

Copper isotope signatures in modern marine sediments

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Abstract

The development of metal stable isotopes as tools in paleoceanography requires a thorough understanding of their modern marine cycling. To date, no Cu isotope data has been published for modern sediments deposited under low oxygen conditions. We present data encompassing a broad spectrum of hydrographic and redox regimes, including continental margin and euxinic (sulphide-containing) settings. Taken together with previously published data from oxic settings, these data indicate that the modern oceanic sink for Cu has a surprisingly homogeneous isotopic composition of about +0.3‰ ($\delta^{65}\text{Cu}$, relative to NIST SRM 976). We suggest that this signature reflects one of two specific water-column processes: (1) an equilibrium isotope fractionation between soluble, isotopically heavy, Cu complexed to strong organic ligands and an isotopically light pool sorbed to particles that deliver Cu to the sediment, or (2) an equilibrium isotope fractionation between the same isotopically heavy ligand-bound pool and the particle reactive free Cu^{2+} species, with the latter being scavenged by particulates and thereby delivered to the sediment. An output flux of about +0.3‰ into sediments is isotopically light relative to the known inputs to the ocean (at around +0.6‰) and the seawater value of +0.6 to +0.9‰, suggesting the presence of an as yet unidentified isotopically light source of Cu to the oceans. We hypothesize that this source may be hydrothermal, or may result from the partial dissolution of continentally derived particles.

1 **1. Introduction**

2
3 Copper (Cu) is biologically essential, but the free Cu²⁺ form is also toxic, even at
4 extremely low concentrations (e.g., Moffett and Brand, 1996). Aqueous Cu speciation is,
5 however, almost universally dictated by complexation to strong organic ligands (e.g.,
6 Elderfield, 1981; Coale and Bruland, 1988; Gordon et al., 1996; Skrabal et al., 1997; 2000;
7 Wells et al., 1998; Muller et al., 2001; Laglera and van den Berg, 2003; Shank et al.,
8 2004a; 2004b; Bruland and Lohan, 2003; Moffett and Dupont, 2007). In addition to its
9 biological function, Cu is particle reactive, and its speciation and solubility are sensitive to
10 changes in redox conditions. Understanding the balance of these competing processes in
11 controlling the oceanic distribution of Cu and its isotopes has been the subject of a large
12 number of studies (e.g., Boyle et al., 1977; Bruland, 1980; Saager et al., 1992; Bermin et
13 al., 2006; Vance et al., 2008; Thompson et al., 2014; Takano et al., 2014; Little et al.,
14 2014a,b).

15
16 Isotopes provide insight into the mechanisms of metal cycling, with specific isotope
17 signatures attributable to particular processes (e.g., Welch et al., 2003; Barling and Anbar,
18 2004; Severmann et al., 2008; Wasylenki et al., 2011; Peacock and Moon, 2012; Xue et al.,
19 2013; Little et al., 2014b; Vance et al., 2016a). Isotopic measurements are also a useful
20 way to place constraints on oceanic mass balance (e.g., Zhu and Macdougall, 1998;
21 Schmitt et al., 2003; Tipper et al., 2006; 2010; Nielsen et al., 2006; Archer and Vance,
22 2008; Conway and John, 2014; Little et al., 2014a). Based on an analysis of the known
23 inputs and outputs of Cu and its isotopes to the modern ocean, Little et al. (2014a)
24 highlighted an imbalance in the oceanic budget of Cu. Assuming that the cycle is in steady
25 state, these authors suggested the presence of an as yet unidentified isotopically heavy Cu
26 sink (Little et al., 2014a).

27
28 No Cu isotope data exist to date for reducing sedimentary settings, making them a prime
29 candidate for the missing Cu sink. Reducing depositional environments include locations
30 where the water column is euxinic (sulphide-containing), such as the Black Sea and
31 Cariaco Basin, and those in which dissolved oxygen concentrations are negligible but
32 sulphide is either absent or restricted to pore-waters. The latter are typical of oxygen
33 minimum zones (OMZs) along productive continental margins. Copper is insoluble under

34 reducing conditions. Consequently, water column removal of Cu is nearly quantitative
35 below the redoxcline of the euxinic Black Sea and Cariaco Basin (Jacobs et al., 1987;
36 Haraldsson and Westerlund, 1988; Tankéré et al., 2001), and variable Cu enrichments have
37 previously been observed in reducing sediments (e.g., Francois, 1988; Calvert and
38 Perderson, 1993; Algeo and Maynard, 2004; Brumsack, 2006; Little et al., 2015). An iron-
39 rich (ferruginous) pore water profile from the oxygen-poor Santa Monica basin
40 (California) shows evidence of Cu diffusion into sediments and no detectable Cu in pore
41 waters within a few centimetres of the sediment-water interface, suggesting diagenetic
42 removal of Cu into sedimentary sulphide phases (Shaw et al., 1990). Generally, however,
43 there is a lack of similar pore water studies from sediment underlying anoxic ocean waters.
44

45 Reduction of Cu(II) to Cu(I) is likely to be associated with a light isotope fractionation into
46 the reduced phase (e.g., Zhu et al., 2002; Ehrlich et al., 2004; Fujii et al., 2013, Sherman,
47 2013), i.e., fractionation in the opposite direction to that required for an isotopically heavy
48 Cu sink. However, quantitative removal from the water column implies that the authigenic
49 Cu isotope values of sediments deposited under euxinic conditions should reflect the Cu
50 isotope composition of the dissolved pool of the oceans, as observed previously for similar
51 metal isotope systems (e.g., Mo, Zn, Cr; Barling et al., 2001; Nägler et al., 2011; Reinhard
52 et al., 2014; Vance et al., 2016a). The dissolved Cu pool in seawater is, indeed, isotopically
53 heavy, at +0.6 to +0.9‰ (Vance et al., 2008; Thompson et al., 2014; Takano et al., 2014).
54

55 Euxinic sites play a relatively minor role as a global sink for trace metals in the modern
56 ocean, however, due to the restricted areal extent of such conditions (e.g., Emerson and
57 Huested, 1991; Morford and Emerson, 1999; Poulson Brucker et al., 2009; Little et al.,
58 2015). Today, upwelling margins with prominent OMZs are likely a much more important
59 sink for trace metals (e.g., Morford and Emerson, 1999; Böning et al., 2004; 2009;
60 McManus et al., 2006; Poulson Brucker et al., 2009; Little et al., 2015; 2016), and
61 forecasts suggest their expansion in a warming world (Stramma et al., 2008; Keeling et al.,
62 2010). To date, only one estimate has been made of the role of upwelling margin sediments
63 in the oceanic mass balance of Cu (Little et al., 2015), and the isotope composition of the
64 flux of Cu into margin sediments is unknown. In this study, we present Cu isotope data for
65 a wide range of reducing environments, including the euxinic Black Sea and Cariaco
66 Basin, and multiple continental margin sites. This dataset provides considerably improved
67 constraints on the reducing sedimentary sink for Cu.

68

69 **2. Study sites**

70

71 *2.1 The Black Sea*

72 Open ocean euxinia is thought to have been more prevalent at times during Earth's history,
73 particularly along productive margins (Canfield, 1998; Li et al., 2010a; Lyons et al., 2014).
74 Today, however, euxinia is largely restricted to marginal basins, with the Black Sea as the
75 world's largest permanently euxinic basin. The Black Sea is thus frequently cited as an
76 analogue of the Precambrian oceans and for periods of widespread anoxia during the
77 Phanerozoic. Euxinia below ~100 m water depth in the Black Sea is the result of a positive
78 water balance, moderate primary production, and restricted circulation, with limited inflow
79 and outflow to the Mediterranean Sea via the narrow (0.76 – 3.6 km wide) and shallow
80 (<110 m deep) Bosphorus Strait. Total sulphide concentrations increase to 380 μM at 2200
81 m water depth and are associated with near quantitative removal of Cu from the dissolved
82 phase (Haraldsson and Westerlund, 1991; Tankéré et al., 2001). The samples analysed in
83 this study have been described previously (Lyons, 1991; Little et al., 2015). Two deep sites
84 underlie the euxinic water column (stations 9 and 14; Fig. 1), while two others are from the
85 shallow shelf and underlie oxic water (stations 16 and 16B; Fig. 1). Station 16B was
86 recovered from a depth close to the modern day chemocline. A broad array of
87 sedimentological observations (Lyons, 1991) and complementary geochemical analyses
88 has been made on these sediments. These include C-S-Fe systematics (Lyons and Berner,
89 1992; Lyons et al., 1993), S-isotope trends (Lyons, 1997), Fe speciation and isotope
90 patterns (Lyons and Severmann, 2006; Severmann et al., 2008), Mo abundance and isotope
91 compositions (Arnold et al., 2004; Algeo and Lyons, 2006), trace metal concentrations
92 (Little et al., 2015) and Zn and Ni isotope analyses (Vance et al., 2016a). We present bulk
93 sediment Cu isotope data for a total of 31 samples from the four locations, all of which are
94 confined to the upper ~25 cm of the sediment pile at each locality (Fig. 1; see also Little et
95 al., 2015).

96

97 *2.2 The Cariaco Basin*

98 The Cariaco Basin is the world's second largest anoxic basin (Fig. 1, Table 1). It is located
99 on the northern continental shelf off Venezuela and contrasts with the Black Sea in that it
100 has a less restricted hydrographic setting, higher productivity, and higher sedimentation
101 rate. The Cariaco Basin has been euxinic since the last deglaciation (Haug et al., 1998;

102 Dean et al., 1999; Peterson et al., 2000), but euxinia in the water column is less extreme
103 than that in the Black Sea, with peak total sulphide concentrations of ~65 μM (Li et al.,
104 2010b; 2011). Again, Cu removal from the water column is observed due to the presence
105 of sulphide (Jacobs et al., 1987). The 22 drill core samples (20 cm to 8 m depth) included
106 in this study from ODP Site 1002 span the oxic-euxinic transition at 14.5 ka and the
107 associated redox-related geochemical changes in the core have previously been studied in
108 detail (Lyons et al., 2003; Werne et al., 2003; Lyons and Severmann, 2006; Reinhard et al.,
109 2014; Little et al., 2015).

