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1   **Controls on the cadmium isotope composition of modern marine sediments**

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13   **Highlights:**

14   1. First constraints on the $\delta^{114}Cd$ composition of modern marine suboxic sediments

15   2. Main sources of sedimentary Cd are from sinking organic particulates and seawater

16   3. Average $\delta^{114}Cd$ value of surface sediments is 0.27‰ lighter than seawater

17   4. Burial of organically-bound Cd in suboxic sediments could satisfy Cd mass balance

18   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 $\Delta^{114/110}Cd_{surface\ sediments—deep\ waters}$ = -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.

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1. Introduction

50   The cadmium (Cd) isotope system has yielded a wealth of insights into the processes that regulate the

51   vertical and horizontal distribution of Cd in the modern ocean and may be used to provide information

52   about past ocean chemistry. Previous studies have reported a biologically-controlled depth profile for Cd,

53   where preferential uptake of light Cd isotopes by marine phytoplankton leaves the surface waters with

54   low Cd concentrations and higher isotope compositions relative to deep waters (Lacan et al., 2006;

55   Ripperger et al. 2007; Abouchami et al., 2011; Boyle et al., 2012; Xue et al., 2013; John and Conway, 2014;

56   Janssen et al., 2014; Conway and John, 2015a; Conway and John, 2015b; Xie et al., 2017; Janssen et al.,

57   2017; John et al., 2018; Sieber et al. 2019). While the availability of Cd isotope data in seawater and

58   particulates continues to expand (Yang et al., 2012; Janssen et al., 2014; Conway and John, 2015b, Yang

59   et al., 2015; Yang et al., 2018; Janssen et al., 2019), our understanding of the global isotopic mass balance

60   of Cd is less clear due to the unknown Cd isotope compositions in modern marine sediments, especially

61   those accumulating in low oxygen settings with significant amounts of organic matter. Furthermore, the

62   effect of shallow sediment diagenesis in altering the isotopic composition of recently buried Cd is not well

63   understood. Characterization of the isotopic composition of Cd in modern marine bulk sediments is

64   critically important to understand how and why the Cd isotopic composition of the oceans might evolve

65   through time, and how we might interpret marine sediment data as an archive of these variations.

66   At a global scale, the Cd cycle is controlled by inputs of Cd to the oceans from three main sources:

67   upper continental crust (with $\delta^{114/110}$Cd = -0.01 ± 0.04‰; Schmitt et al., 2009; Rehkämper et al., 2012),

68   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‰;

69   Bridgestock et al., 2018). Deep ocean seawater has an isotopic composition of 0.35 ± 0.12‰ (Ripperger

70   et al., 2007; Boyle et al., 2012; Conway and John, 2015a; Conway and John, 2015b; Xie et al., 2017; Janssen

71   et al., 2017; John et al., 2018; Sieber et al., 2019) that is isotopically heavier than the known inputs. The

72   burial flux of Cd from the oceans therefore must be isotopically lighter than the weathered input flux,

73   assuming that Cd is in steady state in the oceans. The primary output flux of Cd from the ocean is into

74   continental margin suboxic sediments (Heinrichs et al., 1980; Rosenthal et al., 1995b; van Geen et al.,

75   1995; Little et al., 2015). Some additional, albeit minor, sinks of Cd include incorporation within Fe-Mn

76   oxides in pelagic clays and marine carbonates (Boyle, 1988; Rosenthal et al., 1995b, van Geen et al., 1995;

77   Morford and Emerson, 1999; Schmitt et al., 2009; Horner et al., 2011; Rehkämper et al., 2012 and

78   references therein) and possibly formation of water column cadmium sulfides (Janssen et al., 2014; John

79   and Conway, 2015). However, it is unknown if these species reach the seafloor. Previous measurements

80   of the Cd isotopic compositions of oxygenated sedimentary sinks (Fe-Mn crusts and nodules) produced

81   isotopic values similar to deep ocean seawater (Schmitt et al., 2009; Horner et al., 2010). In contrast, the

82   burial of Cd into sulfides, particularly those accumulating on shallow continental margins, has been

83   postulated to be isotopically light based on data from experimental systems (Guinoiseau et al., 2018) and

84   measurements of oceanic hydrothermal sulfides (Schmitt et al., 2009). Recent work by Janssen et al., 2019

85   measured particulate and dissolved Cd pools, showing an intermediate depth of isotopically light

86   particulate Cd during remineralization in the subarctic northeast Pacific between 200-600 m water depth.

