Controls on the cadmium isotope composition of modern marine sediments

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Highlights:

1. First constraints on the δ^{114}Cd composition of modern marine suboxic sediments
2. Main sources of sedimentary Cd are from sinking organic particulates and seawater
3. Average δ^{114}Cd value of surface sediments is 0.27‰ lighter than seawater
4. Burial of organically-bound Cd in suboxic sediments could satisfy Cd mass balance
5. Sulfide production quantitatively removes seawater Cd at depth in the sediment

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Abstract

Continental margin suboxic sediments have been identified as the dominant sink term in the marine budget of cadmium (Cd). However, the isotopic composition of this important output flux, including the processes that control this isotope composition during the earliest stages of diagenesis, are not well constrained. Here we present the first constraints on the isotopic composition of Cd in modern marine sediments. Surface sediments (0–1 cm) on the Argentine continental margin and adjacent slope and basin below 100 m water depth are isotopically offset from the overlying oxygenated deep water by $\Delta^{114/110}\mathrm{Cd}_{\text{surface sediments—deep waters}}$ = -0.27 ± 0.14‰. We calculate a mass balance of the Cd budget in the surface sediments and find that it is dominated by organically-bound particulate Cd (in addition to some lithogenic Cd). This surface accumulation of isotopically light Cd along margin suboxic sediments can satisfy the global isotopic mass balance of oceanic Cd. All the cores in this study also show distinct sub-surface enrichment peaks in Cd concentration, with a similar isotopic composition as overlying deep water (~0.35‰). This observation is consistent with a downwards diffusive flux of seawater Cd and redox-driven quantitative removal of that Cd during sulfide precipitation. This sulfide hosted Cd dominates the Cd budget at depth in the sediment and leads to isotope values close to that of seawater. These findings suggest two main pathways for Cd removal into suboxic sediments; Cd associated with organic material, and with sulfide minerals.

1. Introduction

The cadmium (Cd) isotope system has yielded a wealth of insights into the processes that regulate the vertical and horizontal distribution of Cd in the modern ocean and may be used to provide information about past ocean chemistry. Previous studies have reported a biologically-controlled depth profile for Cd, where preferential uptake of light Cd isotopes by marine phytoplankton leaves the surface waters with low Cd concentrations and higher isotope compositions relative to deep waters (Lacan et al., 2006; Ripperger et al. 2007; Abouchami et al., 2011; Boyle et al., 2012; Xue et al., 2013; John and Conway, 2014; Janssen et al., 2014; Conway and John, 2015a; Conway and John, 2015b; Xie et al., 2017; Janssen et al., 2017; John et al., 2018; Sieber et al. 2019). While the availability of Cd isotope data in seawater and particulates continues to expand (Yang et al., 2012; Janssen et al., 2014; Conway and John, 2015b, Yang et al., 2015; Yang et al., 2018; Janssen et al., 2019), our understanding of the global isotopic mass balance of Cd is less clear due to the unknown Cd isotope compositions in modern marine sediments, especially those accumulating in low oxygen settings with significant amounts of organic matter. Furthermore, the effect of shallow sediment diagenesis in altering the isotopic composition of recently buried Cd is not well understood. Characterization of the isotopic composition of Cd in modern marine bulk sediments is critically important to understand how and why the Cd isotopic composition of the oceans might evolve through time, and how we might interpret marine sediment data as an archive of these variations.

At a global scale, the Cd cycle is controlled by inputs of Cd to the oceans from three main sources: upper continental crust (with $\delta^{114/110}$Cd = -0.01 ± 0.04‰; Schmitt et al., 2009; Rehkämper et al., 2012), rivers ($\delta^{114/110}$Cd = 0.1‰ to 0.3‰; Lambelet et al., 2013) and dust ($\delta^{114/110}$Cd = -0.19‰ to 0.19‰; Bridgestock et al., 2018). Deep ocean seawater has an isotopic composition of 0.35 ± 0.12‰ (Ripperger et al., 2007; Boyle et al., 2012; Conway and John, 2015a; Conway and John, 2015b; Xie et al., 2017; Janssen et al., 2017; John et al., 2018; Sieber et al., 2019) that is isotopically heavier than the known inputs. The burial flux of Cd from the oceans therefore must be isotopically lighter than the weathered input flux, assuming that Cd is in steady state in the oceans. The primary output flux of Cd from the ocean is into continental margin suboxic sediments (Heinrichs et al., 1980; Rosenthal et al., 1995b; van Geen et al., 1995; Little et al., 2015). Some additional, albeit minor, sinks of Cd include incorporation within Fe-Mn oxides in pelagic clays and marine carbonates (Boyle, 1988; Rosenthal et al., 1995b, van Geen et al., 1995; Morford and Emerson, 1999; Schmitt et al., 2009; Horner et al., 2011; Rehkämper et al., 2012 and references therein) and possibly formation of water column cadmium sulfides (Janssen et al., 2014; John and Conway, 2015). However, it is unknown if these species reach the seafloor. Previous measurements of the Cd isotopic compositions of oxygenated sedimentary sinks (Fe-Mn crusts and nodules) produced isotopic values similar to deep ocean seawater (Schmitt et al., 2009; Horner et al., 2010). In contrast, the burial of Cd into sulfides, particularly those accumulating on shallow continental margins, has been postulated to be isotopically light based on data from experimental systems (Guinoiseau et al., 2018) and measurements of oceanic hydrothermal sulfides (Schmitt et al., 2009). Recent work by Janssen et al., 2019 measured particulate and dissolved Cd pools, showing an intermediate depth of isotopically light particulate Cd during remineralization in the subarctic northeast Pacific between 200-600 m water depth. These authors proposed that this zone is an important sink of isotopically light Cd to margin sediments. A determination of the isotopic composition of margin sediments is required to validate this hypothesis and better constrain the sources of Cd to the seafloor. As of now, the Cd isotopic composition of margin sediments, particularly suboxic sediments, the largest sink of Cd in the modern oceans (Rosenthal et al., 1995b), is currently uncharacterised, leaving a significant gap in our understanding of how seawater Cd isotope compositions evolve across geological time.

In this study, we present new data that characterise the Cd isotope composition of modern sediments accumulating in oxic and suboxic settings from the Uruguayan margin and Argentine Basin and compare these measurements to those of overlying seawater depth profiles. We use these data to answer some key questions: (i) What is the Cd isotopic composition of modern marine sediments accumulating in low-oxygen conditions? (ii) What are the main sedimentary phases that host Cd? (iii) Does the dominating mechanism for Cd removal from sediment porewaters to marine sediments change during shallow diagenesis? (iv) Does the burial of Cd into modern marine sediments balance the isotopic mass balance of Cd?

