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Author(s):

Sieber, Matthias; Conway, Tim M.; [De Souza, Gregory](#) ; Obata, Hajime; Takano, Shotaro; Sohrin, Yoshiki; Vance, Derek

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Physical and biogeochemical controls on the distribution of dissolved cadmium and its isotopes in the Southwest Pacific Ocean

Sieber, M.^{1,*}, Conway, T. M.^{1,2}, de Souza, G. F.¹, Obata, H.³, Takano, S.⁴, Sohrin, Y.⁴, and Vance, D.¹

¹Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zürich, Zürich, Switzerland

²College of Marine Science and School of Geosciences, University of South Florida, Florida, USA.

³Atmosphere and Ocean Research Institute, The University of Tokyo, Tokyo, Japan

⁴Institute of Chemical Research, Kyoto University, Kyoto, Japan

*Corresponding author: sieber.mat@gmail.com Phone: Tel: +41 44 632 93 83

Highlights:

- First $\delta^{114}\text{Cd}$ section in the Southwest Pacific
- Southern Ocean control on the distribution of Cd and $\delta^{114}\text{Cd}$ at low-latitudes
- Southern sourced water masses carry isotopically heavy Cd
- Remineralization of Cd in non-HNLC regions has negligible influence on $\delta^{114}\text{Cd}$ signatures

Keywords:

trace metals; biogeochemistry; GEOTRACES; GP19 section; water mass mixing; complete utilization

Abstract

Cadmium stable isotope ratios ($\delta^{114}\text{Cd}$) have become a useful tool for oceanographers investigating the biogeochemical and physical processes that affect the nutrient-like distribution of the bioactive trace metal cadmium (Cd) throughout the oceans. Here, we present a meridional transect of dissolved Cd and $\delta^{114}\text{Cd}$ from Japanese GEOTRACES section GP19 along 170°W from 64°S in the Southern Ocean to the equatorial Pacific. Along the GP19 section, the deep ocean (>1500 m) shows small variability in dissolved Cd (0.75 – 0.9 nmol kg⁻¹) and a homogeneous $\delta^{114}\text{Cd}$ signature ($+0.26 \pm 0.06\text{‰}$, 2SD, n = 60; relative to NIST SRM-3108). Adding these data to previously published work allows us to calculate a deep Pacific and Southern Ocean (>1500 m) mean $\delta^{114}\text{Cd}$ of $+0.26 \pm 0.1\text{‰}$ (2SD, n = 436). Higher in the water column, depth profiles of Cd along the GP19 section exhibit a strong vertical gradient from a maximum (up to 0.9 nmol kg⁻¹) at 1500–2000 m up to depleted surface waters (<0.001 nmol kg⁻¹ in the equatorial Pacific). This gradient in dissolved Cd concentration is associated with changes in dissolved $\delta^{114}\text{Cd}$, with values higher (+0.4 to +0.6‰) than the deep ocean average at intermediate depths (300 – 1500 m), and then a further increase towards high $\delta^{114}\text{Cd}$ values (up to +0.9‰) in the surface ocean. Both patterns could be explained by one-dimensional biological cycling including preferential uptake of isotopically light Cd by phytoplankton, and such processes likely explain the surface patterns. At intermediate depths, however, the observed strong vertical Cd concentration and isotopic gradients instead result from the lateral isopycnal transport of Antarctic Intermediate Water (AAIW) and Subantarctic Mode Water (SAMW), both of which carry distinctly lower pre-formed Cd concentrations and higher $\delta^{114}\text{Cd}$ values. These pre-formed signatures, which are imparted during water-mass formation in the Southern Ocean, are clearly conserved into the lower latitude Pacific as these water masses travel northward.

Overall, the distribution of Cd and $\delta^{114}\text{Cd}$ along the GP19 section is remarkably well explained by large scale mixing of water mass endmembers with defined $\delta^{114}\text{Cd}$ signatures, emphasizing the importance of surface Southern Ocean processes for the distribution of trace metals such as Cd in the subsurface Southwest Pacific. At the regional scale, however, two other processes may overprint this mixing relationship. First, by comparison with the nearby Southeast Pacific GP16 section, we find that the $\delta^{114}\text{Cd}$ signature of equatorial intermediate water masses shows little zonal variation across the equatorial Pacific, despite becoming enriched in dissolved Cd due to remineralization. We propose that this uniformity is explained by complete utilization of Cd in the surface tropical Pacific and remineralization of Cd with an isotopic signature similar to intermediate waters, therefore conserving the southern-sourced

isotopic signature. Similarly, the observed increase of about 30% in deep ocean Cd concentrations from the South to the North Pacific is associated with a near-constant $\delta^{114}\text{Cd}$ signal. These observations enable us to constrain the net $\delta^{114}\text{Cd}$ of Cd added by remineralization to the deep ocean, with the caveat that such a signal is integrated over the entire Pacific, and that remineralization under different oceanic regimes such as HNLC areas may add Cd with different isotopic compositions to deep waters. Second, at GP19 stations close to the equator, subtle Cd depletion (relative to phosphate) is observed associated with low-oxygen subsurface waters, consistent with other studies from the North Pacific. Discerning the effects of such processes on Cd isotopic distributions is an important step to a more detailed understanding of the biogeochemical cycling of Cd in the modern ocean, and the application of $\delta^{114}\text{Cd}$ as a tracer of past deep water circulation.

1. Introduction

Together with the macronutrients carbon, phosphate, nitrate and silicate, trace elements, particularly transition metals, are essential micronutrients for marine life (e.g. Morel et al., 2014). In the oceans, the element cadmium (Cd) has a distribution similar to the macronutrients, implying a nutrient-type role for marine life. Although the biological function of Cd for phytoplankton is still not well understood, and although Cd is known to be toxic at high concentrations (Sunda and Huntsman, 1996; Horner et al., 2013), several studies have shown that Cd can function as a micronutrient and that it substitutes for zinc (Zn) in the enzyme carbonic anhydrase under Zn-limited conditions (e.g. Price and Morel, 1990; Lane and Morel, 2000). Cd uptake may thus be closely related to the availability and limitation of the other trace metals (e.g. Cullen, 2006; Sunda and Huntsman, 2000, 1998). Cd is also of particular interest as its global distribution is closely correlated to the macronutrient phosphate (PO_4) (Boyle et al., 1976; Bruland, 1980). Though there is some debate over the origin of the Cd/P correlation, the nutrient-type behavior of Cd has been the basis for using Cd/Ca ratios preserved in microfossils as a proxy for reconstructing past variations in deep ocean phosphate concentrations, and the pattern of deep ocean circulation (e.g. Boyle, 1988; Rickaby and Elderfield, 1999). Successful application of this proxy relies on a full understanding of the additional effects of biological processes, over and above those resulting from large-scale water mass mixing, on the local and global Cd: PO_4 relationship. For example, though the global relationship between Cd and PO_4 has been described in numerous studies as a strong linear correlation that can be interpreted in terms of water mass mixing, there is a pronounced break

68 occurring at PO_4 of $\sim 1.3 \mu\text{mol kg}^{-1}$ (e.g. Boyle, 1988; de Baar et al., 1994). While several
69 explanations have been proposed for this ‘kink’ in the global Cd: PO_4 relationship, recent studies
70 in the Atlantic have also highlighted the importance of water mass mixing (e.g. Baars et al.,
71 2014; Quay et al., 2015; Middag et al., 2018).

72 Over the last decade, advances in multi-collector inductively coupled plasma mass
73 spectrometry (MC-ICPMS), combined with the development of clean sampling techniques and
74 the onset of the GEOTRACES program, have allowed the dissolved stable isotope ratios of
75 trace metals to be deployed as a tool for oceanographers to investigate the physical and
76 biogeochemical processes that affect the distributions of bioactive trace metals in the ocean. As
77 a trace element with a clear nutrient-type distribution, Cd stable isotope ratios (here denoted as
78 $\delta^{114}\text{Cd}$) have become a prime tool for gaining further insight into the processes that control
79 relationships between the oceanic distributions of Cd and macronutrients. A number of studies
80 have now documented the $\delta^{114}\text{Cd}$ composition of seawater from different ocean basins, allowing
81 a first characterization of the $\delta^{114}\text{Cd}$ distribution in the global ocean. For all ocean basins, at
82 depths below 500-1500 m, the ocean is relatively homogeneous, and is characterized by a
83 $\delta^{114}\text{Cd}$ value of +0.2 to +0.3‰, with the exception of heavier North Atlantic Deep Water (+0.4
84 to +0.5‰) (Ripperger and Rehkämper, 2007; Ripperger et al., 2007; Xue et al., 2013;
85 Abouchami et al., 2014; Janssen et al., 2014; Conway and John, 2015a, 2015b; John et al.,
86 2018). Similar to other trace metal isotope systems (e.g. Zhao et al., 2014; Little et al., 2014,
87 2016; Vance et al., 2016), the deep ocean isotopic signature is notably heavier than the sources
88 of Cd to the ocean, with riverine inputs and aerosol dust bearing a near-crustal signature
89 (+0.1‰; Lambelet et al., 2013; Bridgestock et al., 2017). Other potential sources, such as
90 sediments and hydrothermal systems, appear to be small for Cd, and in fact may be sinks
91 (Janssen et al., 2014; Conway and John, 2015a). Recent work has hypothesized that sulfide
92 precipitation in anoxic micro-environments associated with regenerating particulate biogenic
93 material, within the water column of oxygen minimum zones, could be a sink for Cd and other
94 trace metals (Janssen et al., 2014).