87   These authors proposed that this zone is an important sink of isotopically light Cd to margin sediments. A

88   determination of the isotopic composition of margin sediments is required to validate this hypothesis and

89   better constrain the sources of Cd to the seafloor. As of now, the Cd isotopic composition of margin

90   sediments, particularly suboxic sediments, the largest sink of Cd in the modern oceans (Rosenthal et al.,

91   1995b), is currently uncharacterised, leaving a significant gap in our understanding of how seawater Cd

92   isotope compositions evolve across geological time.

93   In this study, we present new data that characterise the Cd isotope composition of modern

94   sediments accumulating in oxic and suboxic settings from the Uruguayan margin and Argentine Basin and

95   compare these measurements to those of overlying seawater depth profiles. We use these data to answer

96 some key questions: (i) What is the Cd isotopic composition of modern marine sediments accumulating in

97 low-oxygen conditions? (ii) What are the main sedimentary phases that host Cd? (iii) Does the dominating

98 mechanism for Cd removal from sediment porewaters to marine sediments change during shallow

99 diagenesis? (iv) Does the burial of Cd into modern marine sediments balance the isotopic mass balance of

100 Cd?

101

102 **2. Sampling and analytical methods**

103

104 **2.1. Study Site**

105 Seawaterand sediment samples were collected during the JC068 research expedition, as part of the UK

106 GEOTRACES GA10 section aboard the RRS James Cook from December 2011 to January 2012. The samples

107 were collected along a longitudinal transect extending from the Uruguayan coast to the open ocean. Near-

108 surface sediments were obtained on the margin at three locations at 60m (St 24), 705m (St 23) and 1,483m

109 (St 22) water depths, while a water profile was collected at a fourth location at 3,313m (St 21) water

110 depth. In the Argentine Basin (St 18), a sediment core was retrieved along with a water column profile at

111 5,156m water depth. An additional water column profile was collected at the mid-Atlantic Ridge (St 12)

112 at 3,080m water depth (Fig. 1). The South West Atlantic water masses at 40°S represent a region of high

113 productivity in an ocean basin known for low concentrations of critical micronutrients. An oxygen

114 minimum zone (180 µmol L^{-1}) occurs between ~1–2 km depth that is associated with Upper Circumpolar

115 Deep Water (UCDW). The regional oxygen minimum zone (OMZ) intersects the seafloor at St 22. The main

116 water mass structure is shown in Fig. 1. The bottom waters of the Argentine Basin are complicated by a

117 large benthic nepheloid layer, spanning a thickness of more than 500 m (Gardner et al., 2018).

118 Sedimentation rates in the abyssal plain vary from ~1–5 cm/kyr (Stevenson and Cheng, 1969). While not

119 being determined directly, it is expected that the sites along the continental margin experience far higher

120 sedimentation rates compared to the deep basin (e.g. 0.8 cm/yr on the shelf top; Perez et al., 2016).