2. Sampling and analytical methods

2.1. Study Site

Seawaterand sediment samples were collected during the JC068 research expedition, as part of the UK GEOTRACES GA10 section aboard the RRS James Cook from December 2011 to January 2012. The samples were collected along a longitudinal transect extending from the Uruguayan coast to the open ocean. Near-surface sediments were obtained on the margin at three locations at 60m (St 24), 705m (St 23) and 1,483m (St 22) water depths, while a water profile was collected at a fourth location at 3,313m (St 21) water depth. In the Argentine Basin (St 18), a sediment core was retrieved along with a water column profile at 5,156m water depth. An additional water column profile was collected at the mid-Atlantic Ridge (St 12) at 3,080m water depth (Fig. 1). The South West Atlantic water masses at 40°S represent a region of high productivity in an ocean basin known for low concentrations of critical micronutrients. An oxygen minimum zone (180 µmol L^{-1}) occurs between ~1–2 km depth that is associated with Upper Circumpolar Deep Water (UCDW). The regional oxygen minimum zone (OMZ) intersects the seafloor at St 22. The main water mass structure is shown in Fig. 1. The bottom waters of the Argentine Basin are complicated by a large benthic nepheloid layer, spanning a thickness of more than 500 m (Gardner et al., 2018). Sedimentation rates in the abyssal plain vary from ~1–5 cm/kyr (Stevenson and Cheng, 1969). While not being determined directly, it is expected that the sites along the continental margin experience far higher sedimentation rates compared to the deep basin (e.g. 0.8 cm/yr on the shelf top; Perez et al., 2016).

2.2 Sample collection

Water samples were retrieved through the vertical depth profile from the surface to the bottom waters. All water sampling was completed using a titanium CTD frame equipped with a full sensor array and fitted with 24x 10 litre OTE (Ocean Test Equipment) bottles with external springs. The unit was deployed on a Plasma Rope for optimal trace metal-free sampling. The retrieved bottles were transferred to a class 100 clean air container laboratory. The water samples for Cd isotopes were immediately filtered through a 0.2 µm AcroPak Supor polyethersulfone membrane filter capsules (Pall) into acid-cleaned, low density polyethylene bottles. Each sample was acidified to approximately 0.024 M with UpA HCl (Romil, Cambridge, UK) under a class 100 laminar flow hood.

For the near-surface sediment samples collected along the transect from the Uruguayan coast to the abyssal plain of the Argentine Basin, a Bowers and Connelly Mega Corer was deployed on a Plasma Rope to collect surface sediment cores and porewater samples. The porewater and sediment fractions were collected at 1–2 cm depth resolution in a shipboard temperature-controlled laboratory that replicated bottom water conditions (4°C) using one of two procedures: (1) Recovered sediment was sub-sectioned by Teflon apparatus, and porewaters separated using Decon- and HCl-cleaned polycarbonate centrifuge tubes (spun at 4°C and 9000g for 10 minutes). Supernatant porewater was extracted and filtered by an acid-cleaned syringe (BD Discardit) and cellulose acetate syringe filter (0.2 µm; Whatman Puradisc) all under an oxygen-purged nitrogen atmosphere. (2) Porewaters were subsampled by insertion of Rhizon samplers (0.15 µm CSS-type 50mm, Rhizosphere Research Products) through the sample ports of a pre-drilled core tubes (e.g. Homoky et al., 2013; Klar et al., 2017), and residual sediment inside the core tubes was subsequently extruded and sub-sampled by Teflon sectioning apparatus. The porewater samples were measured for macronutrients and dissolved metals. Nutrient samples were collected exclusively by the Rhizon samplers. Dissolved metals were collected by centrifugation/filtration at St 18 and 22, and by Rhizon samplers at St 23 and 24. Dissolved metal samples were acidified pH<2 prior to analyses (by addition of 6 µl 6M Q-HCl per 1ml of sample). The sediment samples were freeze-dried and homogenized using an agate pestle and mortar prior to total acid digestion, and coulometric determinations of organic and inorganic carbon concentrations as described in Homoky et al. (2013).

2.3 Elemental and isotopic analyses

All samples were prepared for measurement of Cd concentrations and isotopic compositions in a Class 10 laminar flow workstation within a Class 1000 clean lab suite at the University of Oxford. The acids used in this study were purified by sub-boiling distillation in quartz glass stills. Optima^{TM} Grade perchloric acid was purchased from Fisher Scientific Ltd.

2.3.1 Sediment digestion procedures

The digestion of sediments was completed following one of two procedures, depending on the amount of sediment needed to obtain sufficient Cd for isotopic analysis. Digestion of low-volume sediment samples (0.1–0.3 g) was achieved by sequentially heated aqua regia and combined HF and $HClO_4$ acids following Homoky et al. (2013). Digestion of higher-volume sediment samples involved weighing out between 0.3–2 g of dried and homogenized sediments into acid-cleaned Teflon jars and digesting in 4–12 mL of inverse Aqua Regia at 120–150°C for between 48 hours and three weeks. The samples were removed from the oven once digestion was complete, as evidenced by the presence of pale-yellow leached silicates. Samples were evaporated to incipient dryness before 3 mL of HNO_3 and 1 mL of HF were added to dissolve any silicates. The samples were closed and heated overnight and then dried and redissolved in 3 M HNO_3. All of the samples were measured for a range of major and minor elements.

2.3.2 Determination of element concentrations in sediment samples

A suite of sedimentary major and minor elements was determined using an ELEMENT 2 ICP-MS and a Perkin Elmer NexION 350D ICP-MS at the University of Oxford. The digestion method was validated by measuring the USGS Devonian Shale (SDO-1) standard. All the measured concentrations were within 10% of accepted values for all elements. Procedural blanks were near the detection limit for all elements.

Sedimentary authigenic enrichments were determined from enrichment factors (EF, Wedepohl, 1995) normalized to thorium to determine the detrital contribution to the sediments and using the average of the upper continental crust (Wedepohl, 1995), in the following equation:

$$EF_{element} = (element/Th)_{sediment} / (element/Th)_{upper\ continental\ crust} \quad (1)$$

where an EF greater than 1 indicates authigenic enrichment of the trace metal and less than 1 implies depletion in the sediments.

