, together with its close coupling to PO_4 , make Cd a useful tracer of processes associated with biological cycling. Furthermore, dissolved Cd stable isotope ratios ($\delta^{114}\text{Cd}$) can provide insights into global marine nutrient cycles. Dissolved $\delta^{114}\text{Cd}$ can therefore also provide us with a better understanding of the relationship between the spatial distributions of Cd and macronutrients, and help disentangle other processes that affect major nutrient cycling (e.g. nitrogen fixation).

The dissolved $\delta^{114}\text{Cd}$ composition of seawater has now been characterized by multiple studies in most major ocean basins except the Indian Ocean. The surface oceans, where Cd concentrations are most depleted, typically display heavier Cd isotopes than the subsurface ocean (+1 to +5‰). This has been attributed to the preferential biological uptake of light Cd by phytoplankton, consistent with data from culturing experiments (Lacan et al., 2006; John and Conway, 2014). In the Southern Ocean particularly, upper ocean Cd systematics have been modeled following closed-system Rayleigh fractionation, with a fractionation factor (α) ranging from 0.9995 to 0.9998 (Abouchami et al., 2011, 2014; Xue et al., 2013). In several areas of the

global ocean, a heavy $\delta^{114}\text{Cd}$ signal ($\sim +0.5\text{‰}$) extends down to intermediate depths ($\sim 1500\text{ m}$) (e.g. Conway and John, 2015; Xie et al., 2017; Sieber et al., 2019), associated with the presence of intermediate waters carrying preformed signatures that originate in the surface Southern Ocean (Abouchami et al., 2014). The high latitudes, where these southern-sourced intermediate water masses are absent, are strikingly different: both in the Southern Ocean and the North Pacific the heavy Cd isotopes are restricted to the upper ocean (above $\sim 500\text{ m}$; e.g. Xue et al., 2013; Janssen et al., 2017). Below a depth of 500-1500m, the deep ocean displays relatively homogeneous $\delta^{114}\text{Cd}$ ($+0.2$ to $+0.3\text{‰}$; e.g. Xue et al., 2013; Abouchami et al., 2014; Conway and John, 2015a, 2015b; Janssen et al., 2017; Xie et al., 2017, 2018; John et al., 2018; Sieber et al., 2019), with the exception of Cd-poor North Atlantic Deep Water ($+0.4$ to $+0.5\text{‰}$; e.g. Conway and John, 2015).

The Southern Ocean includes all waters south of the Subtropical Front (STF), and holds a unique role in global ocean circulation. The dominant feature of the Southern Ocean is the eastward-flowing Antarctic Circumpolar Current (ACC) that encircles Antarctica and connects the Pacific, Atlantic and Indian ocean basins (Talley, 2013). Within the ACC, wind-driven upwelling brings nutrient-rich Upper Circumpolar Deep Water (UCDW) to the surface (Talley et al., 2011). The upwelling of nutrient-rich waters, combined with Fe and light limitation in this region of the surface ocean, combine to form the world's largest high-nutrient low-chlorophyll (HNLC) region (e.g. Martin et al., 1990). Part of these waters flows southwards where, due to low temperatures in the high southern latitudes and sea ice formation, very dense deep waters are formed that eventually flow northwards in the deepest parts of the oceans. Another portion of the upwelling waters flows northwards where intermediate water masses, Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW), are formed and exported to the low latitudes (e.g. McCartney, 1982; Sloyan and Rintoul, 2001). During the northward surface transport, phytoplankton take up large amounts of Cd, Zn and Si relative to the major nutrients nitrate and phosphate, and imprint a distinct biogeochemical signal on

Southern Ocean surface waters (Sarmiento et al., 2004; Zhao et al., 2014; Vance et al., 2017). During intermediate water formation, the characteristic biogeochemical signatures formed in the surface Southern Ocean are imparted to SAMW and AAIW, before they flow northwards into the low latitude oceans (Sarmiento et al., 2004). Hence, several authors have shown that biogeochemical processes in the surface Southern Ocean have a strong effect on the global distribution of Si, Zn and Cd (e.g. Sarmiento et al., 2007; Abouchami et al., 2014; Vance et al., 2017).

Though most early Cd isotope studies have focused on the Southern Ocean, data remain sparsely distributed (Abouchami et al., 2011, 2014; Gault-Ringold et al., 2012; Xue et al., 2013; Sieber et al., 2019). Together with the concentration-only study of Baars et al. (2014), these earlier studies have shown that Cd signatures in Southern Ocean waters are dominated by upwelling and shallow biological cycling, with elevated Cd uptake relative to PO_4 . We thus have a basic understanding of Cd cycling in the Southern Ocean and its effects on the global Cd distribution, but the published data lack the resolution to fully capture the Cd isotope systematics relating to biological processes in the upper ocean. Here, we present 17 profiles of high-depth-resolution dissolved Cd concentration and $\delta^{114}\text{Cd}$ data from the top 1000 m of the water column in the Pacific and Atlantic sectors of the Southern Ocean, covering all the major zones of the Southern Ocean, from the Antarctic Circumnavigation Expedition (ACE). Our high-resolution dataset allows us to investigate in detail the surface and near-surface cycling processes and their effect on the distribution of Cd and its isotopes in the Southern Ocean. Cd isotopes in the upper Southern Ocean mostly follow Rayleigh systematics, but we also identify how ice edge processes and Southern Ocean islands affect the systematics. Examination of the formation regions of SAMW and AAIW demonstrates how distinct surface Southern Ocean Cd signatures are imprinted on these intermediate water masses by deep winter convection. Furthermore, by combining our data with previous studies, we develop a synthesis of the

manner in which the Southern Ocean controls the large-scale cycling of Cd, and obtain the first complete picture of Cd cycling through the Pacific.