121

122 **2.2 Sample collection**

123 Water samples were retrieved through the vertical depth profile from the surface to the bottom waters.

124 All water sampling was completed using a titanium CTD frame equipped with a full sensor array and fitted

125 with 24x 10 litre OTE (Ocean Test Equipment) bottles with external springs. The unit was deployed on a

126 Plasma Rope for optimal trace metal-free sampling. The retrieved bottles were transferred to a class 100

127 clean air container laboratory. The water samples for Cd isotopes were immediately filtered through a 0.2

128 µm AcroPak Supor polyethersulfone membrane filter capsules (Pall) into acid-cleaned, low density

129 polyethylene bottles. Each sample was acidified to approximately 0.024 M with UpA HCl (Romil,

130 Cambridge, UK) under a class 100 laminar flow hood.

131   For the near-surface sediment samples collected along the transect from the Uruguayan coast to

132 the abyssal plain of the Argentine Basin, a Bowers and Connelly Mega Corer was deployed on a Plasma

133 Rope to collect surface sediment cores and porewater samples. The porewater and sediment fractions

134 were collected at 1–2 cm depth resolution in a shipboard temperature-controlled laboratory that

135 replicated bottom water conditions (4°C) using one of two procedures: (1) Recovered sediment was sub-

136 sectioned by Teflon apparatus, and porewaters separated using Decon- and HCl-cleaned polycarbonate

137 centrifuge tubes (spun at 4°C and 9000g for 10 minutes). Supernatant porewater was extracted and

138 filtered by an acid-cleaned syringe (BD Discardit) and cellulose acetate syringe filter (0.2 µm; Whatman

139 Puradisc) all under an oxygen-purged nitrogen atmosphere. (2) Porewaters were subsampled by insertion

140 of Rhizon samplers (0.15 µm CSS-type 50mm, Rhizosphere Research Products) through the sample ports

141 of a pre-drilled core tubes (e.g. Homoky et al., 2013; Klar et al., 2017), and residual sediment inside the

142 core tubes was subsequently extruded and sub-sampled by Teflon sectioning apparatus. The porewater

143   samples were measured for macronutrients and dissolved metals. Nutrient samples were collected

144   exclusively by the Rhizon samplers. Dissolved metals were collected by centrifugation/filtration at St 18

145   and 22, and by Rhizon samplers at St 23 and 24. Dissolved metal samples were acidified pH<2 prior to

146   analyses (by addition of 6 µl 6M Q-HCl per 1ml of sample). The sediment samples were freeze-dried and

147   homogenized using an agate pestle and mortar prior to total acid digestion, and coulometric

148   determinations of organic and inorganic carbon concentrations as described in Homoky et al. (2013).

149

150   **2.3 Elemental and isotopic analyses**

151   All samples were prepared for measurement of Cd concentrations and isotopic compositions in a Class 10

152   laminar flow workstation within a Class 1000 clean lab suite at the University of Oxford. The acids used in

153   this study were purified by sub-boiling distillation in quartz glass stills. Optima^{TM} Grade perchloric acid was

154   purchased from Fisher Scientific Ltd.

155

156   ***2.3.1 Sediment digestion procedures***

157   The digestion of sediments was completed following one of two procedures, depending on the amount

158   of sediment needed to obtain sufficient Cd for isotopic analysis. Digestion of low-volume sediment

159   samples (0.1–0.3 g) was achieved by sequentially heated aqua regia and combined HF and $HClO_4$ acids

160   following Homoky et al. (2013). Digestion of higher-volume sediment samples involved weighing out

161   between 0.3–2 g of dried and homogenized sediments into acid-cleaned Teflon jars and digesting in 4–12

162   mL of inverse Aqua Regia at 120–150°C for between 48 hours and three weeks. The samples were

163   removed from the oven once digestion was complete, as evidenced by the presence of pale-yellow

164   leached silicates. Samples were evaporated to incipient dryness before 3 mL of HNO_3 and 1 mL of HF were

165   added to dissolve any silicates. The samples were closed and heated overnight and then dried and

166   redissolved in 3 M HNO_3. All of the samples were measured for a range of major and minor elements.

167

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:

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

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

179

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.