2.3.3 Ion exchange chromatography procedures

Cadmium extracted from water and sediment samples was purified by ion exchange chromatography. Cadmium concentrations obtained from ICP-MS were used to spike sample aliquots with a ^{111}Cd and ^{113}Cd double spike solution. The digested sediment samples were purified by a two-stage column procedure detailed in Sweere et al. (2020). For seawater samples, a preconcentration step was completed prior to chemical separation of Cd (Xue et al., 2012). Purified $AlCl_3$ solution was added to the seawater after sample-spike equilibration, and Cd was precipitated with $Al(OH)_3$ by adding aqueous NH_3 solution until the pH reached 8.5. The precipitate was dissolved and processed through the three-stage column separation process developed by Wombacher et al. (2003) and modified by Ripperger and Rehkämper (2007). In preparation for isotopic analysis, all samples were evaporated dry and redissolved in 1 mL of 2% HNO_3.

2.3.4 Cd isotope determination by Multi-Collector ICP-MS

Cadmium isotopic analyses were completed on a Nu Instruments Nu Plasma multi-collector HR-ICP-MS at the University of Oxford in low resolution mode. A sample concentration of 20 ppb was used for all samples. Measurements comprised 40x simultaneous 10 s integrations for ^{110}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd, ^{114}Cd, ^{115}In and ^{117}Sn, with the latter used to correct for isobaric interferences. All samples were preceded with a short measurement of 2% HNO_3 that was used to blank-correct sample voltages. Isotopic compositions are the mean of two to four replicate measurements and the uncertainty is the 2 S.D. of these replicates.

Sample-spike mixtures were deconvolved off-line using an Excel-based routine, with corrections for Sn and In interferences. Isotopic compositions were corrected to NIST 3108 by normalizing to in-run bracketing standards to correct for mass discrimination. Analyses of Cadmium NIST SRM 3108 (Lot# 060531, $\delta^{114/110}\mathrm{Cd}_{\mathrm{NIST}} \equiv 0$), double-spiked to match the concentrations and sample-spike ratios of the samples, bracketed every one or two sample analyses. Cadmium isotopic compositions are reported in delta notation relative to NIST SRM 3108 (Abouchami et al., 2013) using the following equation:

$$\delta^{114/110}\mathrm{Cd} = \left(\frac{^{114}Cd/^{110}Cd_{sample}}{^{114}Cd/^{110}Cd_{standard}} - 1\right) \times 1000 \qquad (2)$$

An in-house standard ‘OXCAD’ (Alfa Aesar Specpure Cd concentration standard, Lot# 81-081192A) was measured repeatedly in each analysis session to assess instrument stability and long-term reproducibility. The δ^{114}Cd of OXCAD was -0.95 ± 0.09 ‰ (n = 139, 2 S.D.) over the course of this study.

Samples that deviated from optimal sample-spike ratios by more than 0.15 were bracketed with NIST 3108 solutions with a similar proportion of double spike. Previous work has shown that this technique produces accurate results (Ripperger and Rehkämper, 2007).

3. Results

3.1 Cd concentration and isotope variations of waters

The dissolved Cd profile in the South West Atlantic Ocean is similar to published profiles from other ocean basins (Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011; Boyle et al., 2012; Gault-Ringold et al. 2012; Xue et al., 2012; Yang et al., 2012; Xue et al., 2013; Baars et al., 2014; John and Conway, 2014; Conway and John, 2015a; Conway and John, 2015b; Janssen et al., 2017; Xie et al., 2017; John et al., 2018; Janssen et al., 2019; Sieber et al., 2019). The three vertical depth profiles for Cd show a nutrient-type distribution (Table 1 and Fig. 2). The behavior of dissolved Cd below 700 m at all sites is relatively uniform, with an average δ^{114}Cd value of 0.35 ± 0.11‰. Near-surface waters are isotopically higher than the deep water, reaching 3.01‰ in the Argentine Basin (St 18).

3.2 Cd concentrations and isotope compositions of near-surface sediments

3.2.2 Porewater geochemical profiles

The redox profiles of the sediments from the coast to the abyssal plain of the Argentine Basin reflect the physical and nutrient parameters in the overlying water column, their location relative to the OMZ, the degree of organic matter remineralization and sedimentation rate (see Fig. 3). Oxygen penetration into sub-surface sediments is greatest in the deep Argentine basin (St 18), beneath the OMZ, but is considerably less in sediment porewaters from the coast and margin sites, as indicated by the shallow minima in dissolved oxygen and nitrate, and maxima in porewater Fe concentrations. Nitrate and iron reduction occur at the shallowest porewater depths in the shelf and slope locations (St 23 and 22). Samples from St. 22, within the OMZ, record the highest TOC of all the core-tops (~4%) presumably due to a higher organic matter burial efficiency than the other stations. Sediments in profiles on the coast and margin transition to inferred sulfidic conditions at depths where dissolved nitrate disappears, and dissolved iron values decrease in the presence sulfide (Homoky et al., 2017).

3.2.3 Sedimentary element concentration profiles

Redox zonations inferred from dissolved porewater cation and anion profiles are also recorded by solid-phase sedimentary Cd, U and Mo enrichments. The highest redox-sensitive element enrichments occur in the margin sites (St 22 and St 23). Cadmium concentrations of near-surface sediments range from 0.04 to 3.31 ug g^{-1}. An early diagenetic feature in all the measured sediment cores are sharp, authigenic Cd enrichment peaks close to redox fronts, most prominently near the oxic-suboxic redox boundary in the deep basin (St 18) and near the inferred suboxic-sulfide redox boundary on the margin and coast (St 22, St 23 and St 24). These levels coincide with an increase in the concentration of other redox-sensitive metals such as Mo and U. The relationship between Cd and U in the down-core redox profiles is shown graphically in Fig. 4. As this study is focused on modern marine sediments, the following discussion will exclude the suboxic sediments from the deep basin (St 18). The slow sedimentation rates within the Argentine Basin indicates that these sediments are unlikely to represent sediments from the Holocene.

3.2.3 Sedimentary Cd concentrations and isotopes

The Cd isotope compositions of near-surface sediments range from -0.08 to 0.71‰. These compositions are generally lower than the overlying seawater along the Uruguayan continental margin and Argentine Basin (Fig. 3). δ^{114}Cd compositions notably shift to higher values that are within error of the overlying deep water (~0.35‰) near sub-surface redox fronts, coinciding with redox fronts at ~1 µM nitrate and increases in sedimentary Cd concentration.

