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Controls on the cadmium isotope composition of modern marine sediments

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24 **Abstract**

25 Continental margin sediments have been identified as the dominant sink in the marine budget of cadmium
26 (Cd). The isotopic composition of this important output flux is, however, unknown. Here we present, with
27 measurements on the Argentine continental margin, the first observational constraints on the isotopic
28 composition of Cd in modern marine oxic and sub-oxic sediments. We identify two main removal
29 mechanisms of Cd; in organic material, and by sulfide formation. Surface margin sediments (0–0.5 cm),
30 with dissolved O₂ below detection from below ~0.5 cm, are isotopically lighter than overlying oxygenated
31 waters. A mass balance for these surface sediments indicates that Cd is present dominantly as organically-
32 bound particulate Cd. In sub-surface sediments, Cd concentrations increase in the zone of nitrate
33 reduction, and attain similar isotopic compositions as the water that overlies the sediment (i.e. ~0.35‰
34 in deep waters). These observations are consistent with a downward diffusive flux of seawater Cd and
35 redox-driven quantitative removal of that Cd during sulfide precipitation. In combination, these two
36 routes of Cd removal lead to burial of isotopically light organic Cd in margin sub-oxic sediments that
37 enables the global isotopic Cd budget to be balanced.

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48 1. Introduction

49 The cadmium (Cd) isotope system has yielded a wealth of insights into the processes that regulate the
50 vertical and horizontal distribution of Cd in the modern ocean and may be used to provide information
51 about past ocean chemistry. Previous studies have reported a biologically-controlled depth profile for Cd,
52 where preferential uptake of light Cd isotopes by marine phytoplankton leaves the surface waters with
53 low Cd concentrations and higher isotope compositions relative to deep waters (Lacan et al., 2006;
54 Ripperger et al. 2007; Abouchami et al., 2011; John and Conway, 2014; Janssen et al., 2014; Conway and
55 John, 2015a; Conway and John, 2015b; Xie et al., 2017; Janssen et al., 2017; John et al., 2018; Sieber et al.
56 2019). While the availability of Cd isotope data in seawater and particulates continues to expand (Yang et
57 al., 2012; Janssen et al., 2014; Conway and John, 2015b; Yang et al., 2018; Janssen et al., 2019), our
58 understanding of the global isotopic mass balance of Cd remains unclear due to the lack of constraints on
59 the Cd isotope composition of modern marine sediments, especially those accumulating in low oxygen
60 settings and with significant amounts of organic matter. Furthermore, the effect of shallow sediment
61 diagenesis in altering the isotopic composition of recently buried Cd is not well understood.
62 Characterization of the isotopic composition of Cd in modern marine bulk sediments is critically important
63 to understand how and why the Cd isotopic composition of the oceans might evolve through time, and
64 how we might interpret marine sediment data as an archive of these variations.

65 At a global scale, the Cd cycle is controlled by inputs of Cd to the oceans from three main sources:
66 upper continental crust (with $\delta^{114/110}\text{Cd} = -0.01 \pm 0.04\text{‰}$; Schmitt et al., 2009; Rehkämper et al., 2012),
67 rivers ($\delta^{114/110}\text{Cd} = 0.1\text{‰}$ to 0.3‰ ; Lambelet et al., 2013) and dust ($\delta^{114/110}\text{Cd} = -0.19\text{‰}$ to 0.19‰ ;
68 Bridgestock et al., 2018). Deep ocean seawater has an isotopic composition of $0.35 \pm 0.12\text{‰}$ (Ripperger
69 et al., 2007; Conway and John, 2015a; Conway and John, 2015b; Xie et al., 2017; Janssen et al., 2017; John
70 et al., 2018; Sieber et al., 2019) that is isotopically heavier than the known inputs. There must therefore
71 be a burial flux of Cd from the oceans that is isotopically lighter than the input flux, assuming that the Cd