95 In surface waters, dissolved Cd isotope ratios are often characterized by a shift towards
96 heavier values, consistent with preferential uptake of light Cd isotopes by phytoplankton, as
97 documented in culture (Lacan et al., 2006; John and Conway, 2014). While early studies in the
98 Southern Ocean and North Pacific showed that this heavy isotope signature was restricted to
99 shallow waters (above ~ 500 m), the North Atlantic has been shown to have a distinctly heavier
100 isotope signature down to intermediate depths (+0.4‰ to +0.5‰ at depths of 500-1500 m,
101 Conway and John, 2015a). This heavy Cd isotope signature in intermediate waters has been

interpreted to be a result of distinct signatures formed by biological fractionation in the Southern Ocean, and subsequent transport of that signal throughout the ocean basins by large scale physical circulation (Abouchami et al., 2014). This phenomenon has been well characterized by several North and South Atlantic GEOTRACES sections (Xue et al., 2013; Conway and John, 2015a; Xie et al., 2017).

This importance of the Southern Ocean for global macro- and micronutrient distributions, as well as the fact that it is the largest of the iron-limited high nutrient low chlorophyll (HNLC) regions, gives it a central and distinctive role in global ocean biogeochemistry (e.g. Marinov et al., 2006). Around Antarctica, nutrient-rich Circumpolar Deep Water (CDW) is upwelled by the wind-driven Antarctic Circumpolar Current (ACC) that connects the three major ocean basins. As the upwelled waters are transported northwards at the surface by Ekman transport, Southern Ocean diatoms take up large amounts of Cd and Zn relative to PO_4 (Twining and Baines, 2013). This biological uptake thus imprints a distinct biogeochemical signature, strongly depleted in Si and Zn and moderately depleted in Cd, on the surface waters that are subducted as Sub-Antarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) in the region of the Antarctic Polar Front. Vance et al. (2017) have recently suggested that the coupling of these processes dominate the global oceanic distribution of Zn, as it does for the major nutrients (Sarmiento et al., 2004). With Cd thought to be taken up into phytoplankton in a similar manner to Zn, possibly able to substitute for it (e.g. Price and Morel, 1990), it is likely that the Southern Ocean plays a similarly important role in the global distribution of Cd. Indeed, while several mechanisms have been proposed to explain the “kink” in the Cd- PO_4 relationship, they all suggest a central role of the Southern Ocean and large scale circulation. For example, the preferential removal of Cd with respect to PO_4 under micronutrient limitation, especially by Fe but also Zn and Mn (Sunda and Huntsman, 2000), has provided the basis for the suggestion that Fe-limitation in HNLC regions may cause the Cd- PO_4 “kink” (Cullen, 2006).

Accordingly, many Cd isotope studies have focused on the Southern Ocean, with the aim of understanding the biological cycling of Cd and its isotopes, and the source of globally-transported biogeochemical signals (Abouchami et al., 2011, 2014; Gault-Ringold et al., 2012; Xue et al., 2013). To date, however, all studies have been limited to the Atlantic sector (Schlitzer et al., 2018). While this has provided us with important insights into the Cd systematics in the Atlantic, we have a very limited understanding of Cd cycling in the Pacific (John et al., 2018) and to what extent the distribution of Cd in this region is affected by Southern Ocean processes. Here, we present a meridional transect of dissolved Cd and $\delta^{114}\text{Cd}$ from the Japanese

GEOTRACES Section GP19 along 170°W, from 64°S in the Southern Ocean to the equatorial Pacific. We use this new dataset to investigate the role of Southern Ocean processes in controlling the distribution of Cd isotopes at lower latitudes in the Southwest Pacific. In particular, we investigate the effect of fractionation of dissolved Cd due to biological uptake in the Antarctic in setting endmember $\delta^{114}\text{Cd}$ values, and the role of large scale water mass mixing in transporting such endmember signatures northwards in the Southwest Pacific, influencing the distribution of $\delta^{114}\text{Cd}$ at low latitudes.

2. Oceanographic setting

The GP19 meridional transect along 170°W traverses three fronts and four major zones in the Southwest Pacific (Orsi et al., 1995). These and other major oceanographic features referred to in the following brief introduction are shown in Fig. 1. The structure of the South Pacific water masses has been well described by Talley et al., 2011, and is summarized here. The Antarctic Zone is located south of the Antarctic Polar Front (APF) at 60°S, where HNLC conditions dominate due to the upwelling of nutrient-rich Circumpolar Deep Water (CDW) and the limitation of phytoplankton productivity by light and micronutrient availability. Immediately north of the APF, within the Subantarctic Zone (SAZ), Antarctic Surface Water (AASW) is converted into Antarctic Intermediate Water (AAIW) and Subantarctic Mode Water (SAMW) through the formation of deep winter mixed layers. Both, SAMW and AAIW, are subducted at the Subantarctic Front (SAF) and are observed at intermediate depths in the southern hemisphere. The remaining nutrient-rich Southern Ocean waters return to the deep ocean near Antarctica. The Subtropical Front at 43°S is the northern border of the SAZ, separating it from the Subtropical Pacific. Here, the influence of the southern-sourced water masses starts to wane and nutrient-rich Pacific Deep Water (PDW) is increasingly dominant towards the equator.

CDW and PDW are the two water masses that dominate the deep South Pacific. CDW is formed in the Antarctic Circumpolar Current (ACC), as deep waters of each ocean basin enter the ACC and mix with locally formed Antarctic waters (Talley et al., 2011). CDW is separated into southward-flowing Upper CDW (UCDW), recognized by the oxygen minimum and the nutrient maximum, and denser Lower CDW (LCDW), identified by the deep salinity maximum and low temperatures. LCDW also has lower nutrient concentrations than both UCDW and PDW due to the influence of nutrient-poor North Atlantic Deep Water. PDW forms within the ocean interior through the diapycnal transformation of deep southern sourced waters in the North Pacific, and is therefore characterized by high ^{14}C ages and high nutrient concentrations

(Talley, 2013). As PDW flows southwards it mixes with the surrounding younger water masses, resulting in lower nutrient contents and an apparent decrease in age.

While the deep Southwest Pacific is dominated by only two major water masses, there are many different water masses in the upper 1500 m, especially in the near-surface ocean. The most prominent feature in the upper ocean is the salinity minimum at intermediate depths, which originates in the Antarctic surface and extends as far north as 15°N (Talley et al., 2011). This “tongue” of low salinity is associated with the northward flow of AAIW and SAMW. Overlying these intermediate water masses north of the SAF is South Pacific Central Water (SPCW), which makes up the thermocline in the subtropics and spans a large range of temperature and salinity. The shallow salinity maximum (down to 200 m) found towards the Equator is associated with Subtropical Underwater (STUW), which results from subduction of surface waters in the center of the subtropical gyre. South of the APF, AASW is the main water mass in the top 200 m of the surface ocean. It is cold and nutrient-rich and most likely originates from UCDW that upwells to the surface in the Antarctic Zone.

We follow the T-S characteristics of major water mass endmembers defined by Talley et al. (2011), and phosphate concentrations from the GP19 section in order to derive endmembers for different parameters along our section (Table 1). Perhaps the most noticeable feature in the distribution of PO₄ along the GP19 section is the tongue of AAIW and SAMW that carries low concentrations of PO₄ (1-2 μmol kg⁻¹) northwards (Fig. 1). Above this, surface waters are increasingly depleted in PO₄ due to biological uptake, north of the APF and towards the Equatorial Pacific (down to <30 nmol kg⁻¹). PO₄ concentrations in AASW are relatively high (1.8 μmolkg⁻¹) due to the upwelling of nutrient-rich deep waters. Compared to the substantial changes in the upper ocean, dissolved PO₄ is significantly less variable in the deep ocean (below 1000 m), with the lowest concentrations found in LCDW in the south (2.25 μmol kg⁻¹) and the highest at the Equator in PDW (2.96 μmol kg⁻¹).

3. Methods

3.1 Seawater sampling

Seawater samples were collected using clean techniques during the Japanese GEOTRACES GP19 section cruise (KH14-6) on board the R/V Hakuho Maru during the period December 2014 – February 2015. Eight stations (GR 8, 10, 12, 13, 15, 17, 19, 21) were sampled for dissolved Cd and δ¹¹⁴Cd, on a transect along 170°W. An additional station was sampled at 30°S and 174°E (GR 6, Fig. 1). Seawater samples were taken from surface to bottom using a

clean CTD Carousel Multi Sampling system (24 Niskin-X (12L) bottles) attached to a Ti-armored cable, except for the bottom water at GR 21 which was collected with an acid-cleaned Niskin-X sampler attached to a Ti wire, closed with a Teflon-coated messenger (Kim et al., 2015). All samples were filtered (0.2 μm) into acid-cleaned 1 and 4 L LDPE bottles. Filtered seawater samples were acidified at ETH Zürich by addition of 1.2 mL 9.6 M Teflon-distilled HCl ($<1 \text{ pg g}^{-1} \text{ Cd}$) per liter of sample and samples were stored for at least 6 months at pH ~ 2 before processing. Supporting hydrographic data were obtained using a Seabird, SBE-9-plus CTD.