4. Discussion

4.1 Mechanisms for Cd incorporation into near-surface sediments

Sedimentary Cd may be bound in detrital minerals, organic matter, associated with Fe-Mn oxyhydroxides, or as authigenic Cd sulfides (Rosenthal et al., 1995a, Rosenthal et al. 1995b; Janssen et al., 2014; John and Conway, 2015).

Calculated Cd enrichment factors relative to detrital Cd for near-surface sediments average 5.1 and range between 2.7 and 8.1. This corresponds to ~63–88% of the Cd accumulating on the seafloor being non-detrital in origin.

Cadmium incorporation in CdS in the water column or at the sediment surface has been suggested in other settings (Janssen et al. 2014; John and Conway 2015) but is not anticipated at the water column O_2 levels observed in this study, which are always above 180 µmol L^{-1}. We confirmed this assumption by calculating the Cd* value at these sites. A useful parameter, Cd*, is a tracer for water column non-biological addition or removal of Cd, including by CdS. It is based on the expected Cd concentration for a given P concentration, using the well-established Cd/P stoichiometry: $Cd^* = Cd_{measured} - (Cd/P_{deep\ water} \times P_{measured})$ (Baars et al., 2014). Cadmium* values for South Atlantic stations 12, 18 and 21 below 200 m are close to zero (0.02 to 0.12 nmol/kg), indicating no significant precipitation of CdS species at these three sites along the Uruguayan margin.

The role of organically-bound Cd as a pathway for Cd burial can be explored by predicting Cd concentrations expected from measured sedimentary TOC values for typical Cd/C ratios of marine phytoplankton (Ho et al., 2003). Cadmium concentrations and stoichiometries corresponding to the range of Cd uptake into phytoplankton are shown in Figure 5 and can account for the majority of the measured Cd concentrations in the near-surface sediments from the margin and basin sites. Non-detrital Cd in surface sediments of most Uruguayan margin sediments can therefore be explained by addition in organic material. Such POC-hosted Cd makes up the majority of the Cd in the near-surface suboxic sediments in this study.

Some surface sediments from Site 24, however, have higher Cd concentrations than can be explained by planktonic Cd/C ratios, suggesting an additional flux of shallow-water Cd. This additional Cd is likely to be incorporated into Fe-Mn oxyhydroxides in this shelf environment where such oxyhydroxides are common. This explanation is supported by an increase in sedimentary Mn concentrations from 0 to 3 cm in this core. The shallow depth of this core means that the Cd is derived from near-surface seawater with a δ^{114}Cd composition that is heavy due to removal of Cd into organic material. This may explain the unusually high δ^{114}Cd values (0.71‰) observed in these Cd-enriched samples (Fig. 6).

4.2 Suboxic sediments as a sink for isotopically light Cd from the ocean

Cadmium isotope values of suboxic margin surface sediments (0.02 to 0.09‰), the dominant sink flux in the ocean, are lighter than deep water values (~0.35‰). This is explained by sinking organic particular matter with a lighter isotopic composition than deep water which settles to form the sediment. That settling water column particulates are isotopically lighter than deep water has been observed previously; particulate δ^{114}Cd compositions from the upper 1200 m of the Atlantic and Pacific water columns span a wider range of -1.47 to 2.08‰, with the heaviest particulate δ^{114}Cd values in surface waters and the lightest particulate δ^{114}Cd compositions at sub-surface water depths (~200 to 600 m), reflecting the uptake and subsequent remineralization of organically-bound Cd in the surface waters (Yang et al., 2012; Janssen et al., 2014; Conway and John, 2015b; Yang et al., 2015; Yang et al., 2018; Janssen et al., 2019).

A mechanistic understanding of the particulate δ^{114}Cd profile in the ocean remains elusive. Recently, Janssen et al. (2019) hypothesized that sinking particulates may be composed of multiple pools with different isotopic compositions and remineralization labilities, where the sub-surface particulate Cd pool is more refractory than the particulate Cd fraction in the surface waters and isotopically lighter than the particulate Cd pools in surface and deep waters (c.f. Janssen et al., 2019). It is this sub-surface, isotopically light particulate Cd fraction that settles and likely represents the burial flux of particulate Cd on the margin sediments. These sediments may therefore be the missing removal term to satisfy the global isotopic mass balance of oceanic Cd.

4.3 Sub-surface diagenetic alteration of Cd in South Atlantic sediments

The most noticeable feature in sub-surface sediment Cd composition are the Cd enrichment peaks which occur near redox fronts. These Cd concentration peaks generally coincide with low porewater nitrate and Fe concentrations in the South Atlantic sediment profiles (Fig. 3). We propose that these observations reflect the precipitation of porewater Cd with H_2S to form CdS species (Fig. 4, Gobeil et al., 1987; Pedersen et al., 1989; Rosenthal et al., 1995a; Rosenthal et al., 1995b).

A sub-surface formation of CdS and/or other sulfide species (e.g. FeS, Framson and Leckle, 1978; Pedersen et al., 1989), would likely reduce porewater Cd concentrations, and thus establish a diffusive gradient that draws overlying seawater Cd downwards towards the Cd-sulfide reaction front and zone of enrichment. The sedimentary Cd isotopic compositions at these enrichment fronts are within analytical uncertainty of overlying deep water (~0.35‰), overprinting the Cd isotopic signature from detrital and sinking organic particulates.

The dominant process governing authigenic Cd burial in modern marine sediments with suboxic and sulfidic porewaters is the precipitation of CdS species (Rosenthal et al., 1995a; Rosenthal et al., 1995b), where diffusion would drives preferential removal of the lighter Cd isotopes from the porewaters (Guinoiseau et al. 2018). Recent experiments show that Cd isotope fractionation during precipitation with H_2S will preferentially capture the lighter Cd isotopes relative to the bulk solution, although more complete Cd precipitation leads to quantitative transfer of the Cd isotopic signature from solution into the solid phase (Guinoiseau et al., 2018). Some suboxic sediments from this study, above the sulfide front, also have Cd concentrations and isotope compositions that suggest such quantitative removal of deep water Cd (see Figure 6).

Overall, the Cd and δ^{114}Cd composition of the sediments in this study can be interpreted as an interplay between three processes:

i. Incorporation of isotopically light Cd in organic matter settling from the water column and making up the bulk of Cd in near surface sediments

ii. Additional input of near-surface seawater Cd into Mn-Fe hydroxides in coastal and shelf sediments

iii. Additional diffusive uptake of deep-seawater Cd and incorporation into CdS at depth in the sediment.

The impact of these three processes is shown in Fig. 6.