72 cycle is in steady state. The primary output fluxes of Cd from the ocean are into continental margin sub-
73 oxic and anoxic sediments (Heinrichs et al., 1980; Rosenthal et al., 1995b; van Geen et al., 1995; Little et
74 al., 2015), due either to the greater burial efficiency of organically-bound Cd (Janssen et al., 2019), or to
75 the burial of cadmium sulfide (CdS) in the presence of aqueous hydrogen sulfide (Schmitt et al., 2009;
76 Janssen et al., 2014; John and Conway, 2015; Guinoiseau et al., 2019; Plass et al., 2020). Both of these
77 pathways have been postulated to be the isotopically light removal pathway needed to balance the global
78 Cd cycle. Some additional, albeit minor, sinks of Cd include incorporation within or adsorption onto Fe-
79 Mn oxides in pelagic clays and marine carbonates (Boyle, 1988; Rosenthal et al., 1995b, van Geen et al.,
80 1995; Schmitt et al., 2009; Horner et al., 2011; Rehkämper et al., 2012 and references therein). Previous
81 measurements of the Cd isotopic compositions of oxygenated sedimentary sinks (Fe-Mn crusts and
82 nodules) produced isotopic values similar to deep ocean seawater (Schmitt et al., 2009; Horner et al.,
83 2010). Direct observations of the isotopic composition of marginal marine sediments are required to test
84 whether organic matter and/or CdS burial control the output flux of Cd from the oceans, and to
85 understand the controls that determine the magnitude of these two burial pathways. However, the Cd
86 isotopic composition of modern margin sediments, particularly sub-oxic sediments, is currently
87 uncharacterised, leaving a significant gap in our understanding of how seawater Cd isotope compositions
88 evolve across geological time.

89 In this study, we present new data that characterise the Cd isotope composition of modern marine
90 sediments accumulating in oxic and sub-oxic settings from the Uruguayan margin and Argentine Basin and
91 compare these measurements to those of overlying seawater depth profiles. We use these data to answer
92 some key questions: (i) What is the Cd isotopic composition of modern marine sediments accumulating in
93 sub-oxic porewaters? (ii) What are the main sedimentary phases that host Cd? (iii) Do sedimentary phases
94 containing Cd change during shallow diagenesis? (iv) Does the burial of Cd into modern marine sediments
95 balance the isotopic mass balance of Cd?

96

97 **2. Sampling and analytical methods**

98

99 **2.1. Study Site**

100 Seawater and sediment samples were collected during the JC068 research expedition, as part of the UK
101 GEOTRACES GA10 section aboard the RRS James Cook from December 2011 to January 2012. The samples
102 were collected along a longitudinal transect extending from the Uruguayan coast to the open ocean. Near-
103 surface sediments were obtained on the margin at three locations at 60m (St 24), 705m (St 23) and 1,483m
104 (St 22) water depths, while a water profile was collected at a fourth location at 3,313m (St 21) water
105 depth. In the Argentine Basin (St 18), a sediment core was retrieved along with a water column profile at
106 5,156m water depth. An additional water column profile was collected at the mid-Atlantic Ridge (St 12)
107 at 3,080m water depth (Fig. 1). The South West Atlantic water masses at 40°S represent a region of high
108 productivity in an ocean basin known for low concentrations of critical micronutrients. The main water
109 mass structure is shown in Fig. 1. Sedimentation rates in the abyssal plain vary from ~1–5 cm/kyr
110 (Stevenson and Cheng, 1969). While not being determined directly, it is expected that the sites along the
111 continental margin experience higher sedimentation rates compared to the deep basin (e.g. 0.8 cm/yr on
112 the shelf top; Perez et al., 2016).

113

114 **2.2 Sample collection**

115 Water samples were retrieved through the vertical depth profile from the surface to the bottom waters.
116 All water sampling was completed using a titanium CTD frame equipped with a full sensor array and fitted
117 with 24x 10 litre OTE (Ocean Test Equipment) bottles with external springs. The unit was deployed on a
118 Plasma Rope for optimal trace-metal-free sampling. The retrieved bottles were transferred to a class 100
119 clean air container laboratory. The water samples for Cd isotopes were immediately filtered through a 0.2

120 μm AcroPak Supor polyethersulfone membrane filter capsules (Pall) into acid-cleaned, low density
121 polyethylene bottles. Each sample was acidified to approximately 0.024 M with UpA HCl (Romil,
122 Cambridge, UK) under a class 100 laminar flow hood.

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

139

140 **2.3 Elemental and isotopic analyses**

141 All samples were prepared for measurement of Cd concentrations and isotopic compositions in a Class 10
142 laminar flow workstation within a Class 1000 clean lab suite at the University of Oxford. The acids used in

143 this study were purified by sub-boiling distillation in quartz glass stills. Optima™ Grade perchloric acid was
144 purchased from Fisher Scientific Ltd.

145

146 **2.3.1 Sediment digestion procedures**

147 The digestion of dried and homogenized sediments was completed by oxidizing organic matter in aqua
148 regia and HClO₄ and dissolving silicates in HNO₃ and HF (Homoky et al., 2013). All of the samples were
149 measured for a range of major and minor elements.