2. Methods

2.1 Oceanographic setting of the Antarctic Circumnavigation Expedition

The study region, the Atlantic and Pacific sectors of the Southern Ocean, encompasses all of the major Southern Ocean zones from the STF to the Antarctic shelf (Fig. 1). Three major ACC fronts separate the broad, dynamically and biogeochemically rather homogeneous zones of the ACC (Orsi et al., 1995). The Subantarctic Front (SAF) and the dynamical Southern ACC Front (SACCF) mark the northern and southern extent of the ACC, respectively, while the Antarctic Polar Front (APF) is the central ACC front. The fronts are associated with transitions in water properties and biogeochemical characteristics. Towards Antarctica to the south, the Southern Boundary (SB) is defined as the southern extent of low-oxygen UCDW. The Southern Zone (SZ) lies between the SB and the Antarctic shelf, and encompasses the Weddell and Ross Gyres. The ACC is strongest within the Antarctic Zone (AZ), located between the SACCF and the APF, where wind-driven upwelling brings nutrient-rich UCDW to the surface (Talley et al., 2011). In the upper ocean of the AZ, Antarctic Surface Water (AASW) is transported northwards across the APF and into the Polar Frontal Zone (PFZ) by Ekman transport. Formation of intermediate water masses, SAMW and AAIW, occurs by deep vertical convection in the PFZ and, north of the SAF, in the Subantarctic Zone (SAZ) (Sallée et al., 2010). Both SAMW and AAIW deepen northwards before they cross the STF, which marks the northern boundary of the Southern Ocean.

2.2 Seawater Sampling

Seawater samples were collected during Legs 2 and 3 of the Antarctic Circumnavigation Expedition on board the R/V Akademik Tryoshnikov during austral summer 2017 (January -

March 2017; Fig. 1). High-depth-resolution profiles (6 to 8 samples in the top 200 m) at seventeen stations (ACE station numbers 08 - 20, 22 - 25) in the Atlantic and Pacific sectors, and covering all the major zones of the Southern Ocean, were sampled for dissolved Cd and $\delta^{114}\text{Cd}$ (Fig. 1). Seawater samples were collected using acid-cleaned, Teflon-coated, externally-sprung, 10-liter Niskin bottles coupled to an autonomous rosette (Model 1018, General Oceanics, USA) attached to a Dynema line. Samples were filtered through AcroPak capsule filters (0.2 μm , Pall) into acid-cleaned 1 L or 4 L LDPE bottles. The filtered seawater samples were later acidified at ETH Zürich by addition of 1.2 mL 9.6 M Teflon double-distilled HCl ($<1 \text{ pg g}^{-1} \text{ Cd}$) per liter of sample (Sieber et al., 2019), and samples were stored for at least 3 months at pH ~ 2 before processing.

2.3 Sample processing and analysis for Cd and $\delta^{114}\text{Cd}$

Prior to sample processing, preliminary Cd concentrations were determined on small (45 mL) subsamples that had been preconcentrated using a seaFAST system (Elemental Scientific; Lagerström et al., 2013), by isotope dilution, on an Element XR HR-ICP-MS at the University of South Florida. These analyses were simply used to guide later double-spike addition for isotope analyses, and the data are not reported here. Larger volume samples (1-4 L) were processed for isotope analysis followed by analysis of Cd concentration and isotopic composition on a Thermo Neptune Plus MC-ICP-MS at ETH Zürich. The methodology, using a ^{111}Cd - ^{113}Cd double-spike, a batch extraction technique using Nobias PA-1 chelating resin, and purification by anion-exchange chromatography using AG-MP1 resin, was identical to recently-published methods (Sieber et al., 2019), and we refer the reader there for further details. The method has a full procedural blank of $<1 \text{ pg}$ per liter of seawater processed. We express Cd stable isotope ratios in delta notation relative to the NIST SRM-3108 Cd standard (Abouchami et al., 2013):

$$\delta^{114/110}\text{Cd} = \left[\frac{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{sample}}}{(^{114}\text{Cd}/^{110}\text{Cd})_{\text{NIST SRM-3108}}} - 1 \right] \times 1000$$

We express precision as 2σ uncertainty on $\delta^{114}\text{Cd}$ as the long-term 2x standard deviation of secondary isotope standards (0.06‰; reported in Sieber et al., 2019), except for low concentration samples where the larger internal error is considered a more conservative estimate of uncertainty. Concentrations were calculated using the isotope dilution technique based on on-peak blank, interference and mass-bias corrected $^{114}\text{Cd}/^{111}\text{Cd}$ ratios measured simultaneously with isotope analyses (Sieber et al., 2019). We assign 2% uncertainty on concentrations measured using this approach (Conway et al., 2013).

2.4 Phosphate analyses and Cd*

Dissolved phosphate concentrations were determined at the Alfred Wegener Institute, using flow injection analysis (QQAatro Seal Analytical autoanalyser, method Q-064-05 Rev 6) with Certipur standard solutions (Merck). The detection limit was $0.013 \mu\text{mol kg}^{-1}$, and accuracy was verified using certified reference materials (KANSO LTD). We calculated Cd*, a parameter that indicates whether the dissolved pool is enriched or depleted in Cd relative to the Cd:PO₄ ratio of the deep ocean, following Janssen et al. (2014). This calculation was based on measured Cd and PO₄ concentrations in this study, using the deep Southern Ocean Cd:PO₄ ratio as a reference point ($0.35 \text{ mmol mol}^{-1}$; Sieber et al., 2019).