4.4 Cadmium Mass Balance

Sedimentary Cd isotopes may serve as a proxy for the extent of past cycling and ocean mixing (Georgiev et al., 2015; Sweere et al., 2020). A critical first step to using this proxy effectively is to constrain the elemental and isotopic mass balance of Cd in the modern ocean. A summary of the global source and sink fluxes of oceanic Cd is presented in Table 3. The estimated fluxes are primarily from Rosenthal et al. (1995b), where the main inputs of Cd are from rivers (4–15 x 10^6 mol Cd/yr) and dust (2–11 x 10^6 mol Cd/yr, Shiller and Boyle, 1991; Rosenthal et al., 1995b; van Geen et al., 1995). While hydrothermal vents are an important local source of Cd, this flux only influences the chemistry of very proximal ocean waters, and thus is assumed to be removed quantitatively near the vent site. The dominant sink of oceanic Cd is into suboxic and anoxic margin sediments, with an estimated removal flux of 15–60 x 10^6 mol Cd/yr (Table 3, Rosenthal et al., 1995b; van Geen et al., 1995; Little et al., 2015).

Other minor output fluxes are pelagic clays, carbonates and Fe-Mn nodules and crusts, although they are unlikely to significantly influence the oceanic budget of Cd. Contribution of Cd from pelagic clays is estimated using the Cd concentration from Heinrichs et al., 1980 (100 to 350 ng g^{-1}) and the burial rate of 0.23 g cm^2/kyr (Hay et al., 1988), producing an estimated output flux of 0.6–2.1 x 10^6 mol Cd/yr. The Cd isotopic composition of this output flux is unknown. The contribution of Cd associated with Fe-Mn deposits to the oceanic Cd budget is negligible (Schmitt et al., 2009; Horner et al., 2010), and this process does not greatly fractionate Cd (Schmitt et al., 2009; Horner et al., 2010). Cadmium burial within carbonates is estimated to be 0.4–1.8 x 10^6 mol Cd/yr (Horner et al., 2011) with an unknown isotopic composition for natural samples.

This study provides new isotopic compositions of Cd in suboxic margin sediments. The burial flux of Cd within suboxic margin sediments from below 100 m water depth (St 22 and St 23) has a range in δ^{114}Cd values of -0.02 to 0.25‰, predominately composed of sinking organic particulates.

An additional flux of Cd becomes important below the sediment-water interface as CdS species start to precipitate at redox fronts. The initial particulate-dominated burial flux of Cd is subsequently modified in the sub-surface during shallow diagenesis to higher isotopic compositions and concentrations as seawater-sourced porewater Cd precipitates with H_2S to form CdS species. This process is expected to drive a downward diffusive flux of seawater Cd into the sub-surface sediments to enrichment zones near redox boundaries where the isotope composition of precipitating Cd overprints the isotopic composition of the surface sediments to values within error of overlying deep water. An additional inferred, albeit minor, source of porewater Cd to form CdS species is newly-released Cd during the redox-driven oxidation of sinking organic particulates during shallow diagenesis. Within anoxic margin sediments, such as the Black Sea (Little et al., 2015), these processes will occur within the water column, where the Cd isotopic composition will reflect global deep water values (~0.35‰).

Cadmium burial within suboxic and anoxic margin sediments satisfies the global oceanic mass balance of Cd, within the uncertainties that exist on all fluxes (Table 3). The measured isotopic output flux of δ^{114}Cd ranges from -0.02 to 0.35‰, using the elemental and isotopic ranges for Cd from suboxic and anoxic margin sediments. This sink term largely balances the budget of Cd in the oceans. Future assessment of Cd output fluxes from a diversity of ocean-sediment boundaries is now recommended to develop further robustness in our assessment of the ocean's Cd cycle.

5. Conclusions

We present the first constraints on the isotopic compositions of Cd in modern marine suboxic sediments using new measurements from the South West Atlantic Ocean. Surface sediments (0–1 cm) below 100 m water depth comprised δ^{114}Cd values between 0.02 and 0.15‰ that are isotopically lower than river inputs and overlying deep seawater ($\Delta^{114/110}\text{Cd}_{\text{surface sediments—deep waters}}$ = -0.27 ± 0.14‰). These observations, coupled to an assessment of the global ocean budget, suggest that suboxic surface sediments provide the missing light isotopic sink and enable the isotopic mass balance of Cd in the oceans to be closed. The primary contributors of Cd to marine sediments are from sinking organic particulates, and from downwards diffusion of seawater Cd to precipitate as CdS species within reducing porewater conditions at depth.

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References

Abouchami, W., Galer, S.J.G., de Baar, H.J.W., Alderkamp, A.C., Middag, R., Laan, P., Feldmann, H., Andreae, M.O., 2011. Modulation of the Southern Ocean cadmium isotope signature by ocean circulation and primary productivity. Earth Planet. Sci. Lett. 305, 83-91. http://dx.doi.org/10.1016/j.epsl.2011.02.044.

Abouchami, W., Galer, S.J.G., Horner, T.J., Rehkämper, M., Wombacher, F., Xue, Z., Lambelet, M., Gault-Ringold, M., Stirling, C.H., Schönbächler, M., Shiel, A.E., Weis, D., Holdship, P.F., 2013. A Common Reference Material for Cadmium Isotope Studies - NIST SRM 3108. Geostand. Geoanal. Res. 37, 5-17. https://doi.org/10.1111/j.1751-908X.2012.00175.x.

Baars, O., Abouchami, W., Galer, S.J.G., Boye, M., Croot, P.L., 2014. Dissolved cadmium in the Southern Ocean: Distribution, speciation, and relation to phosphate. Limnol. Oceanogr. 59, 385-399. https://doi.org/10.4319/lo.2014.59.2.0385.

Bridgestock, L., Hsieh, Y., Porcelli, D., Homoky, W.B., Bryan, A., Henderson, G.M., 2018. Controls on the barium isotope compositions of marine sediments. Earth Planet. Sci. Lett. 481, 101-110. https://doi.org/10.1016/j.epsl.2017.10.019.

Boyle, E.A., 1988. Cadmium: Chemical tracer of deepwater paleoceanography. Paleoceanography. 3, 471-489. https://doi.org/10.1029/PA003i004p00471.

Boyle, E.A., John, S., Abouchami, W., Adkins, J.F., Echegoyen-Sanz, Y., Ellwood, M., Russell Flegal, A., Fornace, K., Gallon, C., Galer, S., Gault-Ringold, M., Lacan, F., Radic, A., Rehkämper, M., Rouxel, O., Sohrin, Y., Stirling, C., Thompson, C., Vance, D., Xue, Z., Zhao, Y., 2012. GEOTRACES IC1 (BATS) contamination-prone trace element isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration. Limnol. Oceanogr.: Methods 10, 653-665. https://doi.org/10.4319/lom.2012.10.653.