191

2.3.4 Cd isotope determination by Multi-Collector ICP-MS

193 Cadmium isotopic analyses were completed on a Nu Instruments Nu Plasma multi-collector HR-ICP-MS at

194 the University of Oxford in low resolution mode. A sample concentration of 20 ppb was used for all

195 samples. Measurements comprised 40x simultaneous 10 s integrations for ^{110}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd, ^{114}Cd,

196 ^{115}In and ^{117}Sn, with the latter used to correct for isobaric interferences. All samples were preceded with

197 a short measurement of 2% HNO_3 that was used to blank-correct sample voltages. Isotopic compositions

198 are the mean of two to four replicate measurements and the uncertainty is the 2 S.D. of these replicates.

199 Sample-spike mixtures were deconvolved off-line using an Excel-based routine, with corrections

200 for Sn and In interferences. Isotopic compositions were corrected to NIST 3108 by normalizing to in-run

201 bracketing standards to correct for mass discrimination. Analyses of Cadmium NIST SRM 3108 (Lot#

202 060531, $\delta^{114/110}Cd_{NIST} \equiv 0$), double-spiked to match the concentrations and sample-spike ratios of the

203 samples, bracketed every one or two sample analyses. Cadmium isotopic compositions are reported in

204 delta notation relative to NIST SRM 3108 (Abouchami et al., 2013) using the following equation:

205 $$\delta^{114/110}Cd = \left(\frac{^{114}Cd/^{110}Cd_{sample}}{^{114}Cd/^{110}Cd_{standard}} - 1 \right) \times 1000 \qquad (2)$$

206 An in-house standard 'OXCAD' (Alfa Aesar Specpure Cd concentration standard, Lot# 81-081192A) was

207 measured repeatedly in each analysis session to assess instrument stability and long-term reproducibility.

208 The $\delta^{114}Cd$ of OXCAD was -0.95 ± 0.09 ‰ (n = 139, 2 S.D.) over the course of this study.

209 Samples that deviated from optimal sample-spike ratios by more than 0.15 were bracketed with

210 NIST 3108 solutions with a similar proportion of double spike. Previous work has shown that this technique

211 produces accurate results (Ripperger and Rehkämper, 2007).

212

213 **3. Results**

214

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).

239

3.2.3 Sedimentary element concentration profiles

240 Redox zonations inferred from dissolved porewater cation and anion profiles are also recorded by solid-

242 phase sedimentary Cd, U and Mo enrichments. The highest redox-sensitive element enrichments occur in

243 the margin sites (St 22 and St 23). Cadmium concentrations of near-surface sediments range from 0.04 to

244 3.31 ug g^{-1}. An early diagenetic feature in all the measured sediment cores are sharp, authigenic Cd

245 enrichment peaks close to redox fronts, most prominently near the oxic-suboxic redox boundary in the

246 deep basin (St 18) and near the inferred suboxic-sulfide redox boundary on the margin and coast (St 22,

247 St 23 and St 24). These levels coincide with an increase in the concentration of other redox-sensitive

248 metals such as Mo and U. The relationship between Cd and U in the down-core redox profiles is shown

249 graphically in Fig. 4. As this study is focused on modern marine sediments, the following discussion will

250 exclude the suboxic sediments from the deep basin (St 18). The slow sedimentation rates within the

251 Argentine Basin indicates that these sediments are unlikely to represent sediments from the Holocene.

252

3.2.3 Sedimentary Cd concentrations and isotopes

254 The Cd isotope compositions of near-surface sediments range from -0.08 to 0.71‰. These compositions

255 are generally lower than the overlying seawater along the Uruguayan continental margin and Argentine

256 Basin (Fig. 3). δ^{114}Cd compositions notably shift to higher values that are within error of the overlying deep

257 water (~0.35‰) near sub-surface redox fronts, coinciding with redox fronts at ~1 μM nitrate and increases

258 in sedimentary Cd concentration.