3.2 General laboratory procedures

All seawater samples were processed within ISO 4 laminar flow air benches inside ISO 6 clean laboratories at the Institute of Geochemistry and Petrology at ETH Zurich, using clean techniques including the wearing of polyethylene gloves to reduce metal contamination from handling. All plastics were LDPE or PFA Teflon, rigorously cleaned using published procedures (Cutter et al., 2010). All water used was ultrapure (UPW; 18.2 M Ω) from a Milli-Q[®] integral water purification system (Merck, Millipore). Concentrated nitric (HNO₃) and hydrochloric (HCl) acids were double distilled in-house from reagent grade, using SavillexTM PFA Teflon stills (TD). Ultrapure hydrogen peroxide, acetic acid, and ammonium hydroxide were obtained from Romil Ltd.

3.3 Double-spike preparation

The ¹¹¹Cd - ¹¹³Cd double-spike was made up from single spikes of ¹¹¹Cd (95 - 97.5 % pure) and ¹¹³Cd (93 - 96 % pure) obtained from Isoflex USA. The single spikes were dissolved in 7 M TD HNO₃ and then diluted with UPW and mixed to achieve 0.3 M HNO₃ solution with a ¹¹¹Cd/¹¹³Cd ratio of 1.63, designed based on Xue et al. (2012). A 1:1 sample - spike ratio minimizes propagated errors (Rudge et al., 2009). We chose not to use a ¹¹⁰Cd - ¹¹¹Cd double-spike, in order to eliminate the need to correct for Pd interferences on Cd, a correction that has been previously found to be problematic in some samples (John et al., 2017). To remove any impurities, the mixed double spike was purified using a modified scaled-up version of the column chemistry for samples: the concentrated double-spike was dried down, taken up in 0.2 M HBr + 0.3 M HNO₃, refluxed and loaded in 2 mL aliquots (containing 2 mg of total Cd each) onto larger AG-MP1 resin columns. We found that, at these high Cd concentrations (and thus Cd:Br ratios), conditioning using 0.1 M HBr + 0.3 M HNO₃ prior to the loading step, and loading with 0.2 M HBr + 0.3 M HNO₃ (Strelow, 1978), were required for quantitative recovery of Cd. Conditioning with 0.2 M HBr solution resulted in a much longer elution curve for Cd,

and so was avoided. Other elements were then eluted from the columns using 0.1 M HBr + 0.3 M HNO₃ before eluting Cd with 0.3 M HNO₃. The clean spike solution was subsequently diluted and calibrated for concentration and isotope ratio.

The isotopic composition of the spike was calibrated by isotopic analysis of mixtures of NIST SRM-3108 and the double spike, with standard – spike mixtures of ratios between 10:1 and 1:10. For normalization, the ¹¹³Cd/¹¹¹Cd of NIST SRM-3108 was taken to be 0.950099 (Wombacher et al., 2004). The mass-bias corrected ¹¹²Cd/¹¹¹Cd and ¹¹⁴Cd/¹¹¹Cd ratios measured for the NIST SRM-3108 during the analytical session for the spike calibration were 1.878708 and 2.228044, respectively. The double spike is calibrated against this set of ratios, with a calculated isotope composition of ¹¹²Cd/¹¹¹Cd = 0.614163; ¹¹³Cd/¹¹¹Cd = 0.029845; ¹¹⁴Cd/¹¹¹Cd = 0.003017. The concentration of the double-spike was determined by reverse isotope dilution, against a gravimetrically prepared in-house Cd concentration standard (Cd foil, Puratronic, 99.9975%, Alfa Aesar).

3.4 Sample Processing and Analysis

Chemical Processing

Sample processing and Cd isotope analyses were carried out following a modification of previously published methods (Xue et al., 2012; Conway et al., 2013). Briefly, a ¹¹¹Cd-¹¹³Cd double-spike was added to the samples to obtain a sample to spike ratio of 1:1, guided by concentration analyses from the same samples. Additionally, 1 mL 10 mmol L⁻¹ hydrogen peroxide (added to control Fe oxidation state for the co-separation of Fe from the same samples) was added per liter of sample. Samples were then left for at least 12 hours for the double-spike to equilibrate. A batch extraction technique using Nobias PA-1 chelating resin was then used to extract trace metals from seawater, following Conway et al (2013). To achieve this, ~0.8 g of Nobias resin beads were added to the sample, and the sample shaken vigorously for 2 hours on an orbital shaker table. Subsequently, the pH was adjusted to 6.2 (± 0.3) using a 5 M ammonium acetate buffer solution and ultrapure 11 M NH₄OH, followed by another 2 hours of shaking. The sample was then filtered through a 47 mm PFA Savillex™ Filter Rig with a 5 µm pore size Nucleopore polycarbonate filter, to collect the resin and the trace metals bound to it. Metals were eluted from the resin with 3 M TD HNO₃. Prior to 2nd stage column purification, samples were dried down at 180 °C, refluxed with conc. HNO₃ + 10% H₂O₂, and dried down again before being taken up in 200 µL 7 M HCl + 0.001% H₂O₂. Metals were purified by anion-exchange chromatography using 20 µL PTFE micro-columns filled with AG-MP1 resin, following a scheme modified from Archer and Vance (2004) and Conway et al. (2013). Major

cations, as well as Cr, Cu and Ni, were eluted with 7 M HCl + 0.001% H₂O₂, Fe with 1 M HCl, Zn with 2 M HNO₃ + 0.1 M HBr, and Cd with 2 M HNO₃. Samples were then evaporated to dryness and redissolved in 0.3 M TD HNO₃ for analysis by MC-ICPMS. The same procedure was used for 1 L and 4 L samples.

Tests of the extraction efficiency by addition of standard to ‘metal-free’ seawater and re-extraction demonstrated that this procedure was sufficient to extract >95% of Cd from the volumes analyzed. Additionally, this method has full procedural blanks of <1 pg for Cd per liter of seawater processed (n = 5) and effectively purifies Cd from major cations and interfering elements (Mo, In, Sn), with <0.3 ng of Mo per liter of seawater eluted in the Cd cut (<0.001% of seawater Mo).

Cd isotope analytical technique

We express Cd stable isotope ratios in delta notation relative to the NIST SRM-3108 Cd standard, which has become the commonly accepted reference material (Abouchami et al., 2013):

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

Cd isotope analyses were performed on a Thermo Neptune Plus Multi-Collector-ICPMS at the Institute of Geochemistry and Petrology at ETH Zurich, using an ESI Apex-Q introduction system, Pt Jet and Ni ‘H-type’ skimmer cones. Cd isotopes were measured in low resolution mode with the cup configuration shown in Table S1 (Supplementary information). Isobaric interferences of Sn on ¹¹²Cd, ¹¹⁴Cd, ¹¹⁶Cd and of In on ¹¹³Cd were corrected by measuring the abundances of ¹¹⁸Sn and ¹¹⁵In, respectively, while ¹¹⁷Sn was measured to monitor hydride formation, and torch z-position tuned to minimize this. Tests showed that, given the low amounts of Mo eluted with Cd (<0.001% of seawater Mo), no correction for MoO⁺ was necessary even at low seawater Cd concentrations in 4 L samples (down to 0.45 pmol L⁻¹) (Fig. S1). The ¹¹¹Cd - ¹¹³Cd double-spike was used in combination with data reduction based on the iterative approach of Siebert et al. (2001).

At the beginning of each analytical session, mixtures of double spike and NIST SRM-3108 at standard - spike ratios between 10:1 and 1:10 were analyzed in order to verify that the spike calibration and the data processing procedure were working (Fig. 2a). Two secondary standards, BAM-I012 and Münster Cd, which have well established $\delta^{114}\text{Cd}$ relative to NIST SRM-3108, were analyzed multiple times in each session as a check on accuracy and day-to-

day instrumental variability, and to provide an estimate of long term instrumental precision. The values of these secondary standards, measured over 12 analytical sessions and on the same timescale as the samples (seven months) were $-1.32 \pm 0.06\text{‰}$ for BAM-I012 (2SD, $n = 98$) and $+4.45 \pm 0.06\text{‰}$ for Münster Cd (2SD, $n = 102$) (Fig. 2b). These values are in good agreement with inter-laboratory consensus values for these standards ($\delta^{114}\text{Cd}$ $-1.332 \pm 0.043\text{‰}$ and $+4.499 \pm 0.053\text{‰}$; Abouchami et al., 2013) and provide an estimate of external precision of 0.06‰ for the analysis of $\delta^{114}\text{Cd}$ by this method. As a second estimate of external precision, we did duplicate analyses of the Cd extracted from 75 seawater samples, over multiple analytical sessions, using the offsets of replicate measurements from the mean as detailed in Steele et al. (2011). The estimate of external precision obtained – 0.05‰ (95% confidence) – is similar to the value estimated from the secondary standards, and separately processed aliquots of the reference materials SAFe D1 and D2 agree within this range (Table S2). In the following, therefore, a 2σ uncertainty of 0.06‰ is assumed, except for low concentration surface 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. We assume a 2% uncertainty on concentrations measured using this approach (Conway et al., 2013).

4. Results

4.1 Data quality and intercomparison

Tests with standard – spike mixtures that had concentrations equivalent to a seawater sample of $<0.2 \text{ ng Cd}$ ($<0.45 \text{ pmol L}^{-1}$ in a 4 L sample) yielded non-reproducible $\delta^{114}\text{Cd}$ and uncertainties of $>1\text{‰}$. We thus regard this as the lower concentration limit for the method used here, and do not report dissolved $\delta^{114}\text{Cd}$ for samples with concentrations below this threshold. To assess the accuracy of seawater $\delta^{114}\text{Cd}$ and Cd concentration measurements, we analyzed the reference materials SAFe S1, D1 and D2 for dissolved Cd concentration and $\delta^{114}\text{Cd}$ alongside our samples, splitting each D1 and D2 sample into two aliquots that were then processed completely separately. The results show excellent agreement with the consensus values for both concentrations and $\delta^{114}\text{Cd}$ (Fig. 3 & Table S2). We also inter-compared one full water column profile with the University of Otago and this showed good agreement throughout the profile (results reported in Conway, in prep.).