Conway, T.M., John, S.G., 2015a. The cycling of iron, zinc and cadmium in the North East Pacific Ocean – Insights from stable isotopes. Geochim. Cosmochim. Acta 164, 262-283. https://doi.org/10.1016/j.gca.2015.05.023.

Conway, T.M., John, S.G., 2015b. Biogeochemical cycling of cadmium isotopes along a high-resolution section through the North Atlantic Ocean. Geochim. Cosmochim. Acta 148, 269-283. https://doi.org/10.1016/j.gca.2014.09.032.

Framson, P.E., Leckie, J.O., 1978. Limits of Coprecipitation of Cadmium and Ferrous Sulfides. Environ. Sci. Technol. 12, 465-469. https://doi.org/10.1021/es60140a012.

Gault-Ringold, M., Adu, T., Stirling, C.H., Frew, R.D., Hunter, K.A., 2012. Anomalous biogeochemical behavior of cadmium in subantarctic surface waters: Mechanistic constraints from cadmium isotopes. Earth Planet. Sci. Lett. 341-344, 94-103. https://doi.org/10.1016/j.epsl.2012.06.005.

Georgiev, S.V., Horner, T.J., Stein, H.J., Hannah, J.L., Bingen, B., Rehkämper, M., 2015. Cadmium-isotopic evidence for increasing primary productivity during the Late Permian anoxic event. Earth Planet. Sci. Lett. 410, 84-96. https://doi.org/10.1016/j.epsl.2014.11.010.

Gobeil, C., Silverberg, N., Sundby, B., Cossa, D., 1987. Cadmium diagenesis in Laurentian Trough sediments. Geochim. Cosmochim. Acta 51, 589-596. https://doi.org/10.1016/0016-7037(87)90071-8.

Guinoiseau, D., Galer, S.J.G., Abouchami, W., 2018. Effect of cadmium sulphide precipitation on the partitioning of Cd isotopes: Implications for the oceanic Cd cycle. Earth Planet. Sci. Lett. 498, 300-308. https://doi.org/10.1016/j.epsl.2018.06.039.

Hay, W.W., Sloan, J.L., Wold, C.N., 1988. Mass/age distribution and composition of sediments on the ocean floor and the global rate of sediment subduction. J. Geophys. Res. 93, 14933-14940. https://doi.org/10.1029/JB093iB12p14933.

Heinrichs, H., Schulz-Dobrick, B., Wedepohl, K.H., 1980. Terrestrial geochemistry of Cd, Bi, Tl, Pb, Zn and Rb. Geochim. Cosmochim. Acta 44, 1519-1533. https://doi.org/10.1016/0016-7037(80)90116-7.

Ho, T.Y., Quigg, A., Finkel, Z.V., Milligan, A.J., Wyman, K., Falkowski, P.G., Morel, F.M.M., 2003. The elemental composition of some marine phytoplankton. J. Phycol. 39, 1145-1159. https://doi.org/10.1111/j.0022-3646.2003.03-090.x.

Homoky, W.B., John, S.G., Conway, T.M., Mills, R.A., 2013. Distinct iron isotopic signatures and supply from marine sediment dissolution. Nat. Commun. 4. https://doi.org/10.1038/ncomms3143.

Homoky, W.B., Conway, T.M., John, S.G., Woodward, E.M., Mills, R.A., 2017. Model evaluations of pore water iron isotope signatures in the South Atlantic Ocean – Implications for benthic exchange. ASLO 2017: Mountains to the Sea. Honolulu, Hawaii. 26 February – 3 March.

Horner, T.J., Schönbächler, M., Rehkämper, M., Nielsen, S.G., Williams, H., Halliday, A.N., Xue, Z., Hein, J.R., 2010. Ferromanganese crusts as archives of deep water Cd isotope compositions. Geochem. Geophys. Geosyst. 11. https://doi.org/10.1029/2009GC002987.

Horner, T.J., Rickaby, R.E.M., Henderson, G.M., 2011. Isotopic fractionation of cadmium into calcite. Earth Planet. Sci. Lett. 312, 243-253. https://doi.org/10.1016/j.epsl.2011.10.004.

Janssen, D.J., Conway, T.M., John, S.G., Christian, J.R., Kramer, D.I., Pedersen, T.F., Cullen, J.T., 2014. Undocumented water column sink for cadmium in open ocean oxygen-deficient zones. Proc. Natl. Acad. Sci. U.S.A. 111, 6888-6893. https://doi.org/10.1073/pnas.1402388111.

Janssen, D.J., Abouchami, W., Galer, S.J.G., Cullen, J.T., 2017. Fine-scale spatial and interannual cadmium isotope variability in the subarctic northeast Pacific. Earth Planet. Sci. Lett. 472, 241-252. https://doi.org/10.1016/j.epsl.2017.04.048.

Janssen, D.J., Abouchami, W., Galer, S.J.G., Purdon, K.B., Cullen, J.T., 2019. Particulate cadmium stable isotopes in the subarctic northeast Pacific reveal dynamic Cd cycling and a new isotopically light Cd sink. Earth Planet. Sci. Lett. 515, 67-78. https://doi.org/10.1016/j.epsl.2019.03.006.

John, S.G., Helgoe, J., Townsend, E., 2018. Biogeochemical cycling of Zn and Cd and their stable isotopes in the Eastern Tropical South Pacific. Mar. Chem. 201, 256-262. https://doi.org/10.1016/j.marchem.2017.06.001.

Klar, J.K., Homoky, W.B., Statham, P.J., Birchill, A.J., Harris, E.L., Woodward, E.M.S., Silburn, B., Cooper, M.J., James, R.H., Connelly, D.P., Chever, F., Lichtschlag, A., Graves, C., 2017. Stability of dissolved and soluble Fe(II) in shelf sediment pore waters and release to an oxic water column. Biogeochemistry. 135, 49-67. https://doi.org/10.1007/s10533-017-0309-x.

Lacan, F., Francois, R., Yongcheng, J., Sherrell, R.M., 2006. Cadmium isotopic composition in the ocean. Geochim. Cosmochim. Acta 70, 5104-5118. https://doi.org/10.1016/j.gca.2006.07.036.