110

111 *2.3 Continental Margin sites*

112 *2.3.1 California Borderland basins*

113 The Southern California Bight is a region of elevated primary production, primarily due to
114 coastal upwelling (e.g., Eppley, 1992; Macías et al., 2012). The resultant carbon flux to
115 depth, in combination with related ocean circulation patterns, generates oxygen-deficient
116 waters at depths of 200 m to 1000 m along the margin. The Southern California Borderland
117 basins exhibit even lower oxygen contents than equivalent depths along the open margin
118 because the silled topography restricts mixing of basin waters with surrounding seawater
119 (e.g. Emery, 1954; Berelson, 1991). The samples used in this study come from four of the
120 Borderland basins: Santa Barbara, Santa Monica, San Nicolas, and Tanner Basin (Fig. 1).
121 These settings have been characterised geochemically, and samples for this study were
122 taken from expeditions described previously (e.g., McManus et al., 1997; McManus et al.,
123 1998; McManus et al., 2006; Poulson-Brucker et al., 2009; Little et al., 2016).

124

125 The Santa Barbara and Santa Monica basins are near shore and have sill depths within the
126 region's OMZ. The Santa Barbara basin is the most reducing of the four Borderland basins
127 included for study, though the core studied was sampled just below the sill (sill: 475 m,
128 core site: 493 m; Poulson-Brucker et al., 2009). Dissolved sulphide is present to varying
129 degrees within the shallow sediment package and has been observed at low (<15 nM)
130 levels in the water column (e.g., Kuwabara et al., 1999; Zheng et al., 2000). These
131 observations, coupled with the fact that the shallow pore fluids (upper 3–8 cm, with
132 sulphide appearing below) are ferruginous (e.g., Kuwabara et al., 1999; Zheng et al.,
133 2000), imply that iron reduction and sulphate reduction are dominant electron transfer
134 pathways within the shallow sediment package. The mass accumulation rate in Santa

135 Barbara is the highest of all the sites studied (Table 1), which is largely the result of high
136 fluxes of lithogenic material (Thunell et al., 1995).

137

138 The Santa Monica sill is at 740 m, the basin floor is at 910 m, and the sediment core was
139 collected at 905 m. Bottom-water oxygen concentrations vary within the basin but are
140 generally 2 - 10 μM (Berelson, 1991; Stott et al., 2000; Berelson et al., 2005; McManus et
141 al., 2006). Like Santa Barbara basin, shallow pore fluids in Santa Monica are ferruginous
142 (e.g., Shaw et al., 1990; McManus et al., 1997; 1998). Although Shaw et al. (1990) report a
143 thin (~ 1 cm) layer of extractable Fe at the sediment-water boundary, transfer of dissolved
144 Fe occurs across this boundary (McManus et al., 1997; Elrod et al., 1991; Severmann et al.,
145 2010). To our knowledge there are no reports of shallow sediment-column or bottom-water
146 accumulation of dissolved sulphide; net sulphate reduction is nevertheless an important
147 pathway for electron transport, as manifest in iron sulphide minerals that form within the
148 sediments (Berelson et al., 1996).

149

150 The offshore basins, San Nicolas and Tanner, have sill depths at 1100 m and 1160 m,
151 respectively, below the depth of the most intense oxygen deficiency. Tanner Basin is
152 further offshore than San Nicolas (Emery, 1960). Maximum water depths in the San
153 Nicolas basin are 1832 m (core collected at 1750 m), with bottom-water oxygen contents
154 of ~ 30 μM (Shaw et al., 1990). Pore fluids from the upper 10 cm are rich in dissolved Mn,
155 with strong increases in Mn appearing just below the sediment-water interface (Shaw et al.,
156 1990). Dissolved Fe concentrations increase below ~ 2 cm, with much lower Fe
157 concentrations in the upper sediment package compared to those in the basins nearer to
158 shore (Shaw et al., 1990). The Tanner Basin reaches a maximum depth of 1550 m, and the
159 core was collected at 1514 m. Bottom water oxygen contents are ~ 30 μM . Sediments in
160 this basin also exhibit pore fluid Fe and Mn enrichments, but the concentrations of both are
161 lower than those in San Nicolas Basin sediments (c.f., Shaw et al., 1990; McManus et al.,
162 1997; 1998). Despite differences in dissolved metal concentrations, these two basins are
163 quite similar diagenetically, with Tanner having an estimated sediment depth of oxygen
164 penetration that is slightly shallower than in San Nicolas (e.g., 0.4 vs. 0.5 cm, Berelson et
165 al., 1996) and slightly higher total organic carbon contents (~ 6 wt% vs. ~ 4.5 wt%; Little et
166 al., 2016).

167

168

169 *2.3.2 Mexican Margin*

170 Oxygen deficiency is more pronounced along the Mexican margin compared to the
171 California margin, with oxygen concentrations of $< 1 \mu\text{M}$ at our study sites (Chong et al.,
172 2012). This OMZ extends more than 1500 km off the coast of Mexico (Sansone et al.,
173 2004), and anaerobic diagenetic processes dominate in sediments where the OMZ
174 intercepts the seafloor (Berelson et al., 2005). Of the three sites included in this study, two
175 are from the open ocean margin off Baja California (Magdalena and the Soledad Basin),
176 and the other is from the Pescadero Slope, which is at the eastern edge of the mouth of the
177 Gulf of California (Chong et al., 2012) (Fig. 1).

178

179 The Magdalena site is situated on the western margin of Baja California at 692 m water
180 depth. The upper 1 - 2 cm of the sediment core is bioturbated, and organic carbon contents
181 are particularly high ($\sim 11\%$). Dissolved sulphide appears in pore waters at 3 cm depth (2
182 μM) and increases rapidly at depths greater than 20 cm (Chong et al., 2012). The Soledad
183 Basin is also on the western side of Baja California and has an effective sill depth of ~ 250
184 m (Silverberg et al., 2004). The core studied here was collected at 544 m water depth, close
185 to the deepest point of the basin (545 m). Sediments at this site are laminated (including
186 extensive traceable coccolith laminae; van Geen et al., 2003), with sulphide ($\sim 10 \mu\text{M}$) in
187 pore waters close to the sediment-water interface and increasing below 8 cm (to $> 40 \mu\text{M}$)
188 (Chong et al., 2012). Because of the high sulphide concentrations, dissolved iron is titrated
189 from the pore fluids at relatively shallow depths (Chong et al., 2012). Clastic input on the
190 open ocean side of Baja California is low, but sediment accumulation rates are high,
191 particularly in the Soledad Basin, due to elevated productivity (Sansone et al., 2004; Table
192 1). Clastic input is high along the Pescadero slope, due to the location of this coring site on
193 the eastern edge of the mouth of the Gulf of California, where it receives continental
194 drainage from the Sierra Madre Occidental Mountains (e.g., Berelson et al., 2005; Chong
195 et al., 2012). The laminated sediment core discussed in this study was taken at 616 m, close
196 to the centre of the OMZ (at ~ 600 m). High concentrations of dissolved Fe have been
197 reported from the pore waters of this site, rising from near zero to $260 \mu\text{M}$ within the first 2
198 cm (Chong et al., 2012), compared to peaks of $\sim 10 \mu\text{M}$ at 3 cm for the Magdalena site and
199 a $\sim 65 \mu\text{M}$ peak in the upper 1 cm of the Soledad sediment core. Chong et al. (2012)
200 classified the Pescadero site as Fe-rich, Magdalena as Fe-rich/sulphidic, and Soledad Basin
201 as sulphidic.

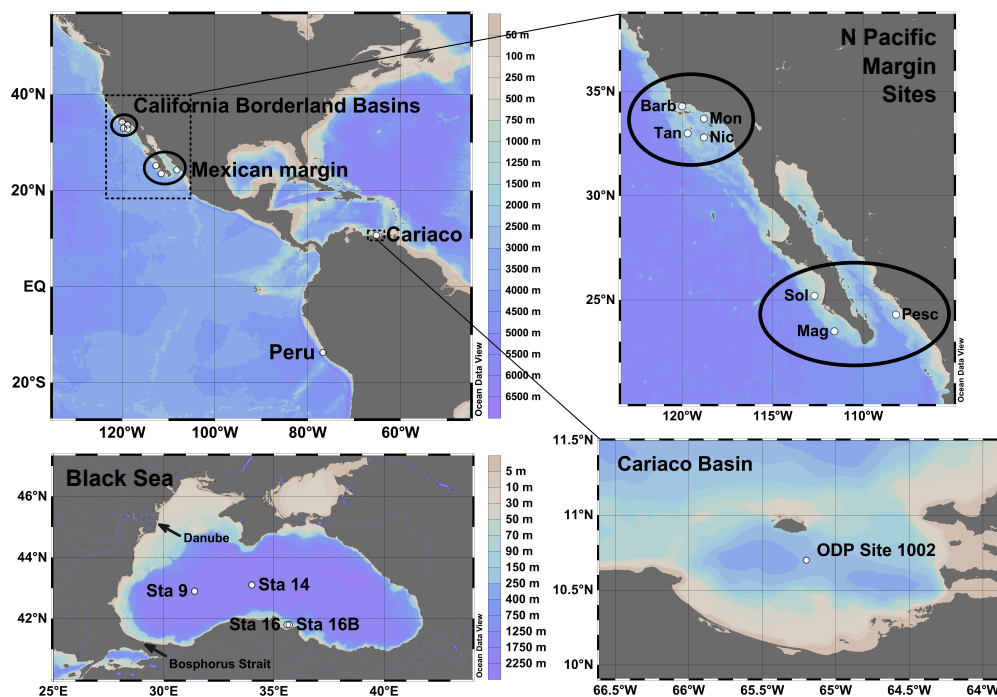
202

203 2.3.3 Peru Margin

204 The Peru margin is an open ocean margin setting with high upwelling-driven productivity
205 and an associated intense OMZ at depths of ~100 to 700 m (Emeis et al., 1991; Lückge and
206 Reinhardt. 2000). The core used in our study (Fig. 1, see also McManus et al., 2006; Little
207 et al., 2015; 2016) was collected at 264 m, with bottom-water oxygen concentrations of
208 <10 μM . Bulk sediments contain ~15% organic carbon and >1% total sulphur (McManus
209 et al., 2006; Little et al., 2016). This combination of high organic carbon and low oxygen
210 results in intense anerobic diagenesis, with prior work demonstrating the potential for
211 reduced iron fluxes across the sediment water interface (Noffke et al., 2012; Scholz et al.,
212 2014). Episodic efflux of sulphide has also been reported further south along the Peruvian
213 margin (Schunck et al., 2013).