150

151 **2.3.2 Determination of element concentrations in sediment samples**

152 A suite of sedimentary major and minor elements was determined using an ELEMENT 2 ICP-MS and a
153 Perkin Elmer NexION 350D ICP-MS at the University of Oxford. Accuracy and precision was assessed using
154 repeated analyses of USGS Devonian Shale (SDO-1). All measured concentrations were within 10% of
155 accepted values.

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

$$159 \text{EF}_{\text{element}} = (\text{Cd/Th})_{\text{sediment}} / (\text{Cd/Th})_{\text{upper continental crust}} \quad (1)$$

160 where an EF greater than 1 indicates enrichment above typical crustal abundances. The enriched Cd
161 isotopic composition of the sediments was calculated using the $\delta^{114/110}\text{Cd}$ of UCC from Schmitt et al.
162 (2009), in the following equation:

$$163 \delta^{114/110} \text{enriched Cd} = \frac{([\text{Cd}]_{\text{bulk}} \cdot \delta^{114}_{110}\text{Cd}_{\text{bulk}}) - ([\text{Cd}]_{\text{UCC}} \cdot \delta^{114}_{110}\text{Cd}_{\text{UCC}})}{[\text{Cd}]_{\text{bulk}} - [\text{Cd}]_{\text{UCC}}} \quad (2)$$

164

165 **2.3.3 Ion exchange chromatography procedures**

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

176

177 **2.3.4 Cd isotope determination by Multi-Collector ICP-MS**

178 Cadmium isotopic analyses were completed on a Nu Instruments Nu Plasma multi-collector HR-ICP-MS at
179 the University of Oxford in low resolution mode. A sample concentration of 20 ppb (natural Cd) was used
180 for all samples. Measurements comprised 40x simultaneous 10 s integrations for ^{110}Cd , ^{111}Cd , ^{112}Cd , ^{113}Cd ,
181 ^{114}Cd , ^{115}In and ^{117}Sn , with the latter used to correct for isobaric interferences. All samples were preceded
182 with a short measurement of 2% HNO_3 that was used to blank-correct sample voltages. Isotopic
183 compositions are the mean of two to four replicate measurements and the uncertainty is the 2 S.D. of
184 these replicates. Cadmium procedural blanks were ≤ 1.1 ng, representing $\leq 2\%$ of the Cd processed in the
185 samples, and thus no blank corrections were applied.

186 Sample-spike mixtures were deconvolved off-line using an Excel-based routine, with corrections
187 for Sn and In interferences. Isotopic compositions were corrected to NIST 3108 by normalizing to in-run
188 bracketing standards to correct for mass discrimination. Analyses of Cadmium NIST SRM 3108 (Lot#
189 060531, $\delta^{114/110}\text{Cd}_{\text{NIST}} \equiv 0$), double-spiked to match the concentrations and sample-spike ratios of the

190 samples, bracketed every one or two sample analyses. Cadmium isotopic compositions are reported in
191 delta notation relative to NIST SRM 3108 (Abouchami et al., 2013) using the following equation:

$$192 \quad \delta^{114/110}\text{Cd} = \left(\frac{{}^{114}\text{Cd}/{}^{110}\text{Cd}_{\text{sample}}}{{}^{114}\text{Cd}/{}^{110}\text{Cd}_{\text{standard}}} - 1 \right) \times 1000 \quad (3)$$

193 An in-house standard 'OXCAD' (Alfa Aesar Specpure Cd concentration standard, Lot# 81-081192A) was
194 measured repeatedly in each analysis session to assess instrument stability and long-term reproducibility.

195 The $\delta^{114}\text{Cd}$ of OXCAD was $-0.95 \pm 0.09 \text{‰}$ ($n = 139$, 2 S.D.) over the course of this study, which is identical
196 to values determined by inter-laboratory comparison (Abouchami et al., 2012) and in previous studies
197 (Dickson et al., 2019; Sweere et al., 2020).

198

199 **3. Results**

200

201 **3.1 Cd concentration and isotope variations of waters**

202 The dissolved Cd profile in the South West Atlantic Ocean is similar to published profiles from other ocean
203 basins (Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011; Xue et al., 2012; Yang et al.,
204 2012; Baars et al., 2014; John and Conway, 2014; Conway and John, 2015a; Conway and John, 2015b;
205 Janssen et al., 2017; Xie et al., 2017; John et al., 2018; Janssen et al., 2019; Sieber et al., 2019). The three
206 vertical depth profiles for Cd show a nutrient-type distribution (Table 1 and Fig. 2). The behavior of
207 dissolved Cd below 700 m at all sites is relatively uniform, with an average $\delta^{114}\text{Cd}$ value of $0.35 \pm 0.11\text{‰}$,
208 identical to average global deepwater (John et al., 2018). Near-surface waters are isotopically higher than
209 the deep water, reaching 3.01‰ in the Argentine Basin (St 18). We observe very high $\delta^{114}\text{Cd}$ values in the
210 surface waters (<100 m) with Cd concentrations below 0.1 nmol kg^{-1} that were not observed in a previous
211 study of South Atlantic waters by Xie et al. (2017). The sample from 47 m in particular passed all

212 laboratory control checks but the obvious difference with Xie et al. (2019) requires future
213 investigation.