Lambelet, M., Rehkämper, M., van de Flierdt, T., Xue, Z., Kreissig, K., Coles, B., Porcelli, D., Andersson, P., 2013. Isotopic analysis of Cd in the mixing zone of Siberian rivers with the Arctic Ocean—New constraints on marine Cd cycling and the isotope composition of riverine Cd. Earth Planet. Sci. Lett. 361, 64-73. https://doi.org/10.1016/j.epsl.2012.11.034.

Little, S.H., Vance, D., Lyons, T.W., McManus, J., 2015. Controls on trace metal authigenic enrichment in reducing sediments: Insights from modern oxygen-deficient settings. Am. J. Sci. 315, 77-119. https://doi.org/10.2475/02.2015.01.

Morford, J.L., Emerson, S., 1999. The geochemistry of redox sensitive trace metals in sediments. Geochim. Cosmochim. Acta 63, 1735-1750. https://doi.org/10.1016/S0016-7037(99)00126-X.

Pedersen, T.F., Waters, R.D., Macdonald, R.W., 1989. On the natural enrichment of cadmium and molybdenum in the sediments of ucluelet inlet, British Columbia. Sci. Total Environ. 79, 125-139. https://doi.org/10.1016/0048-9697(89)90357-4.

Perez, L., García-Rodríguez, F., Hanebuth, T.J.J., 2016. Variability in terrigenous sediment supply offshore of the Río de la Plata (Uruguay) recording the continental climatic history over the past 1200 years. Clim. Past 12, 623-634. https://doi.org/10.5194/cp-12-623-2016.

Rehkämper, M., Wombacher, F., Horner, T.J., Xue, Z., 2012. Natural and anthropogenic Cd isotope variations. In: Baskaran, M. (Ed.), Handbook of Environmental Isotope Geochemistry. Springer, Berlin, Heidelberg, pp. 125-154. https://doi.org/10.1007/978-3-642-10637-8_8.

Ripperger, S., Rehkämper, M., Porcelli, D., Halliday, A.N., 2007. Cadmium isotope fractionation in seawater — A signature of biological activity. Earth Planet. Sci. Lett. 261, 670-684. https://doi.org/10.1016/j.epsl.2007.07.034.

Ripperger, S., Rehkämper, M., 2007. Precise determination of cadmium isotope fractionation in seawater by double spike MC-ICPMS. Geochim. Cosmochim. Acta 71, 631-642. https://doi.org/10.1016/j.gca.2006.10.005.

Rosenthal, Y., Lam, P., Boyle, E.A., Thomson, J., 1995a. Authigenic cadmium enrichments in suboxic sediments: Precipitation and postdepositional mobility. Earth Planet. Sci. Lett. 132, 99-111. https://doi.org/10.1016/0012-821X(95)00056-I.

Rosenthal, Y., Boyle, E.A., Labeyrie, L., Oppo, D., 1995b. Glacial enrichments of authigenic Cd and U in subantarctic sediments: A climatic control on the elements' oceanic budget? Paleoceanography. 10, 395-413. https://doi.org/10.1029/95PA00310.

Schmitt, A.D., Galer, S.J.G., Abouchami, W., 2009. High-precision cadmium stable isotope measurements by double spike thermal ionisation mass spectrometry. J. Anal. At. Spectrom. 24, 1079-1088. https://doi.org/10.1039/B821576F.

Shiller, A.M., Boyle, E.A., 1991. Trace elements in the Mississippi River Delta outflow region: Behavior at high discharge. Geochim. Cosmochim. Acta 55, 3241-3251. https://doi.org/10.1016/0016-7037(91)90486-O.

Sieber, M., Conway, T.M., de Souza, G.F., Obata, H., Takano, S., Sohrin, Y., Vance, D., 2019. Physical and biogeochemical controls on the distribution of dissolved cadmium and its isotopes in the Southwest Pacific Ocean. Chem. Geol. 511, 494-509. https://doi.org/10.1016/j.chemgeo.2018.07.021.

Stevenson, F.J., Cheng, C.N., 1969. Amino acid levels in the Argentine Basin sediments; correlation with Quaternary climatic changes. J. Sediment. Res. 39, 345-349. https://doi.org/10.1306/74D71C62-2B21-11D7-8648000102C1865D.

Sweere, T.C., Dickson, A.J., Jenkyns, H.C., Porcelli, D., Ruhl, M., Murphy, M.J., Idiz, E., van den Boorn, S.H.J.M., Eldrett, J.S., Henderson, G.M., 2020. Controls on the Cd-isotope composition of Upper Cretaceous (Cenomanian–Turonian) organic-rich mudrocks from south Texas (Eagle Ford Group). (In Press). https://doi.org/10.1016/j.gca.2020.02.019.

van Geen, A., McCorkle, D.C., Klinkhammer, G.P., 1995. Sensitivity of the phosphate-cadmium-carbon isotope relation in the ocean to cadmium removal by suboxic sediments. Paleoceanography 10, 159-169. https://doi.org/10.1029/94PA03352.

Wedepohl, K.H., 1995. The composition of the continental crust. Geochim. Cosmochim. Acta 59, 1217-1232. https://doi.org/10.1016/0016-7037(95)00038-2.

Wombacher, F., Rehkämper, M., Mezger, K., Münker, C., 2003. Stable isotope compositions of cadmium in geological materials and meteorites determined by multiple-collector ICPMS. Geochim. Cosmochim. Acta 67, 4639-4654. https://doi.org/10.1016/S0016-7037(03)00389-2.

Xue, Z., Rehkämper, M., Schönbächler, M., Statham, P.J., Coles, B.J., 2012. A new methodology for precise cadmium isotope analyses of seawater. Anal. Bioanal. Chem. 402, 883-893. https://doi.org/10.1007/s00216-011-5487-0.

Xue, Z., Rehkämper, M., Horner, T.J., Abouchami, W., Middag, R., van de Flierd, T., de Baar, H.J.W., 2013. Cadmium isotope variations in the Southern Ocean. Earth Planet. Sci. Lett. 382, 161-172. https://doi.org/10.1016/j.epsl.2013.09.014.

Xie, R.C., Galer, S.J.G., Abouchami, W., Rijkenberg, M.J.A., de Baar, H.J.W., De Jong, J., Andreae, M.O., 2017. Non-Rayleigh control of upper-ocean Cd isotope fractionation in the western South Atlantic. Earth Planet. Sci. Lett. 471, 94-103. https://doi.org/10.1016/j.epsl.2017.04.024.