4.2 Dissolved Cd and $\delta^{114}\text{Cd}$ in the Southwest Pacific

Dissolved Cd concentrations and isotopic compositions for the Southwest Pacific transect are tabulated in Supplementary Data, along with temperature, salinity, and oxygen and phosphate concentrations. The data are also shown along south-north sections in Fig. 4, and as example depth profiles in Fig. 5. Along the entire GP19 section and over the entire depth range studied, Cd concentrations vary from 0.2 pmol kg⁻¹ up to 0.97 nmol kg⁻¹ (Fig. 4). Variation with depth, in common with previous studies (e.g. Boyle et al., 1976; Bruland, 1980), conforms to nutrient-like profiles, with Cd at its most depleted at the surface while the deep ocean Cd concentration is high and near-constant. Over most of the section (Figs 4, 5) a maximum in Cd concentration is seen at intermediate depths (1500 – 2000 m). Towards the Equator, the Cd maximum reaches increasingly higher concentrations (up to 0.9 nmol kg⁻¹) and extends down to the greater depths of nutrient-rich PDW. However, the Cd concentration profile for the most southerly station (station 8, 64 °S 170 °W, Fig. 5), located in the Southern Ocean, is distinctly different from those further north in that the surface depletion is much less pronounced and the maximum below the surface (~1 nmol kg⁻¹) is much shallower, at a depth of ~200 m (Figs 4, 5).

$\delta^{114}\text{Cd}$ values for the GP19 section exhibit a range between -0.14 and +0.87‰, with the exception of one extreme value ($+3.50 \pm 0.79\text{‰}$, 99m, Station 13). Vertical profiles of dissolved $\delta^{114}\text{Cd}$ generally show little variability in the deep ocean ($+0.26 \pm 0.06\text{‰}$ 2SD, $n = 60$) and an increase towards high $\delta^{114}\text{Cd}$ values (up to +0.8‰) in the Cd-depleted surface ocean (Figs 4, 5). Despite the complex water mass structure, and the variation in surface temperature, salinity, and Cd concentrations along the transect, all stations show relatively uniform “high” surface $\delta^{114}\text{Cd}$ values (+0.6 to +0.8‰). With the exception of the extreme value noted above, we do not observe any other $\delta^{114}\text{Cd}$ values $>1\text{‰}$, as have been reported from heavily depleted surface waters in the North Pacific and North Atlantic (Ripperger et al., 2007; Boyle et al., 2012; Xue et al., 2012; Conway and John, 2015a, 2015b). In fact, we identify a slight return towards slightly lighter $\delta^{114}\text{Cd}$ values at the surface in some samples, albeit close to the uncertainty on these measurements. This latter observation is consistent with recent profiles in the South Atlantic (Xie et al., 2017). As noted above for Cd concentrations, the $\delta^{114}\text{Cd}$ profile for the most southerly Southern Ocean station is very different from those further north (Figs 4, 5), in that the $\delta^{114}\text{Cd}$ maximum is at the surface.

5. Discussion

5.1 Cd isotopes in surface waters and surface ocean cycling

An important feature of the dataset presented here, as described in Section 4.2, is the general lack of high $\delta^{114}\text{Cd}$ values ($>1.3\text{‰}$) associated with the lowest Cd concentrations in this region of the surface ocean, unlike those seen in previous studies (up to 5‰) in parts of the North Pacific and North Atlantic Ocean (Ripperger et al., 2007; Boyle et al., 2012; Xue et al., 2012; Conway et al., 2013; Conway and John, 2015a, 2015b). With the exception of a single elevated data point, our dataset holds this feature in common with the data of Xie et al. (2017) from the South Atlantic, and the data of Janssen et al. (2017) in the North Pacific. In Fig. 6 we compare our new results with all previous data, highlighting the similarity of the finding here with those two studies. While it is possible that heavy values are observed only in some areas of the oceans due to natural oceanographic processes, the presence of very heavy values could also be the result of an unidentified analytical artefact associated with some procedures or samples. Indeed, while good agreement is shown between groups on deep samples (Fig. 3), the heavy isotopic values are associated with some of the lowest Cd concentrations, at the very limit of analytical capability, and have been reported by several different groups using MC-ICPMS but not by the group using TIMS (Janssen et al., 2017; Xie et al., 2017), potentially suggesting an issue with MC-ICPMS techniques. However, it should be pointed out that such highly fractionated values have been replicated in aliquots of the same sample using different chemical separation techniques and analyzed by both Thermo and Nu Instruments multicollector MC-ICPMS, so any analytical or procedural artefact would have to be common to these two instrument platforms. Unfortunately, those specific samples have never been measured by TIMS due to sample volume availability.

Thus, the first challenge for surface water Cd isotope studies is to establish whether heavy isotopic compositions of $1\text{--}5\text{‰}$ are real, or an artefact of analysis. To potentially inform this discussion, we examined the single very heavy $\delta^{114}\text{Cd}$ value in our dataset (Fig. 6, $\delta^{114}\text{Cd} = 3.50 \pm 0.79\text{‰}$, Station 13, 99m), and could not identify a particular analytical problem or obvious oceanographic anomaly. We also investigated the effect of Mo upon $\delta^{114}\text{Cd}$ in seawater samples as MoO^+ is one of the more likely candidates for problematic interference during MC-ICPMS analysis. However, we found that, even at the lowest Cd concentrations reported here, Mo from seawater was effectively removed by the chemical separation and does not systematically bias our $\delta^{114}\text{Cd}$ data to heavier values (see Fig. S1). While this finding provides some new insight into this issue, the question awaits an inter-calibration study of low-concentration Cd samples from regions where high $\delta^{114}\text{Cd}$ has been reported using multiple techniques and by both TIMS and MC-ICPMS. Such an endeavor is currently being pursued by the Cd isotope community.

The second challenge, highlighted by the data in Fig. 6, is identifying the processes that lead to Cd isotope compositions in some surface waters that are relatively unfractionated from high-Cd deep samples, given the widely-held view that surface Cd is controlled by biological uptake with a significant isotope fractionation (e.g. Lacan et al., 2006; John and Conway, 2014). If the Cd uptake process is associated with an isotope fractionation that follows Rayleigh-like systematics, the very small amount of residual Cd remaining in surface waters should be driven to extreme isotope compositions. For the dataset presented here, as for that in Xie et al. (2017) and Janssen et al. (2017), this is not the case. There have been several hypotheses put forward to explain this phenomenon.

The first hypothesis by Xie et al. (2017) is that the “dissolved” Cd pool – in other words, the Cd passing through a 0.2 micron filter – in seawater is partitioned into an organically complexed ligand pool and an inorganic pool, with different isotopic compositions, and different availability for uptake. This hypothesis suggests that only the inorganic pool is biologically available, and is progressively depleted and isotopically fractionated by biological uptake. Thus, at high Cd concentrations this inorganic pool dominates “dissolved” Cd, but at lower concentrations the organic-bound pool is increasingly important and its lighter isotope composition buffers the total “dissolved” pool to lighter isotope compositions. Whilst plausible, this hypothesis remains to be tested. A second potential explanation put forward by Xie et al. (2017) is an open-system model whereby Cd is not just continuously removed by biological uptake, driving the residual dissolved pool towards heavy values, but is also replenished by isotopically un-fractionated Cd. Thus the surface ocean pool is, again, buffered against the development of very extreme Cd isotope values. This idea could explain why heavy isotopic values develop in some regions but not others, depending on the water mass structure, recent physical oceanographic history and the season. Indeed, at Line P in the North Pacific, Janssen et al. (2017) observed very different $\delta^{114}\text{Cd}$ values (+0.8 vs +0.2‰) at similar Cd concentrations (12 vs 6 pmol kg⁻¹) and suggested, amongst other possibilities, that this could be the result of different uptake mechanisms of incorporation of Cd into cells. It has also been suggested that when cells are supply- or diffusion-limited for dissolved Cd, an isotope preference may not be obviously expressed (Gault-Ringold et al., 2012).

Lastly, a source of light Cd could balance out heavy Cd signatures in the surface ocean. One candidate for this would be atmospheric dust input (+0.1‰; Bridgestock et al., 2017). However, if natural dust was the driving force of light Cd in surface waters, it is surprising it was not seen in the North Atlantic GA03 $\delta^{114}\text{Cd}$ section, which crosses a region which receives some of the largest dust fluxes worldwide (Mahowald et al., 2005; Conway and John, 2015a).

Another possibility is that Cd in dust released from anthropogenic processes such as smelting or incinerating, which has been shown to be as light as -0.7‰ (e.g. Cloquet et al., 2006), could be having a seasonal impact on some ocean basins, but not others.

From the available data, it is not clear which of these hypotheses, if any, might explain the relatively unfractionated $\delta^{114}\text{Cd}$ values in some areas of the surface ocean, or why this would change dramatically with ocean regime. Further comprehensive investigation and synthesis of surface ocean variations, once analytical artefacts have been ruled out, together with experiments to test these hypotheses, should thus be a key goal for the Cd isotope community, and we echo previous calls for an intercomparison exercise.