259

4. Discussion

261

4.1 Mechanisms for Cd incorporation into near-surface sediments

263   Sedimentary Cd may be bound in detrital minerals, organic matter, associated with Fe-Mn

264   oxyhydroxides, or as authigenic Cd sulfides (Rosenthal et al., 1995a, Rosenthal et al. 1995b; Janssen et al.,

265   2014; John and Conway, 2015).

266   Calculated Cd enrichment factors relative to detrital Cd for near-surface sediments average 5.1

267   and range between 2.7 and 8.1. This corresponds to ~63–88% of the Cd accumulating on the seafloor

268   being non-detrital in origin.

269   Cadmium incorporation in CdS in the water column or at the sediment surface has been suggested

270   in other settings (Janssen et al. 2014; John and Conway 2015) but is not anticipated at the water column

271   O_2 levels observed in this study, which are always above 180 μmol L^{-1}. We confirmed this assumption by

272   calculating the Cd* value at these sites. A useful parameter, Cd*, is a tracer for water column non-

273   biological addition or removal of Cd, including by CdS. It is based on the expected Cd concentration for a

274   given P concentration, using the well-established Cd/P stoichiometry: Cd* = $Cd_{measured}$ – (Cd/P $_{deep\ water}$ x

275    $P_{measured}$) (Baars et al., 2014). Cadmium* values for South Atlantic stations 12, 18 and 21 below 200 m are

276   close to zero (0.02 to 0.12 nmol/kg), indicating no significant precipitation of CdS species at these three

277   sites along the Uruguayan margin.

278   The role of organically-bound Cd as a pathway for Cd burial can be explored by predicting Cd

279   concentrations expected from measured sedimentary TOC values for typical Cd/C ratios of marine

280   phytoplankton (Ho et al., 2003). Cadmium concentrations and stoichiometries corresponding to the range

281   of Cd uptake into phytoplankton are shown in Figure 5 and can account for the majority of the measured

282   Cd concentrations in the near-surface sediments from the margin and basin sites. Non-detrital Cd in

283   surface sediments of most Uruguayan margin sediments can therefore be explained by addition in organic

284   material. Such POC-hosted Cd makes up the majority of the Cd in the near-surface suboxic sediments in

285   this study.

286   Some surface sediments from Site 24, however, have higher Cd concentrations than can be

287   explained by planktonic Cd/C ratios, suggesting an additional flux of shallow-water Cd. This additional Cd

288   is likely to be incorporated into Fe-Mn oxyhydroxides in this shelf environment where such oxyhydroxides

289   are common. This explanation is supported by an increase in sedimentary Mn concentrations from 0 to 3

290   cm in this core. The shallow depth of this core means that the Cd is derived from near-surface seawater

291   with a δ^{114}Cd composition that is heavy due to removal of Cd into organic material. This may explain the

292   unusually high δ^{114}Cd values (0.71‰) observed in these Cd-enriched samples (Fig. 6).

293

294   **4.2 Suboxic sediments as a sink for isotopically light Cd from the ocean**

295   Cadmium isotope values of suboxic margin surface sediments (0.02 to 0.09‰), the dominant sink flux in

296   the ocean, are lighter than deep water values (~0.35‰). This is explained by sinking organic particular

297   matter with a lighter isotopic composition than deep water which settles to form the sediment. That

298   settling water column particulates are isotopically lighter than deep water has been observed previously;

299   particulate δ^{114}Cd compositions from the upper 1200 m of the Atlantic and Pacific water columns span a

300   wider range of -1.47 to 2.08‰, with the heaviest particulate δ^{114}Cd values in surface waters and the

301   lightest particulate δ^{114}Cd compositions at sub-surface water depths (~200 to 600 m), reflecting the

302   uptake and subsequent remineralization of organically-bound Cd in the surface waters (Yang et al., 2012;

303   Janssen et al., 2014; Conway and John, 2015b; Yang et al., 2015; Yang et al., 2018; Janssen et al., 2019).

304   A mechanistic understanding of the particulate δ^{114}Cd profile in the ocean remains elusive.

305   Recently, Janssen et al. (2019) hypothesized that sinking particulates may be composed of multiple pools

306   with different isotopic compositions and remineralization labilities, where the sub-surface particulate Cd