214

215 **Figure 1.** Locations of sites included for study. The Peru margin site (site MC82; Table 1;
216 McManus et al., 2006) is from the core of the Peruvian OMZ. The California Borderland
217 Basins (N Pacific Margin Sites inset) comprise: Barb – Santa Barbara Basin, Mon – Santa
218 Monica Basin, Nic – San Nicolas Basin and Tan – Tanner Basin. The Mexican margin
219 sites (N Pacific Margin Sites inset) comprise: Sol – Soledad Basin, Mag – Magdalena
220 margin and Pesc – Pescadero Slope. The Cariaco Basin samples are from spliced cores A
221 and B at Site 1002 of Leg 165 of the Ocean Drilling Program (see inset). Samples from
222 four Black Sea stations were analysed: two underly the deep euxinic water column
223 (Stations 9 and 14) and two are from the shallow oxic shelf region (Stations 16 and 16B).
224 Maps were made using Ocean Data View software (odv.awi.de; Schlitzer, 2015).



225
226

227

228 3. Methods

229

230 3.1 Elemental concentrations and Cu isotope data

231 All work was carried out under trace metal clean conditions, with MilliQ water (18.2Ω)
232 and Savillex PFA labware. Acids and reagents used were either ultrapure (HF, H₂O₂) or
233 double distilled (HNO₃, HCl). Sample digestion and analytical methods have been
234 described previously (Little et al., 2014a; 2015). In brief, dilute nitric acid was added
235 dropwise to 50-500 mg of powdered sediment until effervescence ceased (signalling
236 complete dissolution of carbonate). The sediment was then digested in a 3:1 mix of
237 concentrated HF and concentrated HNO₃ for 48 hours. Digestion was followed by triple
238 treatment with concentrated HNO₃ to remove fluoride salts before dissolution in 7M HCl.
239 An aliquot of these solutions was analysed for multi-element concentrations on a
240 ThermoFinnigan Element 2 at the University of Bristol or a ThermoFinnigan Element XR
241 at ETH Zürich.

242

243 After elemental analysis, an aliquot of the total digest solution was taken for Cu isotope
244 purification using a two-stage anion exchange procedure (Bio-Rad AG MP-1M resin)
245 modified from Maréchal et al. (1999) and detailed previously (Archer and Vance, 2004;
246 Vance et al., 2008; Little et al., 2014a). Final Cu concentrations for analysis were ~100
247 ppb, dissolved in ~1 ml 2% HNO₃. Isotopic analyses were carried out on a
248 ThermoFinnigan Neptune MC-ICP-MS at the University of Bristol or a Neptune Plus at
249 ETH Zürich, in low-resolution mode with introduction via a CPI PFA nebuliser (50
250 µl/min) or a Savillex C-Flow PFA nebuliser (50 µl/min) attached to a glass spray chamber.
251 Copper isotope ratios for samples were calculated using a standard bracketing approach by
252 comparison to pure untreated NIST SRM 976 and are reported relative to this standard in
253 delta-notation:

254

$$\delta^{65}\text{Cu} = 1000 \left[\frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{SRM976}}} - 1 \right]$$

255

256 The long-term reproducibility of a secondary pure Cu standard was $\delta^{65}\text{Cu} = +0.11 \pm$
257 0.11‰ (n = 102) and $+0.11 \pm 0.06\text{‰}$ (n = 112) at Bristol and ETH Zürich respectively,
258 compared to $+0.10 \pm 0.06\text{‰}$ measured at the Hebrew University (Asael et al., 2007). The

259 USGS reference materials BHVO-2, BIR-1A, BCR-2, and Nod P1 were analysed to assess
260 accuracy. All uncertainties are given as 2 SD, unless stated otherwise.

261

262 **4. Results**

263

264 Accuracy and reproducibility of measured Cu and Al concentrations for two secondary
265 standards – the commercially available SLRS-5 river standard from the National Research
266 Council Canada and USGS Green River Shale SGR-1 – are reported in Table 2. Note that
267 all Cu/Al ratios are given by mass, in ppm Cu/wt % Al (i.e., $\times 10^{-4}$). Copper isotope data for
268 USGS reference materials are reported in Table 3. Values for BHVO-2, BIR-1A and BCR-
269 2 fall within the ranges recommended in Moynier et al. (2017). Values obtained for Nod-
270 P1 are consistent with that reported by Bigalke et al. (2010), and with the published mean
271 for global Fe-Mn crusts and nodules $+0.31 \pm 0.12\text{‰}$ (1SD, n=31; Data sources: Albarède,
272 2004; Little et al., 2014a).

273

274 *4.1 Cu/Al ratios and Cu isotope data*

275 Down-core Cu/Al and $\delta^{65}\text{Cu}_{\text{bulk}}$ data are presented graphically in Figures 2 – 5 and
276 tabulated in full in the electronic supplementary material (ESM Table 1) and summarised
277 in Table 4 (site-by-site averages). Where available, plotted isotope data are compared to
278 mean values for proximal oxic sediments (Black Sea: oxic Station 16, Cariaco Basin: oxic
279 section of core). In other locations, comparisons are made to the published average
280 lithogenic Cu isotope composition ($\delta^{65}\text{Cu}_{\text{lith}} = +0.08 \pm 0.17\text{‰}$, 1 SD, n = 334; Moynier et
281 al., 2017).

282

283 Aluminium is assumed to be immobile during diagenesis and is used as a tracer of the
284 lithogenic component of the sediment. To accurately define the non-lithogenic sedimentary
285 Cu component, measured Cu/Al ratios should ideally be compared to the Cu/Al ratio of
286 local lithogenic background material (e.g., Böning et al., 2012; Little et al., 2015). In this
287 study, the local background is taken as the minimum measured Cu/Al ratio from proximal
288 oxic sediments where available (Black Sea, Cariaco Basin), following Böning et al. (2012).
289 In the absence of an estimate for the local lithogenic background sedimentation in the
290 California Borderland Basins, we compare Cu/Al ratios in Figure 4 with the most recent
291 upper continental crust (UCC) estimate of 3.5×10^{-4} (Rudnick and Gao, 2003). The
292 lithogenic background for sediments deposited close to Peru has previously been

293 approximated to that of a Peruvian andesite (Böning et al., 2004; Scholz et al., 2011; Little
294 et al., 2015). A Cu/Al ratio of 4.5×10^{-4} can be calculated for average andesite from the
295 Central Volcanic Zone of Peru (values derived from the GEOROC database of the Max-
296 Planck Institute for Chemistry, Mainz, Germany; Sarbas and Nohl, 2009). A similar value
297 of 4.0×10^{-4} can be calculated for a compilation of Trans Mexican Volcanic Belt samples
298 (also derived from the GEOROC database). It is to this range of values ($4.0 - 4.5 \times 10^{-4}$)
299 that samples from the Mexican and Peru margins are compared in Figure 5.

300

301 Elevated Cu/Al ratios compared to the (local) lithogenic background (Figures 2 – 5) are
302 indicative of the presence of authigenic (chemically precipitated or scavenged) and/or
303 biogenic (cellular and/or skeletal) Cu, which together are termed the ‘bioauthigenic’
304 fraction (after Little et al., 2016). Note that the biogenic (or uptake-derived) component of
305 Cu in the sediment is predicted to be small (<20%; Little et al., 2015), but that scavenging
306 of Cu by particulate organic carbon is likely an important route by which Cu is delivered to
307 the sediment.

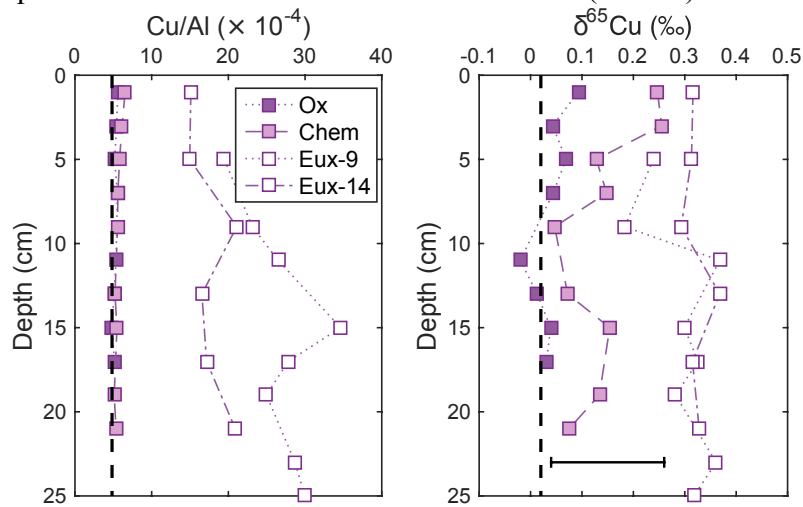
308

309 *4.1.1 Black Sea*

310 Cu/Al and $\delta^{65}\text{Cu}$ data for the four Black Sea sites are presented in Figure 2. Sediments
311 from oxic Station 16 are assumed to represent the local lithogenic background
312 sedimentation (mean Cu/Al = $5.3 \pm 0.5 \times 10^{-4}$, minimum Cu/Al = 4.8×10^{-4}). In support of
313 this assumption, these sediments have a lithogenic Cu isotope composition with an average
314 $\delta^{65}\text{Cu}$ of $+0.04 \pm 0.07\text{‰}$. Chemocline Station 16B shows Cu/Al ratios (mean Cu/Al = $5.7 \pm$
315 0.9×10^{-4}) very close to those of oxic Station 16, suggesting no significant bioauthigenic
316 enrichment, except for the two surface-most samples (Cu/Al = 6.5 and 6.1×10^{-4} at 0 – 2
317 cm and 2 – 4 cm respectively). However, despite dominantly lithogenic Cu/Al ratios,
318 samples from Station 16B exhibit heavier and more variable $\delta^{65}\text{Cu}$, with an average of
319 $+0.14 \pm 0.15\text{‰}$. The two upper-most samples (both at $+0.25\text{‰}$) again exhibit the greatest
320 deviation from lithogenic values. The two euxinic stations 9 and 14 are indistinguishable
321 and isotopically heavy compared to lithogenic Cu (Station 9: $+0.30 \pm 0.12\text{‰}$, Station 14:
322 $+0.32 \pm 0.05\text{‰}$), despite slightly more elevated Cu/Al ratios at Station 9 compared to
323 Station 14 (mean Cu/Al at Station 9 = $26.9 \pm 9.2 \times 10^{-4}$ compared to $17.6 \pm 5.5 \times 10^{-4}$ for
324 Station 14). The mean $\delta^{65}\text{Cu}$ for all Black Sea euxinic samples is $+0.31 \pm 0.10\text{‰}$.