214

215 **3.2 Cd concentrations and isotope compositions of near-surface sediments**

216

217 ***3.2.2 Porewater geochemical profiles***

218 The redox profiles of the sediments from the coast to the abyssal plain of the Argentine Basin reflect the
219 physical characteristics and nutrient concentrations in the overlying water column, the extent of organic
220 matter remineralization and sedimentation rates (see Fig. 3). Dissolved O₂ is present only in the surface
221 sediment levels (~0.5 cm) of stations 22, 23 and 24, and to ~9 cm depth in station 18. Below these levels
222 O₂ is undetectable and NO₃⁻ concentrations decline with depth to levels well below those in overlying
223 seawater (~30 μmol L⁻¹), signifying the primary role of NO₃⁻ as an electron acceptor in the sub-oxic redox
224 zone. Thus the bulk of the enriched sedimentary Cd isotope compositions reported below are from the
225 sub-oxic (nitrate reducing) zone of the sediments (Fig. 3). Samples from St. 22 record the lowest overlying
226 dissolved oxygen concentration at 180 μmol L⁻¹ and the highest TOC of all the core-tops (~4%) presumably
227 due to a higher organic matter burial efficiency than the other stations.

228

229 ***3.2.3 Enriched sedimentary element concentration profiles***

230 Redox zonations inferred from dissolved porewater cation and anion profiles are also recorded by solid-
231 phase sedimentary Cd and U concentrations and enrichments. Uranium enrichment factors increase with
232 depth below the zone of oxygen depletion (from 1.6 to 3.1 at station 22, from 1.3 to 2.7 at station 23 and
233 from 1.4 to 2.1 at station 24), consistent with observations of U(VI) reduction occurring within the zone
234 of NO₃⁻ reduction in seafloor sediments (e.g. Morford et al., 2009, Piper and Calvert, 2009).

235 Non-detrital Cd concentrations of all measured sediments range from 0 to 3.21 $\mu\text{g g}^{-1}$. A notable
236 feature in all the sedimentary successions are sub-surface increases in non-detrital Cd concentrations. Cd
237 concentrations generally increase as nitrate concentrations decrease downcore at all stations.

238

239 **3.2.4 Enriched sedimentary Cd isotope compositions**

240 The enriched Cd isotope compositions of all measured sediments range from -0.07 to 0.89‰.
241 Compositions are generally lighter than in overlying seawater except at St. 24, where the uppermost few
242 cm of sediment have values higher than overlying seawater (Fig. 3). $\delta^{114}\text{Cd}$ compositions increase with
243 depth to values that are within uncertainty of the overlying seawater when nitrate concentrations
244 decrease to $\leq 2 \mu\text{M}$, coinciding with increases in Cd concentrations.

245

246 **4. Discussion**

247

248 **4.1 Mechanisms for Cd incorporation into near-surface sediments**

249 Sedimentary Cd may be bound in detrital silicate minerals, incorporated into organic matter,
250 adsorbed onto Fe-Mn oxyhydroxides, or precipitated as Cd sulfides (Rosenthal et al., 1995a, Rosenthal et
251 al. 1995b; Janssen et al., 2014; John and Conway, 2015; Dickson et al., 2019). Calculated Cd enrichment
252 factors average 5.1 and range between 2.7 and 8.1, indicating that ~64–88% the Cd accumulating on the
253 seafloor at stations 22, 23 and 24, and up to 97% at station 18, is non-detrital in origin.