5.2 Spatial patterns in dissolved Cd concentration: vertical cycling or a Southern Ocean control?

The “classical” view of nutrient-type depth profiles is that they are largely controlled by vertical cycling, uptake in the photic zone and regeneration at depth. Over most of the GP19 section, the strong vertical gradient within the uppermost 1500 m is consistent with that view. For example, all stations north of the APF have very similar profile shapes: surface waters are strongly depleted in Cd at all stations north of the Polar Front, with $<30 \text{ pmol kg}^{-1}$ in the SAZ and $<5 \text{ pmol kg}^{-1}$ for all stations north of the SAF (Figs 4, 5). The lowest surface concentrations anywhere along the section are observed in the subtropical Pacific where Cd is $<1 \text{ pmol kg}^{-1}$, similar to other open ocean gyres (Conway and John, 2015a; Xie et al., 2015). In the subsurface ocean, below a depth of 100 m, Cd concentrations rapidly increase to a maximum of $\sim 0.8 \text{ nmol kg}^{-1}$ at depths of 1000-2000 m.

Thus, in part, the downward increase in dissolved Cd could be the result of release of Cd from sinking organic matter. However, the strong vertical gradient could also primarily result from the horizontal advection of different subsurface water masses (AAIW and SAMW) from the Southern Ocean, with distinct pre-formed Cd concentrations (Xie et al., 2015). In this view, the Cd concentration profile for the Southern Ocean station is important as it is distinct from all other stations on the transect. Although Cd is depleted in the Antarctic surface ocean, the depletion is much less pronounced here than in the surface ocean along the rest of the section, with dissolved Cd concentrations as high as $\sim 0.4 \text{ nmol kg}^{-1}$ at the surface, probably due to the local upwelling of nutrient-rich UCDW. Below the surface, a shallow Cd maximum (1 nmol kg^{-1}) is located at a depth of $\sim 200 \text{ m}$. These two distinct features match the profile shape that has been observed previously in other HNLC areas of the Southern Ocean (Xue et al., 2013; Abouchami et al., 2014).

Fig. 4 clearly shows that the surface Southern Ocean concentrations of Cd are imprinted on water masses exported from this region, and that the distribution further north can also, to a large extent, be viewed as controlled by these low-Cd intermediate water masses (Xie et al., 2015). Thus AAIW-like ($\sim 0.55 \text{ nmol kg}^{-1}$) and SAMW-like ($\sim 0.30 \text{ nmol kg}^{-1}$) concentrations dominate intermediate waters at depths of 300-1500 m as far north as 30°S (Fig. 4, 7). Cd concentrations increase in both AAIW and SAMW as they flow northwards towards the Equator and mix with the underlying, nutrient-rich UCDW and PDW (Fig. 7), leading to a steeper increase in Cd concentration and a progressively shallower Cd maximum (Fig. 4). Set against variation and mixing in surface and intermediate waters, the Cd concentration in northward-flowing LCDW, remains fairly constant throughout the whole transect (Fig. 7), with only a slight increase in the equatorial Pacific.

Stations 6 and 15, located at 30°S but over a longitudinal spread of 16° , display almost identical Cd distributions (Fig. 5) due to the fact that both stations have similar water mass structures. This highlights the importance of water mass structures and their associated pre-formed Cd concentrations which strongly influence the distribution of Cd at lower latitudes. In the next section we explore the Southern Ocean control further, using relationships between Cd and phosphate concentrations.

5.3 Biogeochemical Controls on the Cd/P relationship in the South Pacific

We observe strong and coherent relationships between dissolved Cd and PO_4 in the Southwest Pacific Ocean (Fig. 8). But, the distribution of Cd: PO_4 follows two different slopes: a shallow slope of $0.05 \text{ nmol } \mu\text{mol}^{-1}$ at $\text{PO}_4 < 0.68 \text{ } \mu\text{mol kg}^{-1}$, and a ten-times steeper slope of $0.41 \text{ nmol } \mu\text{mol}^{-1}$ at $\text{PO}_4 > 0.68 \text{ } \mu\text{mol kg}^{-1}$. The entire water column of the station south of the APF falls on the steep slope. For all stations north of the APF, most of the upper ocean as well as the entire intermediate and deep ocean ($>200 \text{ m}$) follow the steep slope of $0.41 \text{ nmol } \mu\text{mol}^{-1}$, consistent with previous observations for deep waters in the Pacific (e.g. Bruland, 1980; Abe, 2002). However, the shallow subsurface ocean ($<200 \text{ m}$) lies close to the lower slope, pointing to a different behavior. The slope is similar to the one observed in the surface South Atlantic (0.031 ; Baars et al., 2014). The distribution of Cd: PO_4 is reminiscent of the correlation between Zn and PO_4 and suggests that similar processes control both distributions (Vance et al., 2017; de Souza et al., 2018). In this view, the lower slope would represent uptake of Cd at an extremely low Cd/P ratio in the Cd-depleted upper ocean north of the APF. The steep slope would track the biogeochemistry of water masses exported from the Southern Ocean, determined by removal of Cd at a high Cd/P ratio by diatoms in the surface Southern Ocean.

Intermediate and deep water masses in the Pacific are all ultimately Southern Ocean-derived and subsequently they follow the same slope, although they bear different Cd:PO₄ ratios. Along our section, intermediate waters exhibit Cd:PO₄ ratios in the range of 0.2 – 0.3 nmol μmol⁻¹, whereas the deep-ocean Cd:PO₄ ratio is constant (0.35 nmol μmol⁻¹). Interestingly, this deep-ocean Cd:PO₄ ratio is the same as calculated for the North Pacific (Janssen et al., 2014), while the ratio measured in the deep subtropical Pacific is slightly lower (0.317 nmol μmol⁻¹, Conway and John, 2015b). Mixing between water masses follows the slopes, with deep waters at the high end of the steep slope and AAIW and SAMW located closer to the kink. In comparison, data for Atlantic intermediate and deep waters show deviations from a single linear relationship due to the mixing of southern-sourced water masses with North Atlantic Deep Water (Middag et al., 2018)

We use Cd* to further highlight the influence of the Southern Ocean on the distributions of dissolved Cd and PO₄ in the Southwest Pacific ocean (Fig. 4). Dissolved Cd* is a parameter that highlights whether Cd is enriched or depleted relative to deep-ocean Cd:PO₄, and is here calculated following Janssen et al., 2014 based on measured Cd and PO₄ concentrations using the deep South Pacific Ocean Cd:PO₄ ratio as a reference point (0.35 nmol μmol⁻¹).

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

Dissolved Cd* values are close to 0 nmol kg⁻¹ below a depth of 1500 m across the entire section, highlighting the homogeneity of the deep ocean with regards to Cd:PO₄ ratios (Fig. 4). In the upper ocean, we observe three prominent features: (1) an excursion to positive Cd* values in the shallow subsurface Southern Ocean while overlying AASW shows negative values; (2) a negative Cd* signal that coincides with the northward-spreading ‘tongue’ of AAIW, and extends towards the surface ocean; and (3) negative Cd* values at shallow depths from 10°S towards the equator associated with the lower oxygen waters of the Tropical Pacific Oxygen Minimum Zone.

On closer examination, the Cd* signal for the Southern Ocean station shows a very large shift, from -0.19 nmol kg⁻¹ in AASW to >+0.1 nmol kg⁻¹ in the subsurface below 50 m. The strong negative Cd* signal in the Antarctic surface ocean can be explained by preferential uptake of Cd relative to PO₄ under Fe-limited conditions (Sunda and Huntsman, 2000), which leaves surface waters depleted in Cd relative to PO₄. The underlying shift to positive Cd* values at shallow depths coincides with a steep increase in Cd. The shallow Cd maximum is a result of both upwelling and shallow remineralization of Cd from organic matter. However, the upwelling UCDW carries a Cd* = 0 nmol kg⁻¹ and we can identify shallow remineralization as

the source of the positive Cd^* signal. The second feature, a negative Cd^* in AAIW and SAMW, can be linked to the negative Cd^* in AASW, as both water masses derive from AASW. This pre-formed Cd-depletion can be traced in intermediate waters across the entire section. The negative Cd^* signal does start to weaken north of 30°S due to increased mixing of SAMW and AAIW with other water masses. The water overlying SAMW also show negative Cd^* values (down to $-0.13 \text{ nmol kg}^{-1}$) throughout the section. Most likely, this signal originates in the underlying water masses SAMW and AAIW, via upwelling or diapycnal mixing. The return to Cd^* values $\sim 0 \text{ nmol kg}^{-1}$ in the surface ocean results purely from the concomitant depletion of Cd and PO_4 in subtropical surface waters, and does not bear any large-scale process information.

At Stations 19 and 21 in the equatorial Pacific, a more negative Cd^* signal is observed at depths of 200 – 600 m, coinciding approximately with the region of oxygen concentrations below $110 \mu\text{mol kg}^{-1}$ (300 – 500 m) (Fig. S2). This signal cannot be simply explained by the waning influence of southern-sourced water masses in this region, as it is at shallower depths than the salinity minimum of AAIW, and is more negative. Instead, this signature corresponds with the top of low-oxygen waters, and may instead be related to the removal of Cd into particulate micro-environments as has been hypothesized previously (see Section 5.6 for further discussion).

5.4 Distribution of dissolved $\delta^{114}\text{Cd}$ along GP19

Along the meridional GP19 section, the vertical profiles of dissolved $\delta^{114}\text{Cd}$ generally show little variation in the deep ocean ($+0.26\text{‰} \pm 0.06$, 2SD, $n = 60$) and an increase towards high $\delta^{114}\text{Cd}$ values (up to $+0.8\text{‰}$) in the surface ocean (Fig 4). This trend towards heavy values coincides with an associated depletion of Cd in the surface ocean and is consistent with preferential uptake of isotopically light Cd by phytoplankton (Lacan et al., 2006; John and Conway, 2014).