325

326 **Figure 2.** Down-core Cu/Al and bulk $\delta^{65}\text{Cu}$ data for the four Black Sea sites. Ox – Station
 327 16, Chem – Station 16B, Eux-9 – Station 9, Eux-14 – Station 14. The local lithogenic
 328 background, which is taken as the minimum Cu/Al and mean $\delta^{65}\text{Cu}$ at oxic Station 16, is
 329 given as a dashed black line. The error bar represents 2 SD external reproducibility on Cu
 330 isotope measurements from Bristol MC-ICP-MS (0.11‰).



331

332

333 4.1.2 Cariaco Basin

334 Cu/Al and $\delta^{65}\text{Cu}$ data for the Cariaco Basin drill-core samples are presented in Figure 3.

335 The lowermost four samples represent deposition under oxic conditions linked to the sea-
 336 level low stand of the last glacial period (Lyons et al., 2003). These four oxic samples have

337 a lithogenic $\delta^{65}\text{Cu}$ of $+0.08 \pm 0.06\text{‰}$ and an average Cu/Al ratio of $5.2 \pm 1.0 \times 10^{-4}$, which
 338 is elevated compared to average UCC (at $3.1 - 3.5 \times 10^{-4}$). The euxinic (interglacial)

339 sediments have a lower average Cu/Al ratio ($4.5 \pm 0.8 \times 10^{-4}$) and significantly heavier Cu
 340 isotope values compared to those deposited under oxic conditions, with a mean $\delta^{65}\text{Cu} =$

341 $+0.20 \pm 0.06\text{‰}$. If the four oxic samples are assumed to represent the local lithogenic

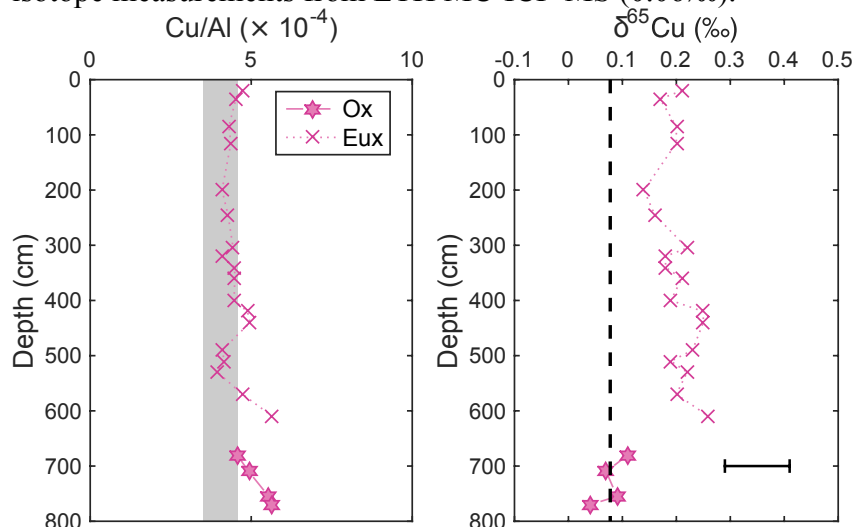
342 input, euxinic sediments in the Cariaco Basin show no bioauthigenic enrichment in Cu

343 over the lithogenic background value (Fig. 3).

344

345

346 **Figure 3.** Down-core Cu/Al and bulk $\delta^{65}\text{Cu}$ data for the Cariaco Basin core. Lowermost
 347 four samples (filled stars, ‘Ox’) were deposited during the last glacial period, under oxic
 348 conditions. The remainder of the sediment core was deposited during the present
 349 interglacial, when the water column was euxinic (crosses, ‘Eux’). The grey bar represents a
 350 range of possible lithogenic Cu/Al ratios (including UCC and the local oxic minimum from
 351 the glacial period samples). The dashed line represents global mean lithogenic $\delta^{65}\text{Cu}$
 352 (Moynier et al., 2017). The error bar represents 2 SD external reproducibility on Cu
 353 isotope measurements from ETH MC-ICP-MS (0.06‰).



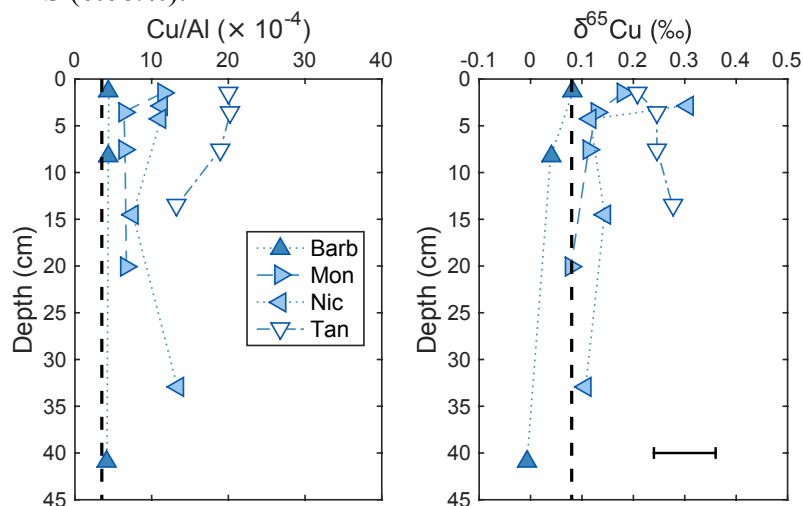
354
 355

356 4.1.3 California Borderland Basins

357 The most reducing of the four California Borderland sites, Santa Barbara, exhibits little or
 358 no bioauthigenic enrichment of Cu (mean Cu/Al = $4.5 \pm 0.8 \times 10^{-4}$) with $\delta^{65}\text{Cu}$ values
 359 ($\delta^{65}\text{Cu} = +0.04 \pm 0.09\text{‰}$) that are unfractionated from lithogenic values. Santa Monica
 360 Basin, which has ferruginous porewaters, exhibits higher Cu/Al ratios and slightly
 361 isotopically heavy Cu, particularly the surface-most sample (Cu/Al at 1.5 cm = 11.4×10^{-4}
 362 cf. mean Cu/Al at depths >1.5 cm = $6.5 \pm 0.3 \times 10^{-4}$; $\delta^{65}\text{Cu}$ at 1.5 cm = $+0.18\text{‰}$ cf. mean
 363 $\delta^{65}\text{Cu}$ >1.5 cm = $+0.11 \pm 0.05\text{‰}$; Fig. 4). Note that an anthropogenic source of metals has
 364 been identified at this site, and this may contribute to the enrichment observed in the
 365 surface 1 – 2 cm (Finney and Huh, 1989; Bruland et al., 1994). San Nicolas, where
 366 porewaters can be defined as manganoous, also has a surface-most sample that is
 367 isotopically heavier than the remainder of the sediment core (at $+0.31\text{‰}$ versus $+0.12 \pm$
 368 0.04‰ ; Fig. 4). Copper throughout this core is significantly enriched (mean Cu/Al = $10.9 \pm$
 369 4.8×10^{-4}) relative to UCC. The most Cu enriched of the California Borderland Basin sites
 370 is Tanner Basin. Mean Cu/Al ratios at this site are $18.1 \pm 6.5 \times 10^{-4}$ and Cu is isotopically
 371 heavy compared to lithogenic Cu at $+0.24 \pm 0.06\text{‰}$.

372

373 **Figure 4.** Down-core Cu/Al and bulk $\delta^{65}\text{Cu}$ data for the California Borderland basins. Barb
 374 – Santa Barbara basin, Mon – Santa Monica basin, Nic – San Nicolas basin, Tan – Tanner
 375 basin. Estimates of the lithogenic background (UCC Cu/Al: Rudnick and Gao, 2003;
 376 global mean lithogenic $\delta^{65}\text{Cu}$; Moynier et al., 2017) are given as a dashed black line. Error
 377 bar represents 2 SD external reproducibility on Cu isotope measurements from ETH MC-
 378 ICP-MS (0.06‰).



379
 380

381 4.1.4 Mexican and Peru Margins

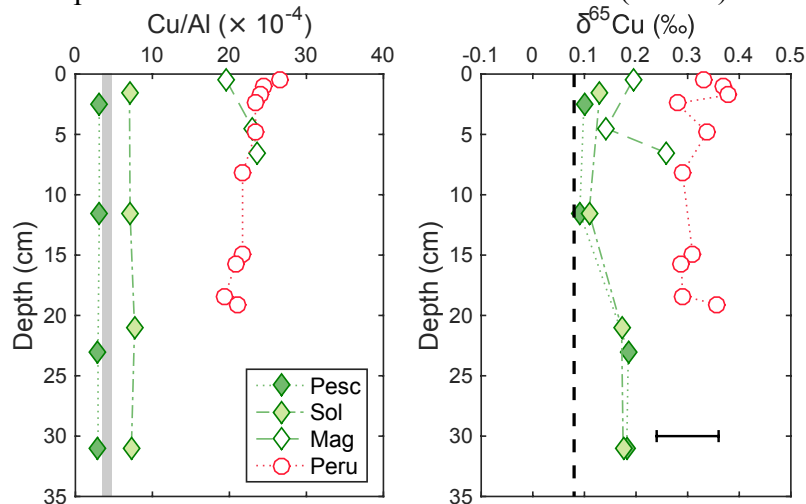
382 The Peru margin exhibits the highest absolute Cu concentrations of any of the sites
 383 analysed here (up to 75 ppm). Enrichment is greatest close to the sediment surface and
 384 declines with depth (Fig. 5; mean $\text{Cu}/\text{Al} = 22.6 \pm 4.2 \times 10^{-4}$). Copper isotope values at this
 385 site are homogeneous with depth and isotopically heavy compared to the lithogenic
 386 baseline ($\delta^{65}\text{Cu} = +0.32 \pm 0.07\text{‰}$; Fig. 5).