$$\text{Cd}^* = \text{Cd} - \text{PO}_4 \times 0.35 \text{ mmol mol}^{-1}$$

3. Results

Dissolved Cd depth profiles exhibit nutrient-type behavior at all stations, consistent with previous observations (Boyle et al., 1976; Schlitzer et al., 2018). Cadmium concentrations range from 4 pmol kg^{-1} in surface waters up to $1.02 \text{ nmol kg}^{-1}$ at depth (Figs 2, 3, Supplementary Data). While stations within each dynamic-biogeochemical zone of the Southern Ocean display

remarkably similar profile shapes, even across different sectors, there are systematic differences between stations located in different zones (Fig. 2). Stations south of the APF exhibit elevated surface Cd concentrations ($>0.2 \text{ nmol kg}^{-1}$), a sharp increase to a shallow maximum (100 – 200 m; up to 1 nmol kg^{-1}), and near-constant concentrations below (Fig. 2c-d). The highest open ocean surface Cd concentrations ($>0.5 \text{ nmol kg}^{-1}$) occur in the Ross and Weddell gyres (Fig. 3a), but we observe the highest surface Cd concentrations in our dataset at station 14, located near the Balleny Islands ($0.62 \text{ nmol kg}^{-1}$). An exception to this pattern are surface waters at the two stations (11, 12) located on the Antarctic shelf close to the Mertz Glacier, that show the lowest surface Cd concentrations ($<0.1 \text{ nmol kg}^{-1}$) observed south of the SAF (Fig. 3c). Stations located in the SAZ (Fig 2a) show the lowest surface concentrations observed in this study ($<0.01 \text{ nmol kg}^{-1}$), and a gradual increase in concentrations in deeper water that continues throughout the profiles. Previous studies in the SAZ region suggest that Cd concentrations continue to increase with depth, to a maximum at $\sim 1500 \text{ m}$ (Xie et al., 2017; Sieber et al., 2019), which would be consistent with our findings, but is below the depth range studied here. The stations in the PFZ (Fig. 2b) depict the transition from the AZ to the SAZ, with a northward decrease in surface concentrations and a deepening of the Cd maximum towards the SAF.

For all stations, dissolved $\delta^{114}\text{Cd}$ ranges between $+0.11$ and $+0.96\text{‰}$, and depth profiles typically show an inverse relationship to Cd concentrations (Figs 2, 3, Supplementary Data). Thus, consistent $\delta^{114}\text{Cd}$ profiles are seen within zones, but systematic changes are observed between zones. Stations south of the APF exhibit elevated $\delta^{114}\text{Cd}$ in the surface ocean, with $\delta^{114}\text{Cd}$ increasing ($+0.45$ to $+0.92\text{‰}$) as Cd concentrations decrease northwards towards the APF (Fig. 2c). Surface waters at stations close to the Mertz Glacier (11, 12) exhibit similar $\delta^{114}\text{Cd}$ ($\sim +0.5\text{‰}$), despite their low concentrations (Fig. 3c). The high-Cd surface waters at stations near the Balleny Islands (13, 14), show the lowest $\delta^{114}\text{Cd}$ across all stations studied here ($+0.34\text{‰}$; Fig. 3b). Below $\sim 300 \text{ m}$, $\delta^{114}\text{Cd}$ profiles at all stations south of the APF return to a constant deep ocean value ($+0.23 \pm 0.09\text{‰}$, 2SD, $n = 29$; Fig 2c-d). In the PFZ, surface

water $\delta^{114}\text{Cd}$ gets increasingly higher (up to +0.96‰) as Cd concentrations continue to decrease northwards towards the SAF (Fig. 2c). Furthermore, high surface $\delta^{114}\text{Cd}$ extends to greater depths in the PFZ than in the AZ, before also returning to a constant deep ocean value ($+0.29 \pm 0.05\text{‰}$, 2SD, $n = 4$; Fig. 2b). While surface Cd concentrations continue to decrease further in the SAZ, this change does not appear to significantly affect the isotopic signal, with surface $\delta^{114}\text{Cd}$ in the SAZ similar to those observed further south (up to +0.81‰; Fig. 2a). However, elevated $\delta^{114}\text{Cd}$ is observed over the entire depth range studied here.

4. Discussion

We first discuss the coherence of Cd and $\delta^{114}\text{Cd}$ within the zones of the ACC before examining the differences observed in regions influenced by ice edge processes and islands. We then discuss the Cd isotope systematics in the upper Southern Ocean, and identify how these Cd signatures are imparted to intermediate waters and exported out of the Southern Ocean. Finally, we consider the role of the Southern Ocean in the global distribution of Cd and $\delta^{114}\text{Cd}$, and present the first complete picture of Cd cycling in the Pacific Ocean.

4.1 Cd and $\delta^{114}\text{Cd}$ in the ACC

Here, we aim to unravel the influence on Cd and $\delta^{114}\text{Cd}$, of the two major processes operating in the upper Southern Ocean, namely biological cycling and upwelling of deep waters. Our high-resolution data allows us to examine the influence of these processes, previously identified as important for Cd cycling in the Southern Ocean (Abouchami et al., 2011, 2014; Xue et al., 2013; Baars et al., 2014), in unprecedented detail. In order to identify the key features, we combine our observations of Cd concentrations, $\delta^{114}\text{Cd}$, and Cd*.

The relatively high Cd concentrations found in AASW throughout the AZ are a result of upwelling of Cd-rich UCDW within the ACC. However, uptake of Cd by phytoplankton in

surface waters leads to lower surface Cd concentrations than in the upwelling deep waters (Figs 2, 3). This surface uptake, with its preference for lighter Cd isotopes, also results in a high remnant dissolved $\delta^{114}\text{Cd}$ pool, as well as strongly negative Cd^* due to higher phytoplankton uptake of Cd relative to PO_4 (Abouchami et al., 2014; Baars et al., 2014). The surface signals observed in Cd concentrations, $\delta^{114}\text{Cd}$, and Cd^* display a consistent pattern with latitude: from south to north, concentrations decrease, $\delta^{114}\text{Cd}$ increases and Cd^* becomes more negative, driven by continuous biological uptake during northward advection of AASW. This pattern extends into the PFZ, where we find the most extreme $\delta^{114}\text{Cd}$ and Cd^* in surface waters (Fig. 2b).