At depths of 100 – 1500 m, as with Cd concentrations, the single Southern Ocean station exhibits a distinctly different shape in subsurface waters from the stations north of the APF (Fig. 5). In the Antarctic, $\delta^{114}\text{Cd}$ values show a sharp drop from heavy surface values ($+0.6\text{‰}$) down to a constant deep ocean value ($+0.23\text{‰}$) as shallow as 150 m. While otherwise similar to Atlantic Southern Ocean Cd isotope profiles (Xue et al., 2013), the shallow maximum in Cd concentrations (up to 1 nmol kg^{-1}) does not coincide with a resolvable shift to lighter $\delta^{114}\text{Cd}$ values. Both, the upwelling of nutrient-rich UCDW to very shallow depths of $\sim 200\text{m}$ at the Pacific station, as reflected by the low oxygen, and the addition of remineralized light Cd,

associated with a shift to positive Cd* values (Section 5.3), contribute to the shallow Cd maximum. The superposition of a slightly heavier $\delta^{114}\text{Cd}$ signature carried by UCDW (Section 5.5) on top of the shallow regeneration of isotopically light Cd could subsequently impart an average $\delta^{114}\text{Cd}$ signature similar to the deep ocean, masking the shift to lighter $\delta^{114}\text{Cd}$ values driven by local remineralization. At the Atlantic Southern Ocean stations, UCDW is not this close to the surface and therefore does not overlap with the shallow regeneration signal. Further south of this station, where UCDW has already reached the surface ocean, we would expect to see an excursion to lighter $\delta^{114}\text{Cd}$ values due to the shallow remineralization, similar to what has been observed in other sectors of the Southern Ocean (Xue et al., 2013).

By contrast, at intermediate depths at stations north of the APF we observe the most striking feature in $\delta^{114}\text{Cd}$ isotope signatures. Along with low Cd concentrations, AAIW and SAMW show heavy $\delta^{114}\text{Cd}$ values (+0.4 to +0.6‰), and these signatures are clearly conserved northwards into the lower latitude Pacific, with little change as far north as 20°S (Figs 7, 9), analogous to $\delta^{30}\text{Si}$ in the southeastern Pacific (de Souza et al., 2012). As these intermediate water masses transit into the tropical Pacific regime, they mix increasingly with the underlying nutrient-rich PDW and the distinctly heavier signatures at intermediate depths start to wane (Figs 7, 9). This mixing leads to a less pronounced gradient in the subsurface, and an equatorward shoaling of the deep ocean homogeneity with the decreasing influence of AAIW and SAMW. Below intermediate waters, the two major water masses in the deep ocean, LCDW and PDW, cannot be distinguished by their $\delta^{114}\text{Cd}$ signatures, despite their significantly different Cd concentrations (Fig. 4, 9). Therefore, the slight northward increase in Cd concentrations observed in LCDW is not accompanied by a change in $\delta^{114}\text{Cd}$ (Fig. 7). Also, the transition from PDW to UCDW in the subtropical Pacific is not visible in $\delta^{114}\text{Cd}$ as both water masses carry the same deep ocean $\delta^{114}\text{Cd}$ value. Hence, as has been shown for the deep North Pacific (Janssen et al., 2017), the deep South Pacific shows little variation in $\delta^{114}\text{Cd}$. When adding the GP19 dataset to Pacific data from the literature (Conway and John, 2015b; Janssen et al., 2017; John et al., 2018), we can calculate an updated deep Pacific and Southern Ocean (>1500 m) Cd isotope signature of $+0.26 \pm 0.10\text{‰}$ (2SD, $n = 436$).

Similar to Cd concentrations, $\delta^{114}\text{Cd}$ profiles for the two stations at 30°S show little to no differences (Fig. 5). The two stations differ slightly in the surface ocean but exhibit the same trends as described above and differences are mostly within error. Below the surface ocean the $\delta^{114}\text{Cd}$ distributions are remarkably similar. Again, this highlights the extent to which southern-sourced water masses dominate the distribution of $\delta^{114}\text{Cd}$ at lower latitudes.

5.5 The influence of water mass mixing on Cd cycling along GP19

In the southwest Pacific, we can investigate how upwelling and surface processes in the Southern Ocean may set preformed Cd isotope signatures in a manner analogous to their influence on Cd* (Baars et al., 2014). Furthermore, ocean circulation control on $\delta^{114}\text{Cd}$ signatures by water mass mixing has been described previously for the Atlantic (Abouchami et al., 2014; Xie et al., 2017), and our section demonstrates exceptionally well how water mass mixing controls the distribution of Cd in the subsurface South Pacific in similar fashion. Here, we explore how the preformed signatures of water mass endmembers evolve as they interact with the effects of large scale circulation and regeneration. To do this, we take the endmembers defined on the basis of physical properties (Section 2) and identify their Cd signatures. Figure 7 shows these endmembers and how Cd concentrations and $\delta^{114}\text{Cd}$ signatures change as subsurface water masses flow across fronts. Fig. 10 illustrates how binary mixing between water mass endmembers can explain the distribution of Cd along the section.

The mixing diagram (Fig. 10) allows us to identify the controls on different features occurring along the GP19 section. Firstly, the observed trend to higher $\delta^{114}\text{Cd}$ values and lower Cd concentrations in the low-oxygen tongue of UCDW, as it shoals southwards across the fronts of the ACC, can clearly be associated with the mixing of isotopically heavy AAIW, such that Subantarctic UCDW is Cd-poorer, and isotopically heavier, than UCDW in the deep Pacific. Secondly, we see that AAIW is higher in Cd and slightly isotopically lighter than AASW. While the isotopically heavy, Cd-depleted, signal found in AASW influences AAIW during formation of intermediate waters north of the SAZ, Fig. 10 shows that Cd signatures in AAIW cannot be derived only by simple mixing of water mass endmembers, indicating that there are other processes that influence the formation of the Cd signal of AAIW. Compared to Atlantic AAIW ($0.65 \text{ nmol kg}^{-1}$, $+0.45\text{‰}$; Xie et al., 2017), Pacific AAIW is slightly more depleted in Cd but carries a similar isotopic signature, the result of the different formation regions and processes of Pacific and Atlantic AAIW (Sallée et al., 2010). As AAIW flows northwards, the Southern Ocean $\delta^{114}\text{Cd}$ signal is conserved up to 20°S , before Cd concentrations increase further and the heavy $\delta^{114}\text{Cd}$ signal subsides quickly towards the equatorial Pacific (Fig. 7). This shift in the equatorial Pacific could result either through diapycnal mixing with underlying PDW that carries abundant Cd and a lighter $\delta^{114}\text{Cd}$ signature (Fig. 10), or the input Cd-rich upper-ocean waters of North Pacific origin (e.g. North Pacific Intermediate Water, NPIW, 0.8 nmol kg^{-1} , $+0.3\text{‰}$; Conway and John, 2015b) into intermediate equatorial waters. Due to their similar isotopic signatures it is not yet possible to attribute relative importance to these two different

sources but it is likely that both contribute to the changing $\delta^{114}\text{Cd}$ signal as intermediate waters transition into the equatorial Pacific regime.

Looking more closely at the relationship between $\delta^{114}\text{Cd}$ and Cd^* signatures along the section (Fig. 11), there is a clear correlation. All heavy $\delta^{114}\text{Cd}$ signatures below a depth of 200 m are associated with a negative Cd^* . The majority follows the mixing of water mass endmembers showing that the heavy $\delta^{114}\text{Cd}$ signatures in AAIW and SAMW originate in the Southern Ocean where a high Cd/P uptake ratio imprints water masses with a negative Cd^* signal while deep water $\delta^{114}\text{Cd}$ signatures cluster around a Cd^* value of zero. This emphasizes the two regimes dominating the distribution of Cd isotopes in the Southwest Pacific. One such regime is the deep ocean, which is isotopically homogenous throughout the whole section and over a range of Cd concentrations. The other is represented by the heavy signatures originating in the surface Southern Ocean. These southern-sourced signatures in intermediate waters reveal the Southern Ocean to be the driving force of varying signatures in the subsurface Southwest Pacific. The export of heavy $\delta^{114}\text{Cd}$ signatures in AAIW originating in the Southern Ocean is in good agreement with previous observations in the Atlantic (Abouchami et al., 2014; Conway and John, 2015a; Xie et al., 2017). In contrast to the Atlantic, the heavy $\delta^{114}\text{Cd}$ signatures are not preserved as far north in the Pacific. Because there is no deep water formation in the North Pacific, southward flowing intermediate and deep waters (e.g. NPIW and PDW) carry high Cd concentrations and it is the increasing influence of these Cd-rich waters that overprints other $\delta^{114}\text{Cd}$ signals in the equatorial Pacific, similar to the distribution described for $\delta^{30}\text{Si}$ (de Souza et al., 2012).