387

388 The Magdalena and Peru margin sites are similar in their Cu geochemistry. The Magdalena
 389 margin also exhibits high Cu/Al ratios ($22.1 \pm 4.4 \times 10^{-4}$) and isotopically heavy $\delta^{65}\text{Cu}$
 390 ($+0.20 \pm 0.12\text{‰}$). By contrast, the sites of Soledad Basin ($\text{Cu}/\text{Al} = 7.3 \pm 0.6 \times 10^{-4}$) and
 391 Pescadero Slope ($\text{Cu}/\text{Al} = 3.0 \pm 0.2 \times 10^{-4}$) are only moderately elevated or not enriched (or
 392 even slightly depleted), respectively. These two sites are isotopically indistinguishable and
 393 exhibit slightly heavier Cu isotope values compared to typical lithogenic signatures
 394 (Soledad: $+0.15 \pm 0.06\text{‰}$; Pescadero: $+0.14 \pm 0.10\text{‰}$).

395
 396

397 **Figure 5.** Down-core Cu/Al and bulk $\delta^{65}\text{Cu}$ data for the Mexican and Peru margin sites.
 398 Pesc – Pescadero slope, Sol – Soledad basin, Mag – Magdalena margin, Peru – Peru
 399 margin. Grey bar gives range of Peruvian andesite-Mexican volcanic zone Cu/Al ratios,
 400 see text in section 4.1 for details. Dashed black line represents global mean lithogenic
 401 $\delta^{65}\text{Cu}$ (Moynier et al., 2017). Error bar represents 2 SD external reproducibility on Cu
 402 isotope measurements from ETH MC-ICP-MS (0.06‰).



403
404

405 5. Discussion

406

407 5.1 Covariation of $\delta^{65}\text{Cu}$ and Al/Cu in marine sediments

408

409 As a whole, the dataset presented here shows limited variability in $\delta^{65}\text{Cu}$ values, from –
 410 0.02‰ to +0.37‰. For comparison, the measured range in $\delta^{65}\text{Cu}$ found for typical Earth
 411 surface materials spans approximately –1.5‰ to +2‰ (e.g., Moynier et al., 2017), though
 412 this range is extended considerably with the inclusion of Cu-bearing ore minerals (–16.5‰
 413 to +10.0‰; Mathur et al., 2009).

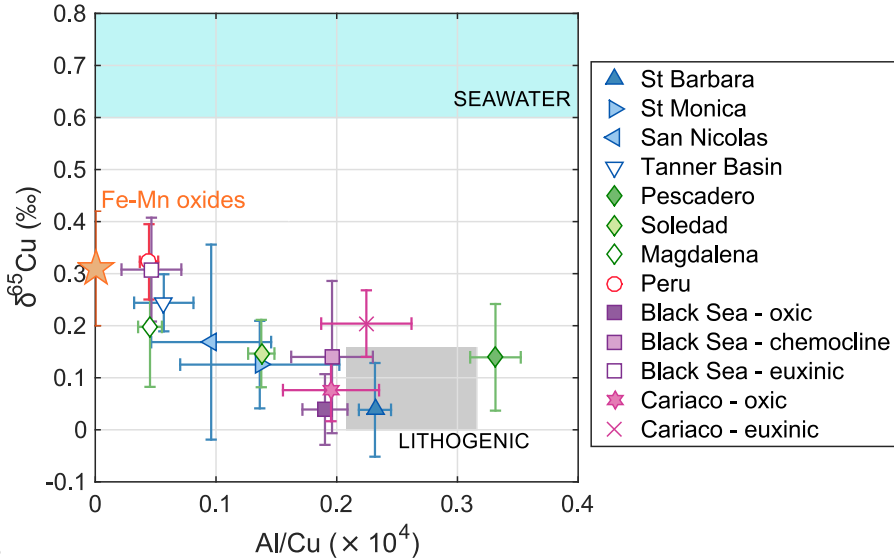
414

415 All samples from this study are isotopically lighter than data for the dissolved phase in
 416 seawater (at +0.6 to +0.9‰, Fig. 6; Vance et al., 2008; Thompson et al., 2014; Takano et
 417 al., 2014). A negative correlation (Fig. 6; $R^2_{\text{all data}} = 0.40$, $p < 0.001$) is observed between
 418 $\delta^{65}\text{Cu}$ values and Al/Cu ratios. This relationship can be explained, to a first order, by
 419 mixing of two distinct end-member sources of Cu. The first is a lithogenic source, with a
 420 high Al/Cu ratio and a lithogenic Cu isotope composition of ~0 to +0.1‰ (grey box, Fig.
 421 6). The second mixing component can be termed the bioauthigenic Cu end member. It has
 422 a low Al/Cu ratio and an isotope composition of about +0.3‰. While the presence of a
 423 lithogenic end member is intuitive, the fact that just one other component can explain a

424 significant fraction of the variability in the remainder of the dataset is unexpected and
 425 merits further discussion.

426

427 **Figure 6.** Covariation of $\delta^{65}\text{Cu}$ with Al/Cu in marine sediments. Each site is represented
 428 by its mean $\delta^{65}\text{Cu}$ and Al/Cu values ± 2 SD error bars. Symbols for each site are the same
 429 as in Figures 2 – 5. The range of estimated bulk seawater isotopic compositions (+0.6 to
 430 +0.9‰) is shown as a shaded blue bar. The range and mean of lithogenic Al/Cu values and
 431 $\delta^{65}\text{Cu}$ ratios are shown as a grey box. For comparison, the mean and 1 SD of the surface
 432 layers of global Fe-Mn oxide sediments is shown as an orange star.



433

434 The isotope composition of the bioauthigenic Cu component of the sediment can be
 435 calculated for individual samples by mass balance, assuming a Cu/Al ratio and $\delta^{65}\text{Cu}$ value
 436 of the lithogenic background material ($\text{Cu}/\text{Al}_{\text{lith}}$ and $\delta^{65}\text{Cu}_{\text{lith}}$). First, the lithogenic fraction
 437 (X_{lith}) of the total Cu is calculated:

438

$$439 \quad X_{\text{lith}} = \frac{\frac{\text{Cu}}{\text{Al}_{\text{lith}}} \times \text{Al}_{\text{sample}}}{\text{Cu}_{\text{sample}}},$$

440

441 where $\text{Al}_{\text{sample}}$ and $\text{Cu}_{\text{sample}}$ are the measured bulk Al and Cu concentrations of the sample.

442 The bioauthigenic $\delta^{65}\text{Cu}_{\text{auth}}$ value can then be calculated:

443

$$444 \quad \delta^{65}\text{Cu}_{\text{auth}} = \frac{(\delta^{65}\text{Cu}_{\text{bulk}} - \delta^{65}\text{Cu}_{\text{lith}} \cdot X_{\text{lith}})}{X_{\text{auth}}},$$

445

446 where $\delta^{65}\text{Cu}_{\text{bulk}}$ is the measured $\delta^{65}\text{Cu}$ ratio of the sample, and X_{auth} is the fraction of
 447 bioauthigenic Cu (i.e., $X_{\text{auth}} = 1 - X_{\text{lith}}$). This calculation is straightforward but gives
 448 unreasonable values when the lithogenic fraction is very large (>90%). This situation

449 applies to the Cariaco Basin, the Santa Barbara Basin, and the Pescadero Slope sites, which
450 all show little or no bioauthigenic enrichment. Excluding these three sites, and assuming
451 lithogenic $\text{Cu}/\text{Al}_{\text{lith}}$ and $\delta^{65}\text{Cu}_{\text{lith}}$ values for the remaining sites as detailed in section 4.1, the
452 calculated bioauthigenic end member has a Cu isotope composition of $+0.31 \pm 0.11\%$ (1
453 SD, $n = 43$; see ESM Table 1 for sample-by-sample calculated $\delta^{65}\text{Cu}_{\text{auth}}$ values). Exclusion
454 of the Black Sea data yields a margin-only $\delta^{65}\text{Cu}_{\text{auth}}$ of $+0.28 \pm 0.11\%$ (1 SD, $n = 29$).
455 Note that using a single $\text{Cu}/\text{Al}_{\text{lith}}$ value for all sites and varying this ratio between 3.0 and
456 4.5×10^{-4} alters the calculated $\delta^{65}\text{Cu}_{\text{auth}}$ by less than $\pm 0.02\%$. The calculation is somewhat
457 more sensitive to the assumed $\delta^{65}\text{Cu}_{\text{lith}}$ value. Taking the published mean $\delta^{65}\text{Cu}_{\text{lith}} \pm 1$ SD
458 (where $\delta^{65}\text{Cu}_{\text{lith}} = 0.08 \pm 0.17\%$; Moynier et al., 2017) – i.e. using a range for $\delta^{65}\text{Cu}_{\text{lith}}$ of –
459 0.09 to $+0.25\%$ – gives a range in the calculated mean $\delta^{65}\text{Cu}_{\text{auth}}$ of $+0.39$ to $+0.23\%$.

460

461 The calculated bioauthigenic end member isotope composition of about $+0.3\%$ closely
462 corresponds to observed values for the surface layers of Fe-Mn crusts and nodules (orange
463 star in Fig. 6; mean $\delta^{65}\text{Cu}_{\text{Fe-Mn oxides}} = +0.31 \pm 0.12\%$, 1SD, $n = 31$, data sources: Albarède,
464 2004; Little et al., 2014a). Fe-Mn crusts have previously been used as an analogue for the
465 dispersed Fe-Mn oxide phases found throughout deep-sea pelagic sediments that are
466 thought to be responsible for Cu removal from the ocean under normal ‘oxic’ marine
467 conditions (Little et al., 2014a). Somewhat surprisingly, therefore, the data presented here
468 suggest that Cu is removed from the ocean with a homogeneous isotopic composition (of
469 about $+0.3\%$) in all oceanic settings. Particularly surprising is the observation that, despite
470 near quantitative removal of Cu from the sulphidic water columns of the Black Sea and
471 Cariaco Basin (Jacobs et al., 1987; Haraldsson and Westerlund, 1991; Tankéré et al.,
472 2001), bioauthigenic Cu isotope values from these two basins do not appear to record the
473 $\delta^{65}\text{Cu}$ of global mean seawater (at $+0.6$ to $+0.9\%$; Vance et al., 2008; Thompson et al.,
474 2014; Takano et al., 2014). We return to this observation in section 5.3.