The shallow-subsurface Cd maximum found in the AZ is associated with a dramatic shift to positive Cd^* , while $\delta^{114}\text{Cd}$ shifts to values similar to deep waters. The positive Cd^* signal indicates that there is a Cd excess relative to PO_4 that cannot originate from upwelling UCDW (which has a $\text{Cd}^* = 0 \text{ nmol kg}^{-1}$ by definition) or deep mixing of AASW (which has low Cd and $\text{Cd}^* < 0$), but instead derives from shallow remineralization of Cd-enriched biological particles (Xue et al., 2013; Sieber et al., 2019). This is reinforced by the fact that the Cd maximum occurs at shallower depths than the oxygen minimum associated with the core of upwelling UCDW (Talley, 2013). Variation in Cd^* (+0.1 to +0.2 nmol kg^{-1}) associated with the Cd maximum are likely the result of regional differences in export, and hence in the extent to which local regeneration of Cd is superimposed upon the upwelling signal. Despite the expected input of isotopically lighter Cd to the dissolved pool during regeneration of biological material, we do not observe any $\delta^{114}\text{Cd}$ minimum in the subsurface of any stations in the AZ (in contrast to the SZ; see below), and $\delta^{114}\text{Cd}$ remains fairly constant below ~100 m.

This absence of a subsurface $\delta^{114}\text{Cd}$ minimum can, in part, be explained by mixing processes, with convection during winter transferring the heavier $\delta^{114}\text{Cd}$ signals from the Cd-depleted summer surface into the shallow subsurface (~100 m), counteracting the addition of

isotopically light Cd by regeneration. However, seasonal mixing cannot explain the lack of lower $\delta^{114}\text{Cd}$ values below the mixed layer (~200 m). Sieber et al. (2019) showed that this is the result of the superposition of two processes occurring at similar depths: upwelling of subantarctic UCDW carrying slightly heavier Cd (+0.30‰), and input of regenerated, isotopically light Cd. This argument is strengthened by evidence from stations located south of the SB, beyond the southernmost reach of UCDW: these stations (e.g. 15, 18) show slightly lower $\delta^{114}\text{Cd}$ associated with the Cd maximum resulting from shallow remineralization (Fig. 2d). However, Janssen et al. (2019) have shown that the interaction between particulate and dissolved $\delta^{114}\text{Cd}$ appears to be more complex than a simple one-dimensional process. Further work on Cd in marine particles will be required to better understand the influence of particulate Cd on dissolved $\delta^{114}\text{Cd}$.

The homogeneity of the deep ocean in Cd concentration (0.75 nmol kg⁻¹), $\delta^{114}\text{Cd}$ (+0.23‰) and zero Cd*, reflects the fact that this part of the water column is dominated by LCDW, which does not interact directly with the surface ocean or processes occurring there. The lack of Cd, $\delta^{114}\text{Cd}$ and Cd* variations in LCDW is therefore a consequence of the circulation pattern and the relatively shallow regeneration length scales of Cd and PO₄ within the Southern Ocean, confining variability to water masses above 300 m.

The effect of these surface and near-surface processes is reflected in the Cd-PO₄ relationship for the Southern Ocean (Fig. 4), making it distinctly different from the global Cd-PO₄ relationship. While the global relationship shows a nonlinear correlation with a pronounced break in slope, largely as a result of water mass mixing (e.g. Quay et al., 2015; Middag et al., 2018), Fig. 4 shows a single linear relationship between Cd and PO₄ in the upper Southern Ocean. This is due to the strong influence of biological cycling on the distributions of these two elements in the upper Southern Ocean. The high-depth-resolution of our dataset permits a detailed examination of the effects of these processes on the Cd-PO₄ relationship south of the

APF. As expected, LCDW is consistent with the global relationship and plots near the upper end of the global trend line. In contrast, surface waters plot on the lower end and below the global trend, due to uptake by Southern Ocean phytoplankton (Baars et al., 2014). Increased Cd uptake rates are likely related to Fe limitation in the Southern Ocean (Sunda and Huntsman, 2000; Cullen et al., 2003). Shallow remineralization in the subsurface Southern Ocean leads to a relative enrichment of Cd in shallow subsurface waters, which therefore plot above the global trend. Figure 4b also highlights the exceptionally systematic variability of $\delta^{114}\text{Cd}$ within the Cd-PO₄ relationship, variations that correlate well with Cd*, i.e. the depletion of Cd relative to PO₄ (Abouchami et al., 2011). Together, these systematics clearly reveal biological cycling (surface uptake and shallow sub-surface remineralization) to be the dominant driver of Cd isotope variations within the ACC.

4.2 Ice edge processes

On the Antarctic shelf, in the vicinity of the Mertz Glacier, surface waters exhibit significantly lower Cd ($<0.1 \text{ nmol kg}^{-1}$) and PO₄ ($<1 \text{ } \mu\text{mol kg}^{-1}$; Fig. 5a) concentrations than at other stations south of the SB. In the upper few tens of meters, where Cd concentrations are lowest, salinity is also significantly lower than in open ocean waters (down to 32.5 psu, Fig. 5a). This freshening is likely an indication of the influence of meltwater from the Mertz Glacier. However, a salinity normalization of Cd concentrations (Fig. 5a) shows that the low surface concentrations cannot be explained by a simple dilution associated with the freshening. These low Cd concentrations must thus point to increased biological uptake in this region, consistent with the depletion in macronutrients observed here (e.g. PO₄). Enhanced productivity could potentially be driven by Fe supply transported to surface waters via glacial meltwater (Sherrell et al., 2015) or some other means of continental input. However, the gradient to very low Cd concentrations in the uppermost 50 m of the water column is not accompanied by a