254 Cadmium precipitation as CdS in the water column or at the sediment-water interface has been
255 demonstrated in oceanographic studies and in laboratory precipitation experiments (Janssen et al. 2014;
256 John and Conway 2015; Guinoiseau et al., 2019) but is not anticipated to occur at the water column O_2
257 levels observed in this study, which are always above $180 \mu\text{mol L}^{-1}$. We explored this assumption by
258 calculating the $[\text{Cd}]^*$ value at these sites. $[\text{Cadmium}]^*$ records the deviation of measured Cd from deep

259 water Cd/PO₄ ratio, where $[Cd]^* = [Cd]_{\text{measured}} - ([Cd]/[P]_{\text{deep water}} \cdot [P]_{\text{measured}})$ (Baars et al., 2014).
260 [Cadmium]* values for South Atlantic stations 12, 18 and 21 below 200 m are close to zero (0.02 to 0.12
261 nmol/kg), indicating no significant precipitation of CdS species at these three sites along the Uruguayan
262 margin, and thus no significant flux of CdS particulates from seawater onto the seafloor. However, a recent
263 study from Bourne et al. (2018) hypothesize that changes in Cd:P ratios can also reflect differences in
264 remineralization rates rather than CdS precipitation, and thus this tracer should be considered alongside
265 other oceanographic parameters to support formation of water column CdS species.

266 The role of organically-bound Cd as a pathway for Cd burial can be explored by predicting Cd
267 concentrations expected from measured sedimentary TOC values for Cd/C ratios of marine phytoplankton
268 (Ho et al., 2003). These ratios are at the low end of documented Cd/C stoichiometries (e.g. Twining and
269 Baines, 2013) and thus are minimum estimates for organic-bound Cd in our studied sediments. Predicted
270 organic-bound Cd concentrations are shown in Figure 4 and can account for the majority of the non-
271 detrital Cd in the near-surface sediments from the margin and basin sites.

272 Some near-surface sediments from the shallow shelf environment at Site 24, however, have
273 higher Cd concentrations than calculated for organic-bound Cd, suggesting an additional flux. This source
274 may be from sinking particulates with elevated Cd:P ratios (Bourne et al., 2018; Ohnemus et al., 2019) and
275 higher $\delta^{114}\text{Cd}$ compositions (Janssen et al., 2014) compared to the other study sites that are located below
276 the euphotic zone. Global profiles of particulate Cd:P ratios exhibit a shallow sub-surface maximum near
277 the transition from the euphotic to the aphotic zone (Bourne et al., 2018; Ohnemus et al., 2019).
278 Furthermore, the higher $\delta^{114}\text{Cd}$ composition of near-surface sediments at St 24 relative to the other sites
279 in this study are in agreement with sinking particulates from a similar water depth in previous publications
280 (Janssen et al., 2014; Conway and John, 2015b; Yang et al., 2018; Janssen et al., 2019).

281

282 **4.2 Organic matter as a sink for isotopically light Cd from the ocean**

283 Cadmium isotope values of the sediments accumulating in the oxic surface levels (0–0.5 cm) of stations
284 22 and 23 are isotopically lighter than overlying deep water values (~0.35‰). This difference is most
285 readily explained by the dominant contribution of isotopically light Cd associated with particulate organic
286 matter. Exported water column particulates have been observed to be isotopically lighter than deep
287 waters: particulate $\delta^{114}\text{Cd}$ compositions from the upper 1200 m of the Atlantic and Pacific water columns
288 span a wide range of -1.47 to 2.08‰, with the heaviest particulate $\delta^{114}\text{Cd}$ values in surface waters and the
289 lightest particulate $\delta^{114}\text{Cd}$ compositions at intermediate water depths (~200–600 m) (Yang et al., 2012;
290 Janssen et al., 2014; Conway and John, 2015b; Yang et al., 2018), reflecting the uptake in the surface
291 waters and subsequent remineralization of organically-bound Cd (Janssen et al., 2019).

292 A mechanistic understanding of the particulate $\delta^{114}\text{Cd}$ profile in the ocean remains elusive.
293 Recently, Janssen et al. (2019) hypothesized that sinking particulates may be composed of multiple pools
294 with different isotopic compositions and remineralization liabilities, where the sub-surface particulate Cd
295 pool is more refractory than the particulate Cd fraction in the surface waters and isotopically lighter than
296 the particulate Cd pools in surface and deep waters. It is this sub-surface, isotopically light particulate Cd
297 fraction that settles and likely represents the burial flux of particulate Cd on the margin sediments. These
298 sediments may therefore be the missing removal term to satisfy the global isotopic mass balance of
299 oceanic Cd (c.f. Janssen et al., 2019). We note that the surface sediments from St. 22 and St. 23 may
300 already contain some CdS, as porewaters have NO_3^- concentrations lower than overlying seawater (e.g.
301 compare to the porewaters in St. 18 in Table 2).