475

476 *5.2 Bioauthigenic Cu in sediments: the isotopic counterpart to strong organic ligand-* 477 *bound Cu in the dissolved pool?*

478

479 The vast majority of dissolved copper in all aqueous environments, from rivers and their
480 estuaries (e.g., Dryden et al., 2004; Laglera and Van den Berg, 2003) to the open ocean
481 (e.g., Coale and Bruland, 1988, 1990; Moffett et al., 1990; Lucia et al., 1994; Leal and Van
482 den Berg, 1998; Moffett and Dupont, 2007; Jacquot and Moffett, 2015), is complexed to

483 strong organic ‘L1-type’ ligands, which have binding constants (log K) in the range of
484 about 12–16. Both *ab initio* calculations (Sherman, 2013) and experiments (Bigalke et al.,
485 2010; Ryan et al., 2014) indicate that strong organic ligands preferentially complex the
486 heavy Cu isotope. Isotopically heavy Cu in the dissolved pool of rivers and the ocean has
487 thus previously been hypothesised to result from preferential complexation of heavy Cu
488 isotopes by these strong organic ligands (Vance et al., 2008; Thompson et al., 2014; Little
489 et al., 2014b). Specifically, Vance et al. (2008) proposed that an equilibrium fractionation
490 occurs directly between an organically complexed dissolved pool and the surface of
491 scavenging particles (Vance et al., 2008). This scenario could also be invoked to explain
492 the homogenous composition of the bioauthigenic Cu output flux observed here. The
493 homogeneous composition of the oceanic Cu sink would, in this case, require open system
494 steady-state fractionation with a fractionation factor ($\Delta = \delta^{65}\text{Cu}_{\text{seawater}} - \delta^{65}\text{Cu}_{\text{sinks}}$) of
495 $\sim 0.4\text{‰}$ between the aqueous and particulate phase.

496

497 Another plausible explanation for the homogeneous isotopic composition of the
498 bioauthigenic Cu output flux, regardless of *sedimentary* redox state, is that an equilibrium
499 isotopic fractionation exists between two species in the oxygenated *aqueous* phase. First,
500 the organically complexed pool is highly soluble and enriched in heavy isotopes due to the
501 strong binding environment provided by the strong organic ligands. Second, a particle
502 reactive free Cu^{2+} pool, which is $\sim 0.4\text{‰}$ lighter than the organic ligand-bound pool, is
503 scavenged to particulates. Consistent with this scenario, Ryan et al. (2014) measured an
504 isotopic fractionation factor $\Delta_{\text{ligand-free}} = 0.44 \pm 0.40 \text{‰}$ ($n = 3$, 2SD) for a synthetic ligand
505 (NTA) with a similar log K to natural L1-type ligands ($\log K_{\text{NTA}} = 14.4$). In this case,
506 where fractionation occurs between two Cu species in the aqueous phase, the nature of the
507 particulate material to which Cu is scavenged is not relevant to the isotopic fractionation
508 expressed. In the alternative scenario, where an equilibrium fractionation exists between
509 the aqueous and particulate pools, there would need to be a near constant fractionation
510 factor between aqueous Cu and all potential scavenging surfaces.

511

512 In either scenario, we hypothesise that scavenging by particulate organic matter plays a key
513 role in the water column. If this scavenging is a reversible process (e.g., Little et al., 2013),
514 and exchange continues with the dissolved pool as particles sink, then bottom water
515 isotope compositions will determine the isotope composition of particles when they reach
516 the sediment. In turn, this process may contribute to the homogeneity of the output flux,

517 because deep waters exhibit less isotopic variability than the upper water column (Vance et
518 al., 2008; Takano et al., 2014, Thompson et al., 2014). Scavenging associated with Fe-Mn
519 cycling either in the water column or within the sediment is also likely to be important,
520 dependent on the setting. For example, active Fe-Mn oxide cycling close to the sediment-
521 water interface (e.g., San Nicolas, Santa Monica; Fig. 4) appears to enhance fixation of Cu
522 with the bioauthigenic $\delta^{65}\text{Cu}$ signature. Detailed spectroscopic and experimental work at
523 the mineral-organic-water interface increasingly supports the suggestion that organic and
524 oxide-bound phases are often inextricably linked (Lalonde et al., 2012; Johnson et al.,
525 2015; Tribovillard et al., 2015). In the case of an equilibrium isotope fractionation between
526 the dissolved phase and scavenging particles, this organic-oxide linkage may also
527 contribute to the isotopic homogeneity of the sedimentary sink.

528

529 *5.3 Cu in euxinic settings*

530

531 *5.3.1 The Cariaco Basin*

532 Near quantitative removal of Cu is observed from the euxinic water columns of both the
533 Black Sea and Cariaco Basin (Haraldsson and Westerlund, 1991; Tankéré et al., 2001;
534 Jacobs et al., 1987). Despite this removal from the water column, we do not observe
535 significantly elevated Cu/Al in Cariaco Basin sediments (Fig. 3). There is, however, a shift
536 in $\delta^{65}\text{Cu}$ ratios across the oxic-anoxic transition of the sediment core, from about +0.08 in
537 the oxic interval to +0.20‰ in the euxinic interval (Fig. 3). Given the absence of
538 appreciable Cu enrichment, one possible explanation of this isotopic shift is a change in the
539 isotope composition of the local lithogenic background material. A change in the source of
540 lithogenic material to the Cariaco Basin on glacial-interglacial timescales has previously
541 been proposed based on Al/Ti ratios. This change is hypothesised to reflect an increased
542 supply of Ti-rich dust from the Sahara during glacial periods, due to the more southerly
543 position of the ITCZ (Yarincik et al., 2000; Martinez et al., 2010). Alternatively, the data
544 and their uncertainties do permit the presence of a small amount of bioauthigenic Cu in the
545 euxinic interval. For example, assuming an UCC Cu/Al ratio of 3.5×10^{-4} (Note: this ratio
546 is lower than that observed in the oxic interval), and $\delta^{65}\text{Cu}_{\text{lith}}$ of +0.08‰, the mean
547 calculated $\delta^{65}\text{Cu}_{\text{auth}}$ for the euxinic portion of the sediment pile is $+0.66 \pm 0.25\%$, similar
548 to that of modern open ocean seawater $\delta^{65}\text{Cu}$ (at approximately +0.7‰). There is an
549 indication, therefore, that bioauthigenic Cu deposited in sediments under Cariaco Basin-
550 type hydrographic conditions, where euxinia is primarily driven by productivity without

551 strong basin restriction, may indeed record open ocean $\delta^{65}\text{Cu}$. However, due to the very
552 low Cu enrichment observed (see also section 5.4), the local lithogenic background must
553 be carefully characterised and corresponding calculated $\delta^{65}\text{Cu}_{\text{auth}}$ values should be
554 interpreted with caution.

555

556 *5.3.2 The Black Sea*

557 Copper is enriched by a factor of 3 to 7 in sediments from the Black Sea euxinic stations
558 compared to those from the oxic stations (Fig. 2), such that the assumed composition of the
559 local lithogenic background has very little impact on calculated $\delta^{65}\text{Cu}_{\text{auth}}$ values (unlike in
560 the Cariaco Basin). The Black Sea Cu isotope data therefore present us with a puzzle:
561 given near quantitative removal from the water column, why are the $\delta^{65}\text{Cu}$ values of
562 euxinic Black Sea sediments not more similar to the isotopic composition of mean global
563 seawater (at approximately +0.7‰)? Instead we find that the Black Sea bioauthigenic Cu
564 has an isotope composition that is similar to the remainder of the reducing sedimentary
565 dataset presented here (i.e., at around +0.3‰).

566

567 One possibility is that the Cu isotope composition of the upper water column of the
568 Mediterranean, which supplies the Black Sea through the shallow Bosphorus Strait between
569 13 and 110 m water depth, is isotopically lighter than that of mean global seawater.
570 Although Cu isotope data for seawater remains relatively sparse, the data that exist show
571 limited variability in deep waters (at +0.6 to 0.9‰: Vance et al., 2008; Takano et al., 2014;
572 Thompson et al., 2014), but frequent small deviations towards lighter $\delta^{65}\text{Cu}$ values in the
573 upper water column (down to +0.4 to 0.5‰: Takano et al., 2014). These relatively light
574 surface values are most easily explained as the result of the deposition of aerosol dust, and
575 the Mediterranean does receive a high mineral dust flux from the Sahara (Prospero, 1996).
576 However, assuming modern inflow through the Bosphorus Strait of $305 \text{ km}^3 \text{ yr}^{-1}$ (Özsoy
577 and Ünlüata, 1997), and a surface water Cu concentration in the Mediterranean of 2.5
578 nM (Saager et al., 1993), the magnitude of the Mediterranean Cu source is about $7 \times 10^7 \text{ g}$
579 yr^{-1} . The mean calculated authigenic Cu content of euxinic Black Sea sediments is ~35
580 ppm (ESM Table 1, range: 28 – 48 ppm). Given this value, and assuming a sediment
581 density of 2.3 g cm^{-3} , porosity of 80%, anoxic basin area of $318,582 \text{ km}^2$ and a
582 sedimentation rate of $0.0155 \text{ cm yr}^{-1}$, we calculate a Cu output flux to Black Sea euxinic
583 sediments of $8 \times 10^8 \text{ g yr}^{-1}$. This estimate is an order of magnitude higher than the
584 estimated Mediterranean input flux. This imbalance is exacerbated by the fact that there is

585 also a return flux to the Mediterranean from the surface Black Sea, representing a further
586 substantial output of Cu from the basin. Hence, input of Cu from the Mediterranean alone
587 can explain neither the enrichment nor the isotope signature of Cu observed in Black Sea
588 sediments.

589

590 Rivers are the other likely key input of Cu to the Black Sea. The previously measured
591 range of $\delta^{65}\text{Cu}$ in a subset of relatively pristine global rivers is +0.02 to +1.45‰, with a
592 discharge-weighted average of +0.68‰ (Vance et al., 2008). A measurement of Black Sea
593 surface water of +0.92‰ (Table 5; for sample collection and pre-concentration techniques,
594 see Vance et al., 2016a) is within this riverine range and the range of published open ocean
595 values. Though the isotope composition of the Black Sea surface ocean may be
596 anthropogenically perturbed (e.g., Vance et al., 2016a), it seems unlikely – though we
597 cannot definitively rule it out – that the relatively light isotopic composition of Black Sea
598 sediments is a direct result of supply of isotopically light Cu from rivers.