corresponding gradient in $\delta^{114}\text{Cd}$ values (Figs 5a,b), suggesting that an additional process affects the Cd isotope signal in these lower-salinity surface waters, causing a decoupling between Cd concentrations and $\delta^{114}\text{Cd}$ (Fig. 5c). The low-Cd surface waters that are associated with reduced salinity do not follow the same Rayleigh systematics that are observed in other sectors of the Southern Ocean (Fig. 6; Section 4.4). A possible explanation for the decoupling of Cd and $\delta^{114}\text{Cd}$ in the upper few tens of meters could be a small addition of Cd from continental sources with a near-crustal $\delta^{114}\text{Cd}$ signature ($\sim +0.1\text{‰}$; Lambelet et al., 2013). Due to the low surface Cd concentrations, even small inputs of isotopically light Cd could affect $\delta^{114}\text{Cd}$ signatures in these surface waters, pulling them off the general biologically-driven Southern Ocean relationship with Cd concentration (Fig. 5c). We speculate that this Cd input could be associated with glacial meltwater, possibly brought to surface waters in particulate form, or adsorbed to particles. However, we lack additional parameters such as particulate Cd concentrations or transmissivity to unravel the complex interactions in the upper few tens of meters between biological uptake, freshening and a potential Cd source; importantly, given the clear signs of strong biological activity and thus nutrient drawdown in the region, such a source of isotopically light Cd need not be reflected by elevated Cd concentrations. In the subsurface, $\delta^{114}\text{Cd}$ are consistent with Rayleigh systematics observed in other sectors of the Southern Ocean (Fig. 6; Section 4.4) and the steep return to constant Cd concentrations and $\delta^{114}\text{Cd}$ at ~ 150 m suggests that the underlying Continental Shelf Water (CSW) remains mostly unaffected by the surface processes. In fact, a glacial influence may be contained within the very shallow surface layer by the dense CSW ($0.73 \text{ nmol kg}^{-1}$, $+0.27 \pm 0.05\text{‰}$, 2SD, $n = 11$) below.

4.3 Island Influences

At stations 13 and 14, located near the Balleny Islands, both Zn and Fe show elevated surface concentrations and a steep increase in the subsurface to relatively constant values below

(Fig. S1). These high Fe concentrations within the winter mixed layer are indicative of Fe supply from the islands that results in natural Fe fertilization of surface waters around the Balleny Islands, analogous to that observed at other Antarctic Island Chains (e.g. Planquette et al., 2011), and consistent with satellite observations of elevated chlorophyll-a concentrations at the time of sampling (Fig. S2).

Although Cd profiles exhibit similar surface elevation to Fe (Fig. 3b), it is unlikely that higher Cd concentrations can be attributed to an island source. The Cd/Fe ratio of a potential lithological source would be 1.4 $\mu\text{mol/mol}$ (Taylor and McLennan, 1985), orders of magnitude lower than the ratio observed in surface waters (~ 7 mol/mol at station 14). Thus, we propose that elevated surface Cd concentrations stem from reduced phytoplankton demand for Cd when relieved from Fe limitation. To estimate drawdown by phytoplankton uptake in surface waters, relative to supply from the mixed layer, we calculate the difference between surface water and winter mixed layer concentrations (~ 100 m). The relative Cd concentration difference at stations near the islands (13, 14; 0.2 nmol kg^{-1}) is approximately half compared to stations in the Fe-limited AZ (10, 17, 19; $\sim 0.4 \text{ nmol kg}^{-1}$), while relative PO_4 concentration differences are similar in both settings ($0.3 - 0.4 \mu\text{mol kg}^{-1}$). This indicates reduced Cd uptake by phytoplankton relative to PO_4 in waters affected by Fe fertilization, consistent with culturing data showing that elevated concentrations of Zn and Fe reduce the uptake rates of Cd (Sunda and Huntsman, 2000). Consistent with lower Cd utilization, $\delta^{114}\text{Cd}$ in these high-Cd surface waters are the lowest across all stations studied here ($+0.34\text{‰}$), despite a slightly lower fractionation factor (Fig. S3).

4.4 Southern Ocean Cd fractionation systematics

Fig. 6 shows the Cd isotope systematics in the upper 300 m of the Southern Ocean and allows us to identify fractionation trends in different oceanic regimes. Though there are slight

variations between the different zones, the upper ocean at all stations south of the SAF follow similar Rayleigh systematics (Fig. 6a), consistent with a fractionation factor (α , where $\alpha = R_{\text{phytoplankton}}/R_{\text{seawater}}$ and $R = {}^{114}\text{Cd}/{}^{110}\text{Cd}$) of 0.99955 ± 0.00002 , in good agreement with field (Abouchami et al., 2011; Xue et al., 2013) and culturing (e.g. Horner et al., 2013) studies. The data from the stations located on the Antarctic shelf, in the vicinity of Mertz Glacier (11, 12), which do not follow a simple Rayleigh model (Fig. 6a) are an exception, as are data in the Weddell Gyre and near the Balleny Islands, which follow slightly different Rayleigh trends (0.99945 ± 0.00002 and 0.99942 ± 0.00008 respectively; Fig. S3) to the rest of the stations south of the SAF, consistent with previous observations (Abouchami et al., 2011), and could potentially be linked to natural Fe-fertilization (Section 4.3; de Jong et al., 2012). Surface waters north of the SAF are considerably lower in Cd but show similar $\delta^{114}\text{Cd}$, following a shallower trend than those south of the SAF that is consistent with previous observations (Gault-Ringold et al., 2012; Xie et al., 2017). A possible explanation for this trend has been put forward recently by Xie et al. (2017), who suggest that $\delta^{114}\text{Cd}$ in these waters can be explained by an open system, steady-state model, rather than closed system Rayleigh fractionation. While processes that may lead to muted fractionation of surface Cd isotopes are still a matter of debate (Janssen et al., 2017; Xie et al., 2017, 2019; George et al., 2019; Sieber et al., 2019), and whatever the mechanism causing this change in fractionation, there is a dramatic shift north of the SAF in the isotope systematics associated with biological cycling (Abouchami et al., 2011, 2014).