5.6 The influence of low-oxygen waters in the tropical Pacific

As noted in Section 5.2, samples collected from depths corresponding to the subsurface oxygen minimum at near-equatorial stations 19 and 21 show a negative Cd^* (Fig S.2). , Though this occurs at the approximate depth of AAIW, it is also associated with low oxygen concentrations. Indeed, when all GP19 samples below 200 m are plotted on a Cd^* - $\delta^{114}\text{Cd}$ plot (Fig. 11), and grouped by salinity or oxygen, it can be seen that tropical low-oxygen samples (circles on Fig. 11) lie on a off the array controlled by the mixing of preformed signatures in water masses. This suggests that the Cd depletion here is not just caused by the presence of AAIW, which influences the profiles deeper in the water column. Instead, the Cd depletion in these samples may be caused by the removal of dissolved Cd (but not phosphate) to CdS , as has been suggested previously for the North Pacific Oxygen Minimum Zones (Janssen et al., 2014; Conway and John, 2015b). While the Cd^* depletion could be a locally-created signal, it is also

possible that we observe an advected signal reflecting Cd removal in anoxic waters deep within the OMZ. Although there is insufficient information available in this section to constrain the isotope effect such a process may impart on the remnant dissolved pool, the array in Fig. 11 would be consistent with the hypothesis that light Cd is lost preferentially to particles (Janssen et al., 2014).

5.7 Remineralization of Cd in the Pacific Ocean

In previous sections, we defined endmembers of intermediate and deep waters and highlighted the influence of the Southern Ocean and ocean circulation on $\delta^{114}\text{Cd}$ distribution at low latitudes. We can compare the Cd-related characteristics of these water masses and their evolution in the southwest Pacific with recently published data from the Equatorial and North Pacific (Conway and John, 2015b; Janssen et al., 2017; John et al., 2018). Both areas include high-Cd intermediate and deep waters that allow us to constrain the effects of remineralization of Cd on isotopic signatures in the Pacific.

5.7.1 The influence of remineralized Cd on AAIW in the equatorial Pacific

To allow for a direct comparison between recently-ventilated AAIW and equatorial AAIW (eqAAIW), we use data from the US GEOTRACES GP16 Eastern Pacific Zonal Transect (John et al., 2018) to derive the Cd-characteristics of equatorial AAIW. Equatorial AAIW along the GP16 section spans a large range of Cd concentrations from $0.67 \text{ nmol kg}^{-1}$ in the South Pacific oligotrophic gyre up to 1 nmol kg^{-1} in the Peru upwelling zone. Concentrations in the western part of GP16 are similar to the ones we observe at this latitude (10°S) along our section ($0.68 \text{ nmol kg}^{-1}$). High levels of phytoplankton productivity and subsequent remineralization of Cd from sinking organic matter are likely the cause of the extremely high concentrations in the eastern part of GP16. However, while eqAAIW exhibits a substantial gradient in Cd concentrations, $\delta^{114}\text{Cd}$ signatures show no significant change along GP16 ($+0.47 \pm 0.08\text{‰}$, 2SD, $n = 10$). Furthermore, the $\delta^{114}\text{Cd}$ signal of eqAAIW from GP16 matches that along our transect at similar latitudes very well ($+0.46\text{‰}$) which, considering the similarity of $\delta^{114}\text{Cd}$ signatures of AAIW in the southwest Pacific and the Atlantic (Xie et al., 2017), suggests that eqAAIW still carries its southern-sourced $\delta^{114}\text{Cd}$ signature. Comparison of the GP16 data with the previously defined scheme for water mass mixing in the South Pacific (Fig. 10) shows that the Cd signatures in eqAAIW cannot be derived from binary mixing with other water mass endmembers but instead can be attributed to addition of remineralized Cd (Fig. S3).

Here, we propose complete consumption of Cd in the surface equatorial Pacific, equivalent to what has been suggested for nitrogen stable isotopes in nitrate (Rafter et al., 2012) as a possible explanation for the lack of zonal change in $\delta^{114}\text{Cd}$ in the eqAAIW. Nutrients are delivered to the surface by equatorial upwelling from the Equatorial Undercurrent (EUC). The EUC carries a $\delta^{114}\text{Cd}$ signal of $\sim +0.55\text{‰}$ (estimated based on our equatorial St. 21, 99 m water depth) and upwelled Cd would thus bring this heavy signature, only slightly higher than the AAIW $\delta^{114}\text{Cd}$ of $\sim +0.45\text{‰}$, to the surface mixed layer. The complete utilization of Cd within the tropical circulation fed by equatorial upwelling will lead to an integrated $\delta^{114}\text{Cd}$ signal in organic matter that is similarly heavy. Remineralization of this organic matter at depth will therefore supply eqAAIW with Cd with a $\delta^{114}\text{Cd}$ that closely matches the Southern Ocean source signature of AAIW. This interpretation can explain the uniformity of the $\delta^{114}\text{Cd}$ signal in eqAAIW over a large range of concentrations. We can take advantage of the isotope systematics of the data to constrain the range of the integrated $\delta^{114}\text{Cd}$ signal of organic matter that is added to eqAAIW through remineralization via linear regression. This is shown in Fig. 12 based on a numerical Monte Carlo propagation of regression error, including the analytical error of individual measurements (see caption for details). The estimated $\delta^{114}\text{Cd}$ of remineralized Cd in the equatorial Pacific falls within a range of $+0.25$ to $+0.63\text{‰}$, which is consistent with the heavier Cd input we suggest. However, as this is an integrated signal of remineralized Cd for the equatorial Pacific, we cannot exclude the possibility of inputs lighter than $\sim +0.5\text{‰}$ into eqAAIW at this stage. Indeed, the regression shows that slightly lighter Cd inputs could be included without an analytically resolvable change in its $\delta^{114}\text{Cd}$ signature. In fact, we would expect such light remineralized Cd to be added locally in the Peruvian upwelling zone, where Cd is not fully depleted in the surface.

5.7.2 Implications for the deep ocean $\delta^{114}\text{Cd}$ signatures in the Pacific

Focusing on the deep Pacific, we can further add data from Line P in the subarctic North Pacific (Janssen et al., 2017) and the SAFe station in the subtropical Northeast Pacific (Conway and John, 2015b) and compare the Cd signatures of deep waters as they move through the Pacific. As mentioned in Section 5.4, the deep Pacific exhibits widespread isotopic uniformity, despite an increase of about 30% in Cd concentrations from the Southern Ocean to the North Pacific. A major factor that contributes to this uniformity is Southern Ocean control on Pacific deep waters. All Pacific deep waters are Southern Ocean derived: LCDW originates in the Southern Ocean, and because PDW has no surface sources and is formed internally by upwelling and diffusion in the North Pacific from LCDW, the pre-formed $\delta^{114}\text{Cd}$ signal of PDW still originates in the Southern Ocean. The increase in Cd concentrations of deep waters is

mainly through addition of remineralized Cd from sinking organic matter which does not seem to change the isotopic composition of deep waters.

Following the interpretation in the previous section, we would expect the heavy remineralized $\delta^{114}\text{Cd}$ signal that results from complete utilization in the equatorial Pacific to affect the entire water column, including deep waters (albeit to a lesser extent, due to the attenuation of particle flux with depth, and the higher leverage of deep waters with higher pre-formed Cd). However, deep waters carry an integrated $\delta^{114}\text{Cd}$ signal of organic matter remineralized across the entire Pacific. A significant part of this is added in the North Pacific, where deep waters have long residence times and accumulate nutrients by remineralization. In the subarctic Pacific, upwelled waters bring Cd with a $\delta^{114}\text{Cd}$ signal comparable to the deep ocean to the surface (Janssen et al., 2017). Additionally, surface waters are not fully depleted in Cd, resulting in production of organic matter with a light $\delta^{114}\text{Cd}$ signature. This is analogous to the Southern Ocean and we would expect that remineralization of this organic matter carries a lighter $\delta^{114}\text{Cd}$ signal to deeper waters. While the integrative nature of deep-water $\delta^{114}\text{Cd}$ precludes identification of the individual contributions of remineralization in different areas of the Pacific, we can constrain the range of the integrated $\delta^{114}\text{Cd}$ signal of organic matter that is remineralized throughout the entire deep Pacific (Fig. 12). This would mean that the integrated $\delta^{114}\text{Cd}$ signal of remineralized Cd lies within the range of +0.2 to +0.45‰, slightly heavier than what Janssen et al. (2017) have suggested. A combination of the two processes described above - complete utilization in Cd-depleted equatorial waters and remineralization of heavier organic matter, as well as incomplete utilization in high latitudes and remineralization of light Cd - would fit well into that range. This conclusion must, however, remain tentative until the isotopic composition of remineralized Cd is better constrained in the different Pacific regimes, perhaps through the isotopic characterization of sinking particulates or through model simulations that incorporate Cd isotopes (Roshan et al., 2017).

6. Conclusions

Here, we have presented a meridional transect of dissolved Cd and $\delta^{114}\text{Cd}$ from Japanese GEOTRACES Section GP19 along 170°W from 60°S in the Southern Ocean to the equatorial Pacific. Our dataset highlights the extent to which Southern Ocean processes and ocean circulation control the distribution of Cd and $\delta^{114}\text{Cd}$ at lower latitudes in the Southwest Pacific. Specifically, we show that large scale near-conservative mixing of Cd between water masses fingerprinted with pre-formed, southern-sourced $\delta^{114}\text{Cd}$ signatures can explain the $\delta^{114}\text{Cd}$ distribution in the Southwest Pacific. Furthermore, we propose complete utilization of Cd in the

surface equatorial Pacific and remineralization of isotopically heavy Cd to explain the zonal uniformity in equatorial AAIW. In the same way, we can constrain the $\delta^{114}\text{Cd}$ signal of Cd added to the deep Pacific by remineralization based on the near-constant $\delta^{114}\text{Cd}$ signal over a range of concentrations. However, since this signal is integrated over the entire Pacific, it is possible that remineralization in different Pacific regimes adds Cd with different isotopic compositions to the deep waters. Future studies focusing on particulate Cd and its interactions with the dissolved pool are needed to provide a more detailed understanding of the effects of remineralization on Cd isotopic distributions.