599

600 A plausible explanation for the coherent isotopic composition of Black Sea sediments
601 versus those from other marine settings is that the source of Cu to the restricted deep basin
602 has, in fact, been subject to biogeochemical cycling similar to that envisaged in section 5.2.
603 In this view, rivers supply isotopically heavy Cu to the oxic Black Sea surface layer. The
604 transfer of this Cu to the deep euxinic portion of the basin is then mediated by the cycling
605 of Fe and Mn and is associated with an isotopic fractionation between the aqueous and
606 particulate phase similar to that which is proposed for the open ocean. Copper is
607 complexed by organic ligands in Black Sea surface waters (Muller et al., 2001), and
608 significant cycling of trace metals across the redoxcline has been hypothesised associated
609 with the cycling of nanoparticulate Fe and Mn oxides at this depth (e.g., Lyons and
610 Severmann, 2006; Little et al., 2015; Vance et al., 2016a). Specifically, nanoparticulate Fe
611 and Mn oxides may form following their efflux from shelf sediments. These
612 nanoparticulate phases can then be transported to the basin interior, where they are re-
613 reduced and dissolve: this is a version of the *benthic redox shuttle* (Severmann et al., 2008;
614 Scholz et al., 2013; 2014). These Fe-Mn nanoparticles sorb other trace metals, forming a
615 fine particle layer at the redoxcline that is rich in Cu, Ni, Zn, and other metals (Tankéré et
616 al., 2001). The scavenged Cu, which need not be shelf-sediment sourced (as invoked for Fe
617 and Mn), is then released to the euxinic portion of the basin on reduction of the host Fe-Mn
618 nanoparticles. Once there, sulphide minerals quantitatively re-scavenge the supplied Cu. In

619 this view, the ‘shuttled’ Cu would have an isotope composition of the bioauthigenic end
620 member at +0.3‰, i.e., approximately +0.6‰ lighter than organically complexed,
621 isotopically heavy, residual Cu in modern Black Sea surface waters.

622

623 Some support for this hypothesis comes from chemocline site 16B. Here, the upper two
624 data points (upper 4 cm of core) are slightly enriched in Cu and are distinctly isotopically
625 heavy at +0.25‰ – similar to the bioauthigenic end member – compared to lithogenic-like
626 $\delta^{65}\text{Cu}$ values observed deeper in the core (Fig. 2). The sediments at Station 16B were
627 deposited close to the position of the redoxcline at the time of coring, with dissolved
628 oxygen at trace levels (Lyons, 1991). Enrichments in AVS (acid volatile sulphur) were
629 evident in the black-grey, banded upper 2-4 cm of the core, compared to the increasingly
630 bioturbated grey layers below. These observations have been interpreted to reflect an
631 evolution from a more to a less oxygenated environment at this site (Lyons, 1991), i.e., a
632 shoaling of the redoxcline, an assertion that is supported by the $\delta^{65}\text{Cu}$ data presented here.

633

634 *5.4 The lithogenic dilution effect on Cu enrichment in marine sediments*

635

636 Cu/Al data from the Cariaco Basin highlight that anoxia, and even euxinia, is not by itself
637 sufficient to produce strong authigenic Cu enrichments in sediments. Other data presented
638 here also illustrate this point clearly: the most reducing sedimentary environment of the
639 California Borderland basins is the Santa Barbara basin, which shows no authigenic Cu
640 enrichment and a lithogenic isotope composition. In Figure 7 we highlight one key reason
641 for this, the control on Cu enrichment by sediment accumulation rate.

642

643 To isolate the role of lithogenic dilution of Cu contents in marine sediments, Al
644 accumulation rates (S_{Al}) were calculated using estimates of sediment accumulation rates
645 from the literature, summarised in Table 1, and measured Al concentrations from this
646 study. Significant Cu enrichment is observed only at sites with an S_{Al} of considerably less
647 than $0.1 \text{ mg cm}^{-2} \text{ yr}^{-1}$ (Fig. 7). Plotting the $S_{\text{Al}} - \text{Al/Cu}$ relationship in this way allows a
648 quantitative assessment of the lithogenic dilution effect on Cu enrichment, via a box model
649 approach outlined by Jacobs et al. (1985; 1987). Full details of the box model are given in
650 the ESM. In brief, it is assumed that the flux of Cu (or any metal) to the sediment is
651 comprised of two components, the relative magnitude of which will determine metal
652 enrichment in the sediment: (1) a detrital (or lithogenic) flux defined by the Cu/Al ratio of

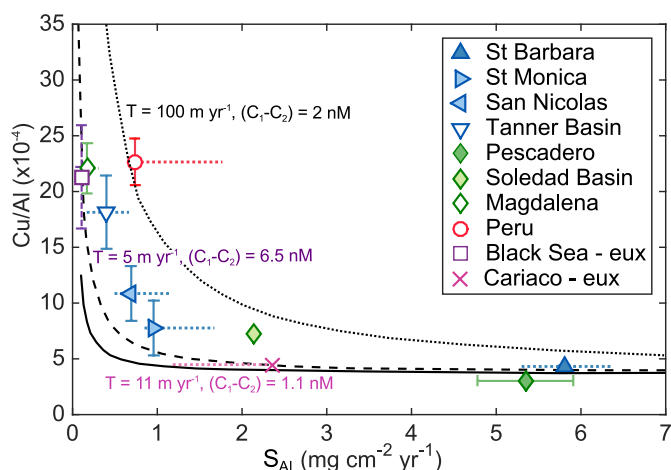
653 upper continental crust $(\text{Cu}/\text{Al})_{\text{lith}}$ and the accumulation rate of Al (S_{Al}) and (2) a
654 bioauthigenic flux derived from removal of dissolved Cu from the water column. We
655 assume that the latter may reflect either sulphidisation or uptake/scavenging by particulate
656 organic carbon and/or Fe-Mn oxides. The model is made up of an oxic surface ocean box
657 (Box 1) and an anoxic deep water box (Box 2), each of which are well mixed and exchange
658 on a timescale, T , in m yr^{-1} (ESM Fig. 1). The authigenic enrichment of a metal, S_{enrich} ,
659 then depends on three parameters: (1) S_{Al} ; (2) the concentration difference between oxic
660 box 1 and anoxic box 2, C_1-C_2 ; and (3) the timescale of mixing, T . We apply this model to
661 the Cariaco Basin (directly following Jacobs et al., 1987) and to the Black Sea. Parameters
662 used are given in Table 6. Note that T is related to the residence time of water in the deep
663 box, τ_2 , by the thickness of this box, z_2 : $T = z_2\tau_2^{-1}$. This mixing timescale is somewhat
664 slower in the Black Sea ($\sim 5 \text{ m yr}^{-1}$) than in the Cariaco Basin ($\sim 11 \text{ m yr}^{-1}$), due to the
665 longer residence time of Black Sea deep waters (Table 6). In addition, the parameter C_1-C_2
666 in the Black Sea (6.5 nM; Tankéré et al., 2001) is quadruple that of the Cariaco Basin (1.1
667 nM, Jacobs et al., 1987), due to the relatively low Cu concentration of the South Atlantic
668 source waters that flow into the Cariaco Basin. The results of the model are plotted as
669 dashed (Black Sea model parameters) and solid (Cariaco Basin model parameters) black
670 lines in Figure 7 for the full range of S_{Al} values observed for sites in this study. Agreement
671 between the model and site-averaged Cu/Al values is observed for the two euxinic sites.

672

673 This simple 2-box model is not directly applicable to open margin sites, like the Peru and
674 Magdalena margin regions, and we have insufficient data to perform a detailed analysis for
675 the other basinal sites included here. We can, however, find parameters that give
676 reasonable results, even for the exceptional Peru margin site (dotted black line, Fig. 7). For
677 this model we assume a removal term of Cu into particulate organic matter of 2 nM, over a
678 depth range of 100 m, and with a very short water residence time (1 year). This result
679 should be considered illustrative only, nevertheless, the model gives clear mechanistic
680 insight into lithogenic dilution of the bioauthigenic flux of Cu.

681

682 **Figure 7.** Al accumulation rate (S_{Al}) versus site average Cu/Al. Black lines show
 683 superimposed box model results (solid – Cariaco Basin; dashed – Black Sea; dotted – Peru
 684 margin; see Table 6 for selected model parameters and ESM for additional model details).
 685 All symbols are the same as in Figs 2 – 5. Coloured dotted ranges in S_{Al} reflect published
 686 range in sediment accumulation rates for nearby sites compiled from the literature (see
 687 Table 1). Error bars on Cu/Al ratios and S_{Al} (where sediment accumulation rates for the
 688 same sediment core have been published) reflect 2 SD variability for the core.
 689



690
 691
 692

693 5.5 Implications for Cu oceanic mass balance: a missing isotopically light Cu source

694

695 One of the motivations for this study was to place constraints on the modern reducing
 696 sedimentary sink for Cu and Cu isotopes. A first order approximation of the net flux of Cu
 697 into continental margin settings can be calculated using an estimate of marine organic C
 698 burial rate and the slope of the C_{org}/Al versus Cu/Al relationship for continental margin
 699 sites. This slope is 0.00041 g Cu/g C (ESM Fig. 3; data from this study and Böning et al.,
 700 2012). Smith et al. (2015) calculate a global marine C_{org} burial rate of $\sim 170 \times 10^{12}$ g C yr⁻¹.
 701 Together, this equates to an organic C associated Cu burial flux of $\sim 11 \times 10^8$ mol yr⁻¹. This
 702 value is an order of magnitude higher than an estimate for the role of continental margin
 703 sediments based on Mo as an analogue (Little et al., 2015) and slightly above the range of
 704 Cu removal estimates to oxic pelagic sedimentary settings, estimated at $1.6 - 9.7 \times 10^8$
 705 mol/yr (Little et al., 2014a; Little et al., 2015). The calculation excludes the additional flux
 706 of Cu to euxinic sediments via the redox-shuttle mechanism proposed for the Black Sea,
 707 which is quantitatively small today ($\sim 0.5 \times 10^8$ mol/yr; Little et al., 2015), but may have
 708 been more significant in the past. Given a total ocean Cu budget of 4.2×10^{12} moles (Little
 709 et al., 2014a) and the sum of the three output fluxes (pelagic, continental margin, redox-

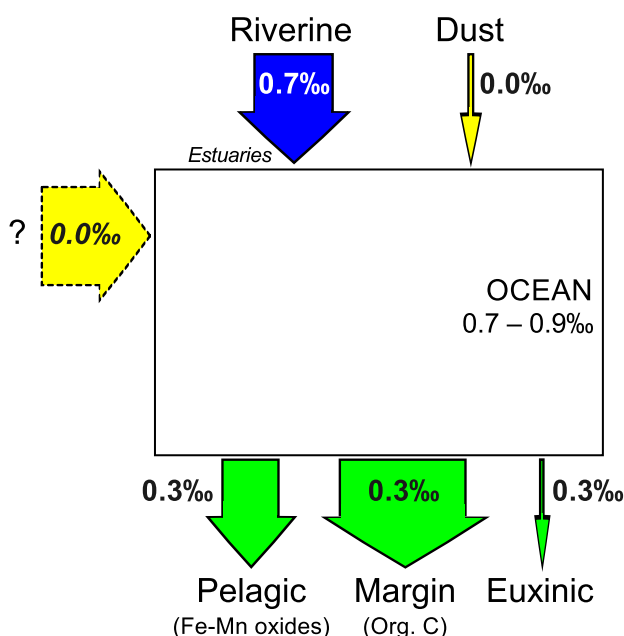
710 shuttle), we calculate a Cu oceanic residence time (where τ = total inventory of element \div
711 annual total input or output flux of element) of 2000 – 3200 years.