302

303 **4.3 Sub-oxic burial of Cd in South Atlantic sediments**

304 Cd concentrations and isotopic compositions ubiquitously increase within the nitrate reduction zones of
305 stations 18, 22, 23 and 24 (Fig. 3). We propose that these observations reflect the precipitation of
306 porewater Cd with trace H_2S to form CdS species (Gobeil et al., 1987; Pedersen et al., 1989; Rosenthal et

307 al., 1995a; Rosenthal et al., 1995b). Precipitation of CdS is the dominant process governing incorporation
308 of authigenic Cd in modern marine sediments with sub-oxic and sulfidic porewaters (Rosenthal et al.,
309 1995a; Rosenthal et al., 1995b). Recent experiments show that Cd isotope fractionation during
310 precipitation with H₂S will preferentially capture the lighter Cd isotopes relative to the bulk solution, with
311 more complete Cd precipitation leading to quantitative transfer of the Cd isotopic signature from solution
312 into the solid phase (Guinoiseau et al., 2018).

313 We are able to postulate the contribution of CdS to the non-detrital Cd fraction of sediments in
314 the nitrate-reducing zone of our studied sediments due to a key line of reasoning: sub-surface increases
315 in $\delta^{114}\text{Cd}$ correspond to increases in Cd concentrations. This correspondence implies that the sub-surface
316 change in $\delta^{114}\text{Cd}$ must be due to the gain of additional authigenic Cd with a composition higher than
317 organic-bound Cd, rather than the remineralisation and loss of an isotopically light non-detrital phase.
318 There are few isotopically heavy Cd phases that could accumulate to explain this observation: Mn and Fe
319 oxyhydroxides, which adsorb Cd with little isotopic fractionation (Horner et al., 2010) are unstable under
320 nitrate-reducing conditions, and organic matter has isotopic compositions lighter than seawater. The
321 importance of sub-surface CdS precipitation is also consistent with recent experimental evidence that
322 organically-bound Cd accounts for less than ~4% of authigenic Cd in deeply buried organic-rich shales
323 (Dickson et al., 2019). It is also supported by the observation that there is no non-detrital Cd contribution
324 to shallow sub-surface sediments (~1–9 cm depth) at station 18, despite total organic carbon accounting
325 for up to 0.8% of the bulk sediments.

326 Sub-surface $\delta^{114}\text{Cd}$ compositions can be modelled as a mixture between an organic-bound Cd
327 endmember (taken as the surface 'oxic' sample from 0–0.5 cm at station 23, ~0.08‰) and a seawater
328 composition of 0.35‰ for CdS, where 'surface' non-detrital Cd concentrations are assumed to be entirely
329 organic-derived, and additional sub-surface authigenic Cd is assumed to be entirely CdS (which
330 precipitates quantitatively). These calculations slightly underestimate the measured $\delta^{114}\text{Cd}$ but the values

331 are within uncertainty of measured compositions if ~20% of the organic matter Cd inventory is assumed
332 to be remineralised and replaced by the precipitation of seawater-derived pore fluids as CdS. This
333 calculation also allows an approximate estimate that a maximum of ~60% of the buried Cd can be organic
334 bound before modelled Cd compositions start to deviate outside of analytical uncertainty of the measured
335 non-detrital compositions.

336 Previous assessments of sub-surface CdS (and FeS) formation showed how low sub-surface
337 porewater concentrations would establish a diffusive gradient that draws overlying porewaters (and
338 dissolved metals) downwards (e.g. FeS, Framson and Leckle, 1978; Pedersen et al., 1989). In sediments
339 from the Uruguayan coast to the Argentine Basin, sub-surface Cd concentrations either remain constant
340 or increase downcore, suggesting that Cd in porewaters must be progressively transferred to the solid
341 phase. TOC (%) does not decrease significantly in the zones of Cd enrichment, further emphasizing that
342 the transfer of Cd from one solid phase to another cannot account for these sub-surface features and thus
343 that seawater must be diffusing into the sediments. The ~2 μM nitrite concentration front seems to
344 correspond closely with the first occurrence of high 'seawater' $\delta^{114}\text{Cd}$ values downcore, and thus may
345 mark the point at which sufficient aqueous H_2S is produced to stimulate CdS precipitation.

346 Overall, the non-detrital Cd and $\delta^{114}\text{Cd}$ composition of the sediments in this study can be
347 interpreted as an interplay between three processes:

- 348 i. Incorporation of isotopically light Cd into organic matter settling from the water column (John
349 and Conway, 2014; Yang et al., 2018; Janssen et al., 2018; Sieber et al., 2019), where the $\delta^{114}\text{Cd}$ value is
350 lighter than overlying seawater.
- 351 ii. Sinking particulates with a higher Cd:P ratio in coastal and shelf sediments (Bourne et al., 2018;
352 Ohnemus et al., 2017) and, although very minor in this study, adsorption of seawater Cd onto Mn-Fe
353 oxyhydroxides, where the $\delta^{114}\text{Cd}$ value is indistinguishable from overlying seawater (Horner et al., 2010).