4.5 Intermediate water formation and export of Southern Ocean signatures

A major feature of the Southern Ocean is the formation of SAMW and AAIW by deep winter convection and subduction, specifically in the subantarctic South Pacific (McCartney, 1982; Sallée et al., 2010). Both water masses also play a dominant role in the large scale distribution of Cd and $\delta^{114}\text{Cd}$, as they carry a negative Cd* signal and high $\delta^{114}\text{Cd}$ to the low

latitudes (Abouchami et al., 2014; Baars et al., 2014; Conway and John, 2015a; Xie et al., 2015; Sieber et al., 2019). Our high-resolution dataset enables us to investigate the formation of the $\delta^{114}\text{Cd}$ signatures found in SAMW and AAIW in more detail than previously possible.

The main formation region of AAIW is located in the Southeast Pacific, close to the Drake Passage, where AASW is subducted by deep winter convection. AAIW is then carried into the Atlantic and Pacific basins (Sallée et al., 2010). ACE stations 19 and 20 close to the Drake Passage are therefore an ideal location to study the processes that preform a Cd signature within AAIW. In winter, wind-driven mixing and strong cooling of surface waters in the Southern Ocean lead to convection within the upper ocean and the formation of deep winter mixed layers (Park et al., 1998). In summer, Winter Water (WW, temperature minimum) remains as the sub-surface remnant of the cold winter surface layer south of the APF. Our analysis of WW throughout the ACC shows that the high $\delta^{114}\text{Cd}$ associated with uptake in the surface are imparted to the winter mixed layer (~100 m) during deep convection. This pattern also holds true for station 19, located in the AZ, close to the Drake Passage, where WW is +0.40‰. However, such binary mixing between AASW and underlying water masses cannot fully explain the $\delta^{114}\text{Cd}$ signals found in WW (Fig. 7a), with WW lying above the mixing line. We suggest that, within the ACC, very shallow regeneration adds isotopically light Cd to WW, and a regeneration signal builds up over the months when the winter mixed layer is separated from the surface. North of the APF, at station 20, the mixed layers extend to greater depths and WW exhibits higher $\delta^{114}\text{Cd}$ (+0.46‰) than in the AZ. This suggests that regeneration of Cd from sinking particles is less influential here, but still contributes to the mixed layer (Fig. 7a). Regardless of the cause, the $\delta^{114}\text{Cd}$ signatures and Cd concentrations observed in WW north of the APF are in good agreement with Cd signatures observed in AAIW in the South Atlantic and Pacific (Xie et al., 2017; Sieber et al., 2019), suggesting that the deep winter mixed layers north of the APF do indeed act as a precursor for the preformed Cd signatures found in AAIW.

North of the SAF, SAMW is formed in very thick mixed layers that are transported eastward along the SAF or subducted northward into the subtropical gyres (McCartney, 1982). We can use stations 08 and 09, located at the STF and SAF, respectively, in the southwest Pacific to investigate in more detail the Cd signatures within these mixed layers. Plotting station 09 in $\delta^{114}\text{Cd} / (1/\text{Cd})$ space (Fig. 7b) shows that a simple binary mixing trend between surface and underlying waters does not explain the Cd signatures observed in the deep winter mixed layers – the mixed layer data are too low in Cd or too low in $\delta^{114}\text{Cd}$, i.e. moving it either to the right or downward in Fig. 7b. This deficit is even more pronounced in SAMW at station 08, which exhibits similar $\delta^{114}\text{Cd}$ but lower Cd concentrations than the deep mixed layers. Therefore, we infer that the subantarctic deep mixed layers and SAMW have an additional component that is either low in Cd or low in $\delta^{114}\text{Cd}$. We can quickly exclude any water masses with low $\delta^{114}\text{Cd}$ because these would also carry high Cd concentrations and would lead to an enrichment in Cd. This leaves a low Cd water mass with a similar $\delta^{114}\text{Cd}$ signal as the isotope signatures observed in the subantarctic thermocline. The prevailing views on the formation of SAMW suggest that a subtropical component, transported southwards and into the ACC by the western boundary currents of the subtropical gyre systems, interacts with southern-sourced waters in the subantarctic thermocline (Sallée et al., 2010). Subtropical waters carry low Cd concentrations with a comparable $\delta^{114}\text{Cd}$ signature (Xie et al., 2017; Sieber et al., 2019), and would fulfil our criteria for the additional component. Hence, we suggest that a subtropical endmember is introduced to the subantarctic thermocline by intense mixing at the SAF, and contributes to the Cd signatures in SAMW, equivalent to the suggestion for the nitrogen stable isotope composition of dissolved nitrate (Sigman et al., 2000).