Yang, S.C., Lee, D.C., Ho, T.Y., 2012. The isotopic composition of Cadmium in the water column of the South China Sea. Geochim. Cosmochim. Acta 98, 66-77. https://doi.org/10.1016/j.gca.2012.09.022.

Yang, S.C., Lee, D.C., Ho, T.Y., 2015. Cd isotopic composition in the suspended and sinking particles of the surface water of the South China Sea: The effects of biotic activities. Earth Planet. Sci. Lett. 428, 63-72. https://doi.org/10.1016/j.epsl.2015.07.025.

Yang, S.C., Zhang, J., Sohrin, Y., Ho, T.Y., 2018. Cadmium cycling in the water column of the Kuroshio-Oyashio Extension region: Insights from dissolved and particulate isotopic composition. Geochim. Cosmochim. Acta 233, 66-80. https://doi.org/10.1016/j.gca.2018.05.001.

Figure 1; Sampling locations for seawater depth profiles (circles) and near-surface sediment cores superimposed onto water mass oxygen concentrations (Schlitzer et al., 2018). The black shapes indicate the location of the sediment cores: square (St 24), diamond (St 23), triangle (St 22) and hexagon (St 18). The approximate location of key water masses is noted on the figure: Antarctic Intermediate Water (AAIW), Upper Circumpolar Water (UCDW), North Atlantic Deep Water (NADW), Antarctic Bottom Water (AABW). Figure produced using Ocean Data View (Schlitzer, 2015).

Figure 2; Vertical water column profiles of dissolved Cd concentrations and isotopic compositions (dCd), along with dissolved oxygen (O_2), PO_4^{3}, NO_3^- and silica (Si) from a) Uruguayan continental slope (St 21), b) Argentine Basin (St 18) and c) South Atlantic Mid-Ocean Ridge (St 12). The measured particulate Cd concentrations and isotopic compositions (pCd) from the Argentine Basin and continental slope are depicted with filled orange squares. The vertical dashed line represents the average SW Atlantic deep ocean water value ($\delta^{114/110}$Cd = 0.35‰). Error bars for the Cd isotopes measurements represent the 2 S.D. on the sample. The Southern Component Water (SCW) includes the AAIW and UCDW. Note scale differences between plots for different samples.

Figure 3; Down-core profiles of sedimentary cadmium concentration and isotopic composition, along with porewater profiles of Fe and NO_3^-, and sedimentary Mn concentrations and total organic carbon (TOC) from a transect of shallow multi-cores obtained from the coast (diamonds), continental shelf (circles), continental slope within an OMZ (squares), and abyssal plain of the Argentine Basin (triangles). The colors indicate the redox conditions of the porewaters: turquoise marks oxic, blue indicates suboxic, and orange denotes sulfidic conditions. The vertical dotted, black line, alongside the measured Cd concentration values, denotes the 'predicted' Cd concentration contributing from organic material and detrital sources: $Cd_{predicted} = TOC_{measured} / (Cd/C_{Ho\ et\ al.,\ 2003})$. The vertical dashed black line at $\delta^{114/110}Cd = 0.35‰$ represents the average SW Atlantic deep ocean water value. The suboxic sediments from the Argentine Basin (grey triangles) are unlikely to represent Holocene sediments due to the slow sedimentation rates in the basin, and thus will not be discussed in this study on modern marine sediments.

Figure 4; Authigenic enrichment of Cd compared to enrichment of U in sediments, using UCC concentrations from Wedepohl (1995) to calculate the enrichment factors. The pattern in the markers represents the redox conditions of the porewaters, defined by porewater chemistry: oxic (dots), suboxic (open) and sulfidic (filled). This figure shows a good relationship between redox-sensitive metals, Cd and U on the Uruguayan coast and margin.

Figure 5; Cadmium concentration versus TOC of all sediment samples within 5 cm of the surface. The straight line represents the average Cd/C ratio in cultured marine eukaryotic phytoplankton species and the grey shaded area is the range in Cd/C ratio of all measured organisms from Ho et al., 2003.

Figure 6; Evidence for redox control on Cd burial in South Atlantic near-surface sediments. Authigenic enrichment of Cd compared to Cd isotopic compositions of near-surface sediments are plotted with the color and shape indicating the redox conditions of the porewaters: oxic (turquois circles), suboxic (blue diamonds), and sulfidic (orange squares). The isotopic composition of detrital Cd (UCC) is marked with a black star. The predicted isotopic composition of Cd associated with sinking organic particulates (Cd_{org}) is determined by hypothesizing the authigenic fraction in near-surface sediments (0–5 cm) is predominately composed of organically-bound Cd, along with using the isotopic composition of the UCC (-0.01‰) for the detrital fraction, in the following equation:

$$\delta^{114/110}\mathrm{Cd}_{\mathrm{organic\ particulates}} = \frac{([\mathrm{Cd}]_{\mathrm{meas.}} \cdot \delta^{114/110}\mathrm{Cd}_{\mathrm{meas.}}) - ([\mathrm{Cd}]_{\mathrm{detrital}} \cdot \delta^{114/110}\mathrm{Cd}_{\mathrm{detrital}})}{[\mathrm{Cd}]_{\mathrm{organic\ particulates}}} \quad (3)$$

where the average predicted δ^{114}Cd value from sinking organic particulates in the top of the core (0–5 cm) is 0.04 ± 0.06‰. The dashed lines denote mixing relationships between detrital Cd (EF value of 1; M_1 and -0.01‰; δ_1) and either shallow-water Cd from the SW Atlantic at 49 m water depth (0.72‰; δ_2), overlying deep ocean water Cd (0.35‰; δ_2), or predicted δ^{114}Cd value of organically-bound Cd (Cd_{org}, 0.04 ± 0.06‰; δ_2) at a starting EF value of 1 ($M_{OBSERVED}$):

$$\delta_{OBSERVED} = \delta_2 + (\delta_1 - \delta_2) \bullet (M_1 / M_{OBSERVED})$$

At oxic porewater conditions, the distribution of Cd versus δ^{114}Cd is best represented by a mixing relationship between a detrital Cd endmember and a mixture of shallow-water- or deep water-sourced porewater Cd adsorbed to Fe-Mn oxyhydroxides and organically-bound Cd from sinking particulates. At suboxic and sulfidic porewater conditions, the sediments depict different stages of mixing between organically-bound Cd and precipitation of CdS species from seawater Cd with trace or appreciable H_2S. The overall trajectory is a shift to higher δ^{114}Cd compositions, within error of overlying deep water, and higher Cd enrichments in reducing sub-surface sediments.