354 iii. Precipitation of CdS at depth in the sediment from diffusing seawater, where the $\delta^{114}\text{Cd}$ value will
355 either be lighter than the overlying seawater with non-quantitative precipitation or, more likely, be
356 isotopically indistinguishable from overlying seawater with quantitative removal (Guinoiseau et al. 2018).
357 In the nitrate-reducing conditions studied here, oxyhydroxides will be unstable and thus the dominant
358 processes controlling the observed $\delta^{114}\text{Cd}$ values at these depths are probably the burial of organically-
359 bound Cd and precipitation of CdS.

360 These three processes are shown in Fig. 5, where we show mixing lines between lithogenic Cd (EF
361 value of 1; M_1 and -0.01‰ ; δ_1 , c.f. Schmitt et al., 2009) and either of the three predicted non-detrital Cd
362 fractions: organically-bound Cd from the surface oxic sediments (0-0.5 cm) at St 23 (Cd_{org} , $0.08 \pm 0.07\text{‰}$;
363 δ_2), particulates at station 24 forming from shallow-water at 49 m water depth (0.72‰ ; δ_2), or CdS forming
364 from deep-waters (0.35‰ ; δ_2) with a starting EF value of 1 (M_{OBSERVED}):

$$365 \delta_{\text{OBSERVED}} = \delta_2 + (\delta_1 - \delta_2) \cdot (M_1 / M_{\text{OBSERVED}}) \quad (4)$$

366 Figure 5 shows how our enriched sedimentary $\delta^{114}\text{Cd}$ dataset might be explained by the end-member
367 mixing of Cd sourced from the different fractions. This figure does not preclude mixing between the non-
368 detrital host phases, but serves as a meaningful starting point for investigating the controls on the isotopic
369 compositions of sediments accumulating in sub-oxic marine sediments such as these. Our model sets up
370 testable hypotheses that could be tackled in future with (e.g.) sequential extractions of authigenic
371 sediments fractions or paired sediment-porewater studies.

372

373 **4.4 Cadmium isotopic mass balance**

374 Sedimentary Cd isotopes may serve as a proxy for past nutrient cycling and ocean mixing (Georgiev et al.,
375 2015; Sweere et al., 2020). A critical first step to using this proxy effectively is to constrain the elemental
376 and isotopic mass balance of Cd in the modern ocean. A summary of the global source and sink fluxes of
377 oceanic Cd is presented in Table 3. The main inputs of Cd are from rivers ($4\text{--}15 \times 10^6$ mol Cd/yr) and dust

378 (2–11 x 10⁶ mol Cd/yr) (Shiller and Boyle, 1991; Rosenthal et al., 1995b; van Geen et al., 1995).
379 Hydrothermal vents are an important local source of Cd, but only influence the chemistry of very proximal
380 ocean waters. Cd is thus assumed to be removed quantitatively near the vent site (van Geen et al., 1995;
381 Schmitt et al., 2009). The dominant sinks of oceanic Cd are into sub-oxic and anoxic margin sediments,
382 with an estimated removal flux of 15–60 x 10⁶ mol Cd/yr (Rosenthal et al., 1995b; van Geen et al., 1995;
383 Little et al., 2015), a flux which probably includes the export of CdS species formed in the water column
384 (Table 3, Janssen et al., 2014; John and Conway, 2015; Guinoiseau et al., 2019).

385 Other minor output fluxes are pelagic clays, carbonates and Fe-Mn nodules and crusts, although
386 they are unlikely to significantly influence the oceanic budget of Cd. The contribution of Cd burial in pelagic
387 clays is estimated using the Cd concentration from Heinrichs et al., 1980 (100–350 ng g⁻¹) and a burial rate
388 of 0.23 g cm²/kyr (Hay et al., 1988), producing an estimated output flux of 0.6–2.1 x 10⁶ mol Cd/yr. The Cd
389 isotopic composition of this output flux into oxic surface sediments is within uncertainty of the $\delta^{114}\text{Cd}$
390 composition of the UCC, as observed at St 18 where samples with no enriched Cd component have an
391 average composition of $-0.03 \pm 0.07\text{‰}$. The contribution of Cd associated with Fe-Mn deposits to the
392 oceanic Cd budget is negligible (Schmitt et al., 2009; Horner et al., 2010), and this process does not in any
393 case greatly fractionate Cd (Schmitt et al., 2009; Horner et al., 2010). Cadmium burial within carbonates
394 is estimated to be 0.4–1.8 x 10⁶ mol Cd/yr (Horner et al., 2011) with an unknown isotopic composition for
395 natural samples.