4.6 Cd-PO₄ in the Pacific and the role of the Southern Ocean

Examination of the Cd-PO₄ relationship in the Pacific sector of the Southern Ocean (Fig. 8a) allows us to identify the shift from the steep Southern Ocean trend, described in section 4.1 (Fig. 4), to the nonlinear relationship between Cd and PO₄ that has been described previously (Fig. 8b; e.g. Frew and Hunter, 1992; de Baar et al., 1994). Surface waters in the AZ are dominated by the strong depletion of Cd relative to PO₄, due to the high Cd uptake rates of Fe-limited Southern Ocean phytoplankton. Surface waters north of the APF, first in the PFZ and then in the SAZ, show even lower Cd concentrations as Cd is continuously stripped out via biological uptake. A major difference, north of the APF, however, is an increase in uptake of PO₄ relative to Cd, which shifts these surface waters to significantly lower PO₄. In the SAZ, once Cd is almost completely depleted (<10 pmol kg⁻¹), Cd cycling in the low latitude surface ocean has only a minimal influence on the Cd-PO₄ relationship (Fig. 8a). Therefore, the shallow slope of the nonlinear Cd-PO₄ relationship is a result of PO₄ cycling over a larger concentration gradient compared to Cd in subantarctic and subtropical surface waters. Below, in intermediate waters, the Cd-PO₄ relationship is controlled by preformed signatures carried in SAMW and AAIW (Section 4.5). Together with the deep mixed layers in the SAZ, they form part of the steep slope of the nonlinear Cd-PO₄ relationship. Water mass mixing connects the intermediate water with the high-Cd deep water masses LCDW and UCDW. The break in the relationship therefore occurs in the subantarctic thermocline, which links the Cd depleted surface waters to SAMW below (cf. de Souza et al., 2018). North of the SAZ, subsurface waters follow the steep slope determined by water mass mixing of preformed water mass endmembers, while biological cycling at very low Cd concentrations in the surface ocean governs the shallow slope (Sieber et al., 2019). Similar systematics have also been suggested for the Zn-PO₄ relationship (Vance et al., 2017).

Consideration of the Cd-PO₄ systematics of data from other recently-published Cd isotope studies in the Pacific (Conway and John, 2015b; Janssen et al., 2017; John et al., 2018; Yang et al., 2018; George et al., 2019; Sieber et al., 2019) shows that the data from the entire

Pacific basin follow the two Southern-Ocean-determined slopes outlined above (Fig. 8b). Therefore, we propose that the Southern Ocean processes described in the previous sections, in combination with water mass formation, transport and mixing, cause this division into two separate regimes, in analogy to that proposed for Si and Zn (Sarmiento et al., 2007; Vance et al., 2017). Outside the Southern Ocean, only a relatively small fraction of the total Cd is available for biological cycling in the upper ocean. The majority of the Cd would be carried in a deep loop, similar to Si (Sarmiento et al., 2004; Holzer et al., 2014). A similar break in the Cd-PO₄ relationship has been observed in the Atlantic sector of the Southern Ocean (Baars et al., 2014). However, within the Atlantic Ocean itself this break is obscured by the formation of North Atlantic Deep Water, which leads to more complex mixing features in the Cd-PO₄ relationship (Middag et al., 2018). These stem largely from the interaction between surface and deep waters in the North Atlantic, which connects the shallow and the steep slopes in the Cd-PO₄ relationship (Baars et al., 2014). In the Pacific, however, all deep waters are ultimately Southern Ocean derived. Due to the lack of deep water formation in the North Pacific, surface waters on the shallow slope and deep waters on the steep slope do not interact directly outside of the Southern Ocean, thus maintaining the separation between them that is created in the Southern Ocean.

Just like the surface Southern Ocean, the upper ocean in the other Pacific HNLC regions, in the Equatorial and North Pacific, are an exception to the basin-wide Cd-PO₄ systematics outlined above (Fig. 8c). In these regions, regional cycling processes likely play a more important role and modulate the transported Cd signatures. More detailed high-resolution studies, similar to this one, are required in the future to understand what causes these deviations from the basin-wide trends in these regions.

A schematic showing the creation and transport of Cd signatures in the Pacific (Fig. 9) highlights the extent to which biogeochemical processes in the surface Southern Ocean,

subsequent water mass formation, and global ocean circulation control the large-scale distribution of Cd and its isotopic composition (Abouchami et al., 2014). In turn, this also means that the relationship between Cd and PO₄ is largely a result of these processes, rather than a local correlation between the two elements. This is an important insight for the application of Cd as a paleoproxy. Cd/Ca ratios have been suggested for reconstructing past variations in phosphate concentration, both in the surface Southern Ocean and the deep ocean (e.g. Boyle, 1988; Rickaby and Elderfield, 1999). However, our findings show that the Southern Ocean plays a central role in setting the global Cd-PO₄ relationship. Specifically, Cd cycling in the upper Southern Ocean is crucial in determining the distinct Cd signatures that are imparted to southern-sourced waters during water mass formation (Frew and Hunter, 1992). Thus, changes in either the global ocean circulation or HNLC conditions in the surface Southern Ocean are likely to have a strong effect on the Cd-PO₄ relationship over time. Therefore, we suggest that Cd would be more suited to investigating the role that the Southern Ocean has played in the global ocean in the past. Specifically, Cd could be used to trace past variations in the biogeochemistry and circulation patterns in the Southern Ocean.

5. Conclusions

Here, we have presented the first high-depth-resolution dissolved Cd and $\delta^{114}\text{Cd}$ data from all major zones of the Southern Ocean, using samples collected as part of the Antarctic Circumnavigation Expedition. Our dataset reveals in detail how the interplay between uptake and regeneration, seasonal mixing, and upwelling, controls the Cd and $\delta^{114}\text{Cd}$ signals in the upper Southern Ocean. Despite the influence of these different processes in the surface and near-surface Southern Ocean, Cd isotopes appear to follow Rayleigh systematics. Regional deviations from the consistent Southern Ocean trends are observed where inputs from islands or glaciers influence the surface waters. Furthermore, the data reveal how Southern Ocean Cd

signatures are incorporated into SAMW and AAIW during intermediate water formation. These and previously published data highlight the importance of the twin Southern Ocean processes of biological cycling and intermediate water mass formation for both the Cd-PO₄ relationship and the large-scale distribution of $\delta^{114}\text{Cd}$. A more complete picture of Cd cycling throughout the Pacific suggests that Southern Ocean processes, in combination with the global ocean circulation, cause a division into two separate Cd regimes, a Cd-depleted surface ocean above a Cd-rich deep ocean loop, analogous to that previously proposed for Si and Zn (Sarmiento et al., 2007; Vance et al., 2017).