307   pool is more refractory than the particulate Cd fraction in the surface waters and isotopically lighter than

308   the particulate Cd pools in surface and deep waters (c.f. Janssen et al., 2019). It is this sub-surface,

309   isotopically light particulate Cd fraction that settles and likely represents the burial flux of particulate Cd

13

310   on the margin sediments. These sediments may therefore be the missing removal term to satisfy the

311   global isotopic mass balance of oceanic Cd.

312

313   **4.3 Sub-surface diagenetic alteration of Cd in South Atlantic sediments**

314   The most noticeable feature in sub-surface sediment Cd composition are the Cd enrichment peaks which

315   occur near redox fronts. These Cd concentration peaks generally coincide with low porewater nitrate and

316   Fe concentrations in the South Atlantic sediment profiles (Fig. 3). We propose that these observations

317   reflect the precipitation of porewater Cd with H_2S to form CdS species (Fig. 4, Gobeil et al., 1987; Pedersen

318   et al., 1989; Rosenthal et al., 1995a; Rosenthal et al., 1995b).

319   A sub-surface formation of CdS and/or other sulfide species (e.g. FeS, Framson and Leckle, 1978;

320   Pedersen et al., 1989), would likely reduce porewater Cd concentrations, and thus establish a diffusive

321   gradient that draws overlying seawater Cd downwards towards the Cd-sulfide reaction front and zone of

322   enrichment. The sedimentary Cd isotopic compositions at these enrichment fronts are within analytical

323   uncertainty of overlying deep water (~0.35‰), overprinting the Cd isotopic signature from detrital and

324   sinking organic particulates.

325   The dominant process governing authigenic Cd burial in modern marine sediments with suboxic

326   and sulfidic porewaters is the precipitation of CdS species (Rosenthal et al., 1995a; Rosenthal et al.,

327   1995b), where diffusion would drives preferential removal of the lighter Cd isotopes from the porewaters

328   (Guinoiseau et al. 2018). Recent experiments show that Cd isotope fractionation during precipitation with

329   H_2S will preferentially capture the lighter Cd isotopes relative to the bulk solution, although more

330   complete Cd precipitation leads to quantitative transfer of the Cd isotopic signature from solution into

331   the solid phase (Guinoiseau et al., 2018). Some suboxic sediments from this study, above the sulfide front,

332   also have Cd concentrations and isotope compositions that suggest such quantitative removal of deep

333   water Cd (see Figure 6).

334   Overall, the Cd and δ^{114}Cd composition of the sediments in this study can be interpreted as an

335   interplay between three processes:

336   i.   Incorporation of isotopically light Cd in organic matter settling from the water column and making

337   up the bulk of Cd in near surface sediments

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

339   sediments

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

341   sediment.

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

343

344   **4.4 Cadmium Mass Balance**

345   Sedimentary Cd isotopes may serve as a proxy for the extent of past cycling and ocean mixing (Georgiev

346   et al., 2015; Sweere et al., 2020). A critical first step to using this proxy effectively is to constrain the

347   elemental and isotopic mass balance of Cd in the modern ocean. A summary of the global source and sink

348   fluxes of oceanic Cd is presented in Table 3. The estimated fluxes are primarily from Rosenthal et al.

349   (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

350   Cd/yr, Shiller and Boyle, 1991; Rosenthal et al., 1995b; van Geen et al., 1995). While hydrothermal vents

351   are an important local source of Cd, this flux only influences the chemistry of very proximal ocean waters,

352   and thus is assumed to be removed quantitatively near the vent site. The dominant sink of oceanic Cd is

353   into suboxic and anoxic margin sediments, with an estimated removal flux of 15–60 x 10^6 mol Cd/yr (Table

354   3, Rosenthal et al., 1995b; van Geen et al., 1995; Little et al., 2015).