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Tables

Table 1. T-S characteristics of the major water mass endmembers in the Southwest Pacific based on Talley et al. (2011).

Water mass	T (°C)	S	σ_θ (kgm ⁻³)	PO ₄ (μmol kg ⁻¹)	characteristic
SAMW	8	34.4	26.8	1.28	pot. vorticity minimum
AAIW	5	34.3	27.1	2.09	salinity minimum
PDW	2-3	34.6	27.6	2.96	high nutrients
UCDW	2.5	34.6	27.6	2.60	O ₂ minimum
LCDW	1-2	34.7	27.8	2.30	salinity maximum

783 distribution of oxygen (lines) overlain on salinity (top), and phosphate concentrations (bottom)
784 along the GP19 transect (based on the World Ocean Circulation Experiment; Schlitzer, 2000).

785 **Figure 2. a)** $\delta^{114}\text{Cd}$ values for mixtures of the NIST SRM-3108 standard with the double spike
 786 at molar ratios of standard to double-spike varying from 0.1 to 10. The analyzed mixtures are
 787 identical within 2σ error (grey bar), showing that accurate results can be obtained for a large
 788 range of standard/spike ratios. Seawater analyses were routinely performed at a ratio of ~ 1 to
 789 maximize analytical precision. **b)** Long term averages for secondary standards BAM-I012 ($-$
 790 $1.320 \pm 0.058\text{‰}$, 2 SD, $n = 98$) and Münster Cd ($4.498 \pm 0.061\text{‰}$, 2 SD, $n = 102$), relative to
 791 NIST SRM-3108, measured over 12 analytical sessions over the same timescale as samples
 792 (seven months). Coloured lines and bars correspond to the established values and 2σ errors,
 793 respectively (Abouchami et al., 2013).

794 **Figure 3.** Inter-comparison of dissolved $\delta^{114}\text{Cd}$ for reference materials SAFe D1 and D2
 795 measured in recent studies (Xue et al., 2012; Conway et al., 2013; Conway and John, 2015a;
 796 Janssen et al., 2017; Xie et al., 2017). We show the weighted average with a 2σ error, with the
 797 number of individual measurements in each study (n) given in brackets. The black line denotes
 798 the weighted average based on all studies ($+0.30\text{‰}$, $n = 27$) and the yellow bar the 2SD
 799 (0.06‰).

800 **Figure 4.** Dissolved Cd concentration (top), Cd* (middle) and $\delta^{114}\text{Cd}$ (bottom) along the GP19
 801 South Pacific section.

802 **Figure 5.** Dissolved Cd concentration, Cd* and $\delta^{114}\text{Cd}$ profiles along the GP19 section. Gray points in the left panel show data from the Atlantic
803 sector of the Southern Ocean (Xue et al., 2013; Abouchami et al., 2014). All three stations at $\sim 30^\circ\text{S}$ (third panel from the right; diamonds - St. 6,
804 circles – St. 13, triangles – St. 15) exhibit the same water mass structure and therefore show almost identical Cd and $\delta^{114}\text{Cd}$ distributions.

805 **Figure 6.** Cd isotope systematics of the global ocean. Blue squares (this study), red squares
 806 (Xie et al., 2017), gray squares (previous studies: (Xue et al., 2013; Abouchami et al., 2014;
 807 Conway and John, 2015a, 2015b; Janssen et al., 2017; John et al., 2018).

808 **Figure 7.** Evolution of Cd (left) and $\delta^{114}\text{Cd}$ (right) signatures of water masses along GP19.
 809 Arrows indicate integrated flow directions for each water mass. Gray bars represent the
 810 Antarctic Polar Front (APF) and Subtropical Front (STF), respectively.

811

812 **Figure 8.** Dissolved Cd – PO₄ relationship along the GP19 section in the South Pacific Ocean.
 813 Surface ocean data (<200m) outside of the Southern Ocean fall on a gentle slope, indicating
 814 uptake at a very low Cd/PO₄ ratio. On the contrary, Southern Ocean and deeper Pacific (>200m)
 815 samples follow a much steeper trend representing uptake at a much higher Cd/PO₄ ratio. Mixing
 816 between nutrient-rich deep waters and Cd-depleted intermediate waters also follows this steeper
 817 slope.

818

819 **Figure 9.** Depth profiles of $\delta^{114}\text{Cd}$ along the GP19 section overlain on a color map of salinity.
 820 The white line for each profile represents the deep Pacific and Southern Ocean average $\delta^{114}\text{Cd}$
 821 (+0.26‰, Section 5.4). Heavy $\delta^{114}\text{Cd}$ values in intermediate waters follow the salinity
 822 maximum northwards, remaining constant up to 20°S before they start to be mixed away due
 823 to the increasing influence of Cd-rich PDW towards the equator.

824 **Figure 10.** Binary mixing of subsurface water mass endmembers along GP19, showing that all
 825 data from samples below 200 m falls on mixing lines (black arrows) between water mass
 826 endmembers (blue circles).

827 **Figure 11.** Relationship of Cd* and $\delta^{114}\text{Cd}$ along GP19, color-coded for salinity (upper panel)
828 and dissolved oxygen (lower panel), showing that water-mass mixing of different preformed
829 endmembers can explain the majority of the distribution of both parameters (solid black lines).
830 Subsurface waters at equatorial stations (circles) fall off this array, and may instead be explained
831 by loss of Cd to CdS in particles in the low-oxygen waters of the tropical Pacific OMZ, with an
832 unconstrained isotope effect.

833 **Figure 12.** Estimation of the integrated $\delta^{114}\text{Cd}$ signal of Cd remineralized from organic matter
 834 in equatorial AAIW (top) and Pacific deep waters below 2000 m (bottom). Intercepts of the y-

835 axis represent the possible range of the integrated $\delta^{114}\text{Cd}$ signal from remineralization, based
836 on a numerical Monte Carlo propagation of regression error including the analytical error of
837 individual measurements (10^4 Monte Carlo iterations). Data for eqAAIW is from the GP19
838 stations in the equatorial Pacific and GP16 (John et al., 2018). Deep ocean data is from all
839 stations from GP19, as well as all previous studies from the Pacific (Conway and John, 2015b;
840 Janssen et al., 2017; John et al., 2018).

Supplementary Material

Table S1. Cup configuration for isotopic analysis of Cd by Thermo Neptune MC-ICPMS.

Isotopic abundances are shown in brackets. All measured Cd isotopes have a molecular interference from MoO⁺.

Faraday cup	L3	L2	L1	C	H1	H2	H3	H4
<i>Measured element</i>	¹¹¹ Cd (12.80 %)	¹¹² Cd (24.13 %)	¹¹³ Cd (12.22 %)	¹¹⁴ Cd (28.73 %)	¹¹⁵ In (95.71 %)	¹¹⁶ Cd (7.49 %)	¹¹⁷ Sn (7.68 %)	¹¹⁸ Sn (24.22 %)
<i>Interference</i>		¹¹² Sn (0.97 %)	¹¹³ In (4.29 %)	¹¹⁴ Sn (0.66 %)	¹¹⁵ Sn (0.34 %)	¹¹⁶ Sn (14.50 %)		

Table S2. Dissolved Cd and $\delta^{114}\text{Cd}$ values for SArFe S1, D1 and D2 seawater standards.

All isotope ratios are shown with 2 σ error, and assumed error on concentrations is 2% (see Section 3.2). 2013 SArFe consensus concentration values are shown in parentheses. Weighted average for $\delta^{114}\text{Cd}$ of SArFe D1 and D2 based on previous studies ($+0.30 \pm 0.06\text{‰}$, 2SD, n = 27)

Sample	Cd (nmol kg ⁻¹)		$\delta^{114}\text{Cd}$ (‰)
S1	0.0011	(0.0011 $\pm$ 0.0003)	nd
D1	0.991	(0.991 $\pm$ 0.031)	0.29 $\pm$ 0.06
D1	0.991		0.29 $\pm$ 0.08
D2	0.986	(0.986 $\pm$ 0.023)	0.24 $\pm$ 0.08
D2	0.986		0.27 $\pm$ 0.07

Figure S1. $\delta^{114}\text{Cd}$ values for low concentration mixtures of the NIST SRM-3108 standard with the double spike at a molar ratio of standard to double-spike of 1, doped with 1 ng of Mo. Cd concentrations range from 0.2 to 5 ng, representing typical Cd concentrations of surface seawater samples. The Mo amount was chosen based on the maximum amount of Mo (1 ng) that elutes with the Cd split after the full extraction procedure on a 4 L sample. Despite the fact that no corrections were applied at all, the analyzed mixtures are identical within 2σ error, showing that no correction for MoO^+ was necessary even at low seawater Cd concentrations in 4 L samples. Error bars represent the internal error which is considered a more conservative estimate of uncertainty for such low concentrations than the external precision (grey bar).

Station 19 (10°S) **Station 21 (0°S)**

855

856 Figure S2: Profiles of Cd*, oxygen concentrations and salinity of the two stations in the
 857 equatorial Pacific.

858

859 Figure S3: Binary mixing of subsurface water mass endmembers along GP19 (gray) with data
 860 added for eqAAIW from GP16 (blue; (John et al., 2018)) and for PDW from LineP (red; Janssen
 861 et al., 2017). Green arrows represent the addition of remineralized Cd, shifting both water
 862 masses away from the signatures of the southern-sourced endmembers (blue circles).

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