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Figures

Figure 1. Bathymetric map of the Southern Ocean, showing the cruise track (red line) and the locations of stations from which samples were collected during Legs 2 and 3 of the Antarctic Circumnavigation Expedition cruises. White lines represent the Subtropical Front (STF), the northern boundary of the Southern Ocean, and the principal fronts of the Antarctic Circumpolar Current (ACC): Subantarctic Front (SAF), Antarctic Polar Front (APF), Southern ACC Front (SACCF), and Southern Boundary (SB). Front locations from Orsi et al. (1995).

Figure 2. Depth profiles of dissolved Cd, $\delta^{114}\text{Cd}$ and Cd^* from ACE stations across the major zones of the Southern Ocean: Subantarctic Zone (SAZ), Polar Frontal Zone (PFZ), Antarctic Zone (AZ) and Southern Zone (SZ). This includes the fronts of the Antarctic Circumpolar Current (ACC): Subantarctic Front (SAF), Antarctic Polar Front (APF) and Southern Boundary (SB); see Fig. 1.

Figure 3. Depth profiles of dissolved Cd, $\delta^{114}\text{Cd}$ and Cd^* from ACE stations located in the Ross and Weddell Gyres (a), downstream of the Balleny Islands (b) and close to the Mertz Glacier (c).

Figure 4. The Cd-PO₄ relationship for all ACE stations south of the APF (excluding stations 11 and 12 at Mertz Glacier), colored for Cd* (a) and for δ¹¹⁴Cd (b), respectively. For comparison, the South Pacific Cd-PO₄ relationship is represented by the dotted line (Sieber et al., 2019).

Figure 5. (a) Depth profiles of the top 300 m for Cd, $\delta^{114}\text{Cd}$, PO_4 , salinity and salinity-corrected Cd of stations 11 and 12, located on the Antarctic shelf, close to the Mertz Glacier. Salinity-corrected Cd is normalized to the subsurface salinity of 34.5 psu. (b) Stations 11 and 12 plotted in Cd vs. salinity space, colored by $\delta^{114}\text{Cd}$; it can be seen that whilst $\delta^{114}\text{Cd}$ increases systematically with decreasing Cd for samples with salinity >33.5, there is no clear change in $\delta^{114}\text{Cd}$ values at lower salinities, despite significantly lower Cd concentrations. (c) Stations 11 and 12 plotted in $\delta^{114}\text{Cd}$ vs. $1/\text{Cd}$ space. Gray area represents the trend observed in the other sectors of the Southern Ocean, driven by biological uptake (Section 4.4); the uppermost samples from Stations 11 and 12 are offset from this trend, indicating a potential influence of isotopically light Cd. The potential influence of a continental source on Cd systematics in low salinity waters, indicated by the arrow, dampens the biological $\delta^{114}\text{Cd}$ signal.

Figure 6. (a) Cd isotope systematics in the upper Southern Ocean (top 300 m). Stations south of the SAF (gray), with the exception of stations located close to the Mertz Glacier (cyan; 11, 12) follow fairly similar Rayleigh fractionation trends. Surface waters north of the SAF (red) do not follow the same trend, and are likely governed by different isotope systematics (Xie et al., 2017). (b-d) Cd isotope systematics for the upper ocean (top 300 m) are consistent within each zone of the Southern Ocean and fractionation factors increase towards the continent. The only difference between Pacific (blue) and Atlantic (orange) sectors can be observed in the Ross and Weddell Gyres. Data from previous studies (Xue et al., 2013 (diamonds); Abouchami et al., 2014 (triangles); Sieber et al., 2019 (squares)) are included in the calculations of α , where $\alpha = R_{\text{phytoplankton}}/R_{\text{seawater}}$ and $R = {}^{114}\text{Cd}/{}^{110}\text{Cd}$.

Figure 7. A plot in $\delta^{114}\text{Cd} - 1/\text{Cd}$ space of stations 19 and 20 (a), located in the southeast Pacific, the major formation region of AAIW, and (b) stations 08 and 09 located in the southwest Pacific at the STF (08) and SAF (09). WW north of the APF exhibits Cd signatures similar to AAIW, and likely acts as a precursor for the Cd signatures exported into the low latitudes. Cd isotope signatures in SAMW are comparable to those found in the deep mixed layers at the SAF. However, Cd concentrations are slightly lower in SAMW, suggesting that low-Cd Subtropical Surface waters contribute to SAMW. Dashed lines represent binary mixing lines between surface and underlying water masses.

Figure 8. (a) Cd-PO₄ relationship from ACE stations located in the three major zones of the ACC (AZ, PFZ, SAZ) in the Pacific sector of the Southern Ocean, colored for δ¹¹⁴Cd, showing the evolution of Cd-PO₄ from the AZ into the SAZ. (b) Nonlinear Cd-PO₄ relationship for the entire Pacific basin north of the SAF, including all previously published data. Data from the upper ocean (top 500 m) in Pacific HNLC regions are excluded here, as waters affected by HNLC conditions appear to be more strongly affected by regional processes, as shown in panel c. Green arrows represent biological cycling at low Cd concentrations in surface waters of the low latitude oceans.

Figure 9. Schematic circulation of the Pacific Ocean (after Sarmiento et al., 2004) with Cd signatures for the major water masses in brackets ([Cd] (nmol kg⁻¹) / $\delta^{114}\text{Cd}$ (‰) / Cd/PO₄ (mmol mol⁻¹)). The Cd signatures observed in intermediate waters are in good agreement with previous studies from the Atlantic (Abouchami et al., 2014; Baars et al., 2014; Xie et al., 2017), while PDW and NADW carry significantly different Cd signatures due to different deep water formation processes in the North Pacific and North Atlantic, respectively.

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