355   Other minor output fluxes are pelagic clays, carbonates and Fe-Mn nodules and crusts, although

356   they are unlikely to significantly influence the oceanic budget of Cd. Contribution of Cd from pelagic clays

357   is estimated using the Cd concentration from Heinrichs et al., 1980 (100 to 350 ng g^{-1}) and the burial rate

358   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

359   isotopic composition of this output flux is unknown. The contribution of Cd associated with Fe-Mn

360   deposits to the oceanic Cd budget is negligible (Schmitt et al., 2009; Horner et al., 2010), and this process

361   does not greatly fractionate Cd (Schmitt et al., 2009; Horner et al., 2010). Cadmium burial within

362   carbonates is estimated to be 0.4–1.8 x 10^6 mol Cd/yr (Horner et al., 2011) with an unknown isotopic

363   composition for natural samples.

364   This study provides new isotopic compositions of Cd in suboxic margin sediments. The burial flux

365   of Cd within suboxic margin sediments from below 100 m water depth (St 22 and St 23) has a range in

366   δ^{114}Cd values of -0.02 to 0.25‰, predominately composed of sinking organic particulates.

367   An additional flux of Cd becomes important below the sediment-water interface as CdS species

368   start to precipitate at redox fronts. The initial particulate-dominated burial flux of Cd is subsequently

369   modified in the sub-surface during shallow diagenesis to higher isotopic compositions and concentrations

370   as seawater-sourced porewater Cd precipitates with H$_2$S to form CdS species. This process is expected to

371   drive a downward diffusive flux of seawater Cd into the sub-surface sediments to enrichment zones near

372   redox boundaries where the isotope composition of precipitating Cd overprints the isotopic composition

373   of the surface sediments to values within error of overlying deep water. An additional inferred, albeit

374   minor, source of porewater Cd to form CdS species is newly-released Cd during the redox-driven oxidation

375   of sinking organic particulates during shallow diagenesis. Within anoxic margin sediments, such as the

376   Black Sea (Little et al., 2015), these processes will occur within the water column, where the Cd isotopic

377   composition will reflect global deep water values (~0.35‰).

378   Cadmium burial within suboxic and anoxic margin sediments satisfies the global oceanic mass

379   balance of Cd, within the uncertainties that exist on all fluxes (Table 3). The measured isotopic output flux

380   of δ^{114}Cd ranges from -0.02 to 0.35‰, using the elemental and isotopic ranges for Cd from suboxic and

381   anoxic margin sediments. This sink term largely balances the budget of Cd in the oceans. Future

16

382 assessment of Cd output fluxes from a diversity of ocean-sediment boundaries is now recommended to

383 develop further robustness in our assessment of the ocean's Cd cycle.

384

385 **5. Conclusions**

386 We present the first constraints on the isotopic compositions of Cd in modern marine suboxic sediments

387 using new measurements from the South West Atlantic Ocean. Surface sediments (0–1 cm) below 100 m

388 water depth comprised δ^{114}Cd values between 0.02 and 0.15‰ that are isotopically lower than river

389 inputs and overlying deep seawater ($\Delta^{114/110}$Cd$_{surface\ sediments—deep\ waters}$ = -0.27 ± 0.14‰). These observations,

390 coupled to an assessment of the global ocean budget, suggest that suboxic surface sediments provide the

391 missing light isotopic sink and enable the isotopic mass balance of Cd in the oceans to be closed. The

392 primary contributors of Cd to marine sediments are from sinking organic particulates, and from

393 downwards diffusion of seawater Cd to precipitate as CdS species within reducing porewater conditions

394 at depth.

395

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555

556   **Figure 1;** Sampling locations for seawater depth profiles (circles) and near-surface sediment cores

557   superimposed onto water mass oxygen concentrations (Schlitzer et al., 2018). The black shapes indicate

558   the location of the sediment cores: square (St 24), diamond (St 23), triangle (St 22) and hexagon (St 18).