396 The Cd isotope compositions of mostly organically-bound Cd in surface sediments in St 23 is
397 $\sim 0.08\text{‰}$. We postulate that an additional flux of dissolved Cd into the sediments becomes important
398 below the nitrate reduction front as CdS species start to precipitate. This additional flux drives that
399 enriched Cd inventory of the sediments to higher isotopic compositions that are within uncertainty of the
400 modern deep ocean Cd composition. This process would be expected to drive a downward diffusive flux
401 of seawater-derived Cd into sub-surface sediments to enrichment zones near redox boundaries. An

402 additional inferred, albeit minor, source of porewater Cd to form CdS species could be from the oxidation
403 of organic matter during shallow diagenesis.

404 Cadmium burial within sub-oxic and anoxic margin sediments satisfies the global oceanic mass
405 balance of Cd, within the uncertainties that exist on all fluxes (Table 3). The measured isotopic output flux
406 of enriched $\delta^{114}\text{Cd}$ ranges from -0.07 to 0.44‰, using the elemental and isotopic ranges for Cd from sub-
407 oxic margin sediments.

408

409 **5. Conclusions**

410 We present the first direct measurements of the isotopic compositions of Cd in modern marine sub-oxic
411 sediments. The composition of surface sediments (~0–0.5 cm), where organic matter is likely to be the
412 primary host for non-detrital Cd, is isotopically lighter than overlying seawater. Within the zone of nitrate
413 reduction, the formation of CdS leads to increased Cd concentrations that overprints the organic Cd
414 signature to a composition close to that of the overlying bottom water. Our study confirms that the burial
415 of isotopically light organic Cd is required to satisfy the global isotopic mass balance of Cd and suggests
416 that sub-oxic sediments, having experienced CdS precipitation, may preserve an archive of past seawater
417 compositions.

418

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428

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588

589 **Figure 1;** Sampling locations for seawater depth profiles (circles) and near-surface sediment cores
590 superimposed onto water mass oxygen concentrations (Schlitzer et al., 2018). The black shapes indicate

591 the location of the sediment cores: square (St 24), diamond (St 23), triangle (St 22) and hexagon (St 18).
592 The approximate location of key water masses is noted on the figure: Antarctic Intermediate Water
593 (AAIW), Upper Circumpolar Water (UCDW), North Atlantic Deep Water (NADW), Antarctic Bottom Water
594 (AABW). Figure produced using Ocean Data View (Schlitzer, 2015).

595

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

602

603 **Figure 3;** Down-core profiles of sedimentary enriched cadmium concentration and isotopic composition,
604 along with porewater profiles of Fe and NO_3^- , and sedimentary Mn concentrations and total organic
605 carbon (TOC) from a transect of shallow multi-cores obtained from the coast (diamonds), continental shelf
606 (circles), continental slope (squares), and abyssal plain of the Argentine Basin (triangles). The colors
607 indicate the redox conditions of the porewaters: blue marks oxic and yellow indicates sub-oxic conditions.
608 The vertical dotted, black line, alongside the measured Cd concentration values, denotes the 'predicted'
609 Cd concentration contributing from organic material and detrital sources: $Cd_{\text{predicted}} = TOC_{\text{measured}} / (Cd/C_{Ho}$
610 et al., 2003). The vertical dashed black line at $\delta^{114/110}Cd = 0.35\text{‰}$ represents the average SW Atlantic deep
611 ocean water value.

612

613 **Figure 4;** Enriched cadmium concentration versus TOC of all sediment samples in this study. The straight
614 line represents the average Cd/C ratio in cultured marine eukaryotic phytoplankton species and the grey
615 shaded area is the range in Cd/C ratio of all measured organisms from Ho et al. (2003).

616

617 **Figure 5;** Evidence for redox control on Cd burial in South Atlantic near-surface sediments. Cadmium
618 enrichment compared to Cd isotopic compositions of near-surface sediments are plotted with the color
619 and shape indicating the redox conditions of the porewaters: oxic (blue circles) and sub-oxic (yellow
620 diamonds). The isotopic composition of detrital Cd (UCC) is marked with a black star. The dash lines denote
621 theoretical mixing relationships between detrital Cd and either $\delta^{114}\text{Cd}$ value of organically-bound Cd from
622 the surface oxic sediments (0-0.5 cm) at St 23, shallow-water Cd from the SW Atlantic at 49 m water depth,
623 or deep-water Cd.