559   The approximate location of key water masses is noted on the figure: Antarctic Intermediate Water

560   (AAIW), Upper Circumpolar Water (UCDW), North Atlantic Deep Water (NADW), Antarctic Bottom Water

561   (AABW). Figure produced using Ocean Data View (Schlitzer, 2015).

562

563   **Figure 2;** Vertical water column profiles of dissolved Cd concentrations and isotopic compositions (dCd),

564   along with dissolved oxygen (O_2), PO_4^3, NO_3^- and silica (Si) from a) Uruguayan continental slope (St 21), b)

565   Argentine Basin (St 18) and c) South Atlantic Mid-Ocean Ridge (St 12). The measured particulate Cd

566   concentrations and isotopic compositions (pCd) from the Argentine Basin and continental slope are

567   depicted with filled orange squares. The vertical dashed line represents the average SW Atlantic deep

568   ocean water value ($\delta^{114/110}Cd = 0.35‰$). Error bars for the Cd isotopes measurements represent the 2 S.D.

569   on the sample. The Southern Component Water (SCW) includes the AAIW and UCDW. Note scale

570   differences between plots for different samples.

571

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.

583

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.

589

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.

593

594 **Figure 6;** Evidence for redox control on Cd burial in South Atlantic near-surface sediments. Authigenic

595 enrichment of Cd compared to Cd isotopic compositions of near-surface sediments are plotted with the

596 color and shape indicating the redox conditions of the porewaters: oxic (turquois circles), suboxic (blue

597 diamonds), and sulfidic (orange squares). The isotopic composition of detrital Cd (UCC) is marked with a

598 black star. The predicted isotopic composition of Cd associated with sinking organic particulates (Cd_{org}) is

599 determined by hypothesizing the authigenic fraction in near-surface sediments (0–5 cm) is predominately

600 composed of organically-bound Cd, along with using the isotopic composition of the UCC (-0.01‰) for the

601 detrital fraction, in the following equation:

602 $$\delta^{114/110}Cd_{organic\ particulates} = \frac{([Cd]_{meas.} \cdot \delta^{114/110}Cd_{meas.}) - ([Cd]_{detrital} \cdot \delta^{114/110}Cd_{detrital})}{[Cd]_{organic\ particulates}} \qquad (3)$$

603 where the average predicted $\delta^{114}Cd$ value from sinking organic particulates in the top of the core (0–5 cm)

604 is 0.04 ± 0.06‰. The dashed lines denote mixing relationships between detrital Cd (EF value of 1; M_1 and

605 -0.01‰; δ_1) and either shallow-water Cd from the SW Atlantic at 49 m water depth (0.72‰; δ_2), overlying

606 deep ocean water Cd (0.35‰; δ_2), or predicted $\delta^{114}Cd$ value of organically-bound Cd (Cd_{org}, 0.04 ± 0.06‰;

607 δ_2) at a starting EF value of 1 ($M_{OBSERVED}$):

608 $\delta_{OBSERVED} = \delta_2 + (\delta_1 - \delta_2) \bullet (M_1 / M_{OBSERVED})$

609 At oxic porewater conditions, the distribution of Cd versus $\delta^{114}Cd$ is best represented by a mixing

610 relationship between a detrital Cd endmember and a mixture of shallow-water- or deep water-sourced

611 porewater Cd adsorbed to Fe-Mn oxyhydroxides and organically-bound Cd from sinking particulates. At

612 suboxic and sulfidic porewater conditions, the sediments depict different stages of mixing between

613 organically-bound Cd and precipitation of CdS species from seawater Cd with trace or appreciable H_2S.

614 The overall trajectory is a shift to higher $\delta^{114}Cd$ compositions, within error of overlying deep water, and

615 higher Cd enrichments in reducing sub-surface sediments.