712

713 Together, the continental margin and pelagic Cu sinks sum to approximately twice the total
714 estimated riverine and dust input flux of Little et al. (2014a) ($6.5 - 9.2 \times 10^8$ mol/yr). In
715 addition, all sedimentary sinks for Cu are isotopically light (at about +0.3‰) compared to
716 the isotope composition of the combined riverine and dust flux (at approximately +0.6‰,
717 Little et al., 2014a). If the Cu oceanic budget is at steady state, these observations require
718 either an additional sink that is isotopically heavy or (a) further source(s) that is/are
719 isotopically light. Given the flux imbalance (i.e., known output fluxes \gg known input
720 fluxes) and the fact that the major output fluxes have now been characterised, a missing
721 input flux appears more probable. Mass balance implies this missing source be $\sim 9 \times 10^8$
722 mol/yr and have an isotope composition of ~ 0 ‰, illustrated schematically in Figure 8.

723

724 **Figure 8.** Schematic illustrating the updated oceanic budget of Cu and Cu isotopes (after
725 Little et al., 2014a; 2015; this study). Arrows are scaled by flux magnitude and labelled
726 and coloured by isotope composition (yellow represents the isotopically light components,
727 blue the isotopically heavier components, and green is intermediate). The projected
728 missing source size and isotope composition is shown as a dashed arrow to the left of the
729 figure (see text for details). For reference to colours, please see online version of this
730 figure.



731

732

733 The main input of Cu to the modern ocean has typically been assumed to be the dissolved
734 phase in rivers (e.g., Little et al., 2014a). Two independent estimates put this riverine

735 dissolved flux at $6 - 9 \times 10^8$ mol/yr (Gaillardet et al., 2003; Vance et al., 2008). This
736 dissolved riverine flux is isotopically heavy, with a discharge-weighted riverine average
737 $\delta^{65}\text{Cu}$ of +0.68‰ (Vance et al., 2008). These estimates assume conservative behaviour of
738 Cu during estuarine mixing, as observed, for example, for two major river systems: the
739 Chiang Jiang and the Amazon (Boyle et al., 1982; Edmond et al., 1985). However, non-
740 conservative behaviour of Cu has also been observed in a spectrum of estuarine systems
741 (e.g., Morris et al., 1978; Windom et al., 1983; Ackroyd et al., 1986). Furthermore, the
742 dissolved flux of Cu accounts for only ~20% of the total riverine flux of Cu to the ocean,
743 with the remainder delivered in particulate form (e.g., Martin and Meybeck, 1979). The
744 partial dissolution of riverine particulates has recently been suggested as a significant
745 oceanic source of several metals (e.g., Oelkers et al., 2012; Jones et al., 2012; 2014).
746 Vance et al. (2008) report isotopically light Cu in the particulate phase of one small river
747 system in the U.K, which is complementary to the heavy dissolved pool. Partial
748 remobilisation of isotopically light riverine particulates, whether lithogenic or other (e.g.
749 terrestrial organic matter) particles, may therefore provide one possible isotopically light
750 flux of Cu to the ocean. Release could be envisaged in, e.g., anoxic estuarine
751 environments, or further out in continental margin or open ocean settings. By analogy,
752 release of neodymium (Nd) from the lithogenic phase has been hypothesised in continental
753 margin settings (e.g., Jeandel et al., 2007; Pearce et al., 2013; Abbott et al., 2015; Abbott et
754 al., 2016).

755

756 The natural (non-anthropogenic) dust flux of Cu to the ocean appears to be isotopically
757 unfractionated from the lithogenic Cu source (at ~0‰), based on analysis of the water-
758 leachable fraction of aerosols and loess particles (Little et al., 2014a; Dong et al., 2013).
759 The magnitude of this natural dust flux has been calculated by two studies, one data-driven
760 (Little et al., 2014a) and one model-based (Takano et al., 2014). In the data-driven
761 approach, the flux is calculated based on a model of global dust deposition (Jickells et al.,
762 2005), an estimate of the Cu concentration in UCC (35ppm; Rudnick and Gao, 2003), and
763 an estimate of mineral dust solubility (27%; Desboeufs et al., 2005), yielding a Cu flux of
764 0.5×10^8 mol/yr (Little et al., 2014a). In the model-derived approach, Takano et al. (2014)
765 invoked a much larger dust flux, at $\sim 10 \times 10^8$ mol/yr, in order to balance their steady state
766 model-derived output flux of 17×10^8 mol/yr. The latter value is, itself, in line with the
767 sum of the pelagic and continental margin sinks proposed here. Assuming a lithogenic
768 isotope composition (0‰) for their postulated dust flux, Takano et al. (2014) further

769 calculate that the Cu isotope composition of the output flux should be +0.3‰ (Takano et
770 al., 2014), also consistent with results in this study. Nevertheless, we consider a very large
771 dust flux to be rather unlikely, due in part to the low solubility of Cu in dust (e.g.,
772 Desboeufs et al., 2005; Sholkovitz et al., 2010). Even if mineral dust were completely
773 soluble – for example, if solubility is enhanced by the presence of organic ligands (as
774 suggested for Fe; Fishwick et al., 2014) – the maximum Cu input flux possible based on an
775 estimate of global mineral dust deposition and the Cu concentration in UCC is five times
776 lower than that required by Takano et al. (2014), at 2.0×10^8 mol/yr.

777

778 Of other possible inputs, a hydrothermal Cu source has to date been assumed to be globally
779 insignificant due its to efficient removal close to the vent (e.g., Trocine and Trefry, 1988;
780 German et al., 1991; 2002). Scavenging within the Atlantic TAG hydrothermal plume
781 indicates that hydrothermal activity may in fact be a net sink of Cu, at least in certain
782 environments (Jacquot and Moffett, 2015; Roshan and Wu, 2015). However, recent water
783 column data for a range of trace elements and their isotopes, collected as part of the
784 international GEOTRACES program, has highlighted significant basin scale heterogeneity
785 in the iron (Fe) and zinc (Zn) hydrothermal flux, indicating that this potential source
786 should be re-evaluated (Resing et al., 2015; Roshan et al., 2016). Sander and Koschinsky
787 (2011) suggest that organic complexation may be one means to stabilise metals from
788 hydrothermal vent sources in the dissolved phase. Primary hydrothermal fluxes are likely
789 to have a lithogenic Cu isotope composition (at ~0‰), though these may be subject to
790 considerable secondary isotope fractionation effects resulting from sulphide precipitation,
791 organic complexation, and/or scavenging to oxide phases.

792

793 Benthic fluxes have long been considered to play a role in the water column distribution of
794 dissolved Cu (e.g., Boyle et al., 1977). In terms of oceanic mass balance, there are two
795 ways in which such a benthic flux can be envisaged, which differ according to the solid
796 phase from which the Cu is released to bottom waters. The first requires that Cu be
797 released from external sources, either via rivers (as discussed above), or hydrothermal
798 particulates. This possibility would then represent a true new source of Cu to the ocean and
799 might be expected to be isotopically light if lithogenic or hydrothermal material is the
800 source. The second type of benthic flux involves re-release to bottom waters of
801 bioauthigenic Cu (i.e., Cu from the water column). This process may occur in porewaters
802 of suboxic sediments, where suboxic denotes negligible dissolved oxygen and sulphide.

803 Under these conditions, Cu carrier phases (Fe-Mn oxides, organic matter) are reduced, and
804 Cu could diffuse into bottom water (Shaw et al., 1990; Elderfield et al., 1981; Heggie et al.,
805 1987; Klinkhammer, 1980; Sawlan and Murray, 1983). This process may be aided by
806 complexation to strong organic ligands in porewaters (Skrabal et al., 1997; 2000; Shank et
807 al., 2004a; 2004b). In itself, this process does not constitute a true new source of Cu to the
808 oceans, because the Cu that is returned to the water column came from the water column –
809 i.e., the Cu is recycled. Note that any such recycling is implicit in the calculation of the
810 organic C burial-associated Cu flux (i.e., this is a net flux). This recycling could, however,
811 be accompanied by an isotopic effect, if isotope fractionation occurs in the sediment pile.
812 An isotopically light signature for such a source would require preferential retention of
813 heavy Cu isotopes in the solid phase. This direction of fractionation would not be
814 consistent, however, with what would be predicted based on organic complexation of Cu in
815 pore waters. This process is likely to favour retention of heavy Cu isotopes in the soluble
816 phase, with the removal of light Cu isotopes to particles.

817

818 Ultimately, we suggest that better resolution of the Cu isotope budget requires future
819 studies focussing on: (1) an improved evaluation of the diagenetic processing of Cu and its
820 isotopes, (2) the fate and isotopic signature of hydrothermally sourced Cu, and (3) the
821 behaviour of continent-derived particulate Cu in the marine environment, both in estuaries
822 and more distally.

823

824

825 **6. Conclusions and Outlook**

826

827 This study presents a Cu isotope dataset for recent organic rich sediments from a range of
828 low oxygen and reducing sedimentary environments. The data indicate that the modern
829 bioauthigenic (i.e., non-lithogenic) oceanic Cu output flux is isotopically homogeneous
830 across many sedimentary environments – at about +0.3‰. This value is significantly
831 lighter than the isotope composition of the open oceans, at +0.6 to +0.9‰. We suggest that
832 the homogeneous isotopic composition of the Cu output flux reflects either (1) an
833 equilibrium isotope fractionation between two species in the dissolved phase, with an
834 isotopically heavy dissolved pool complexed by strong organic ligands and a particle
835 reactive, isotopically light free Cu^{2+} pool, or (2) an equilibrium isotope fractionation
836 directly between the organically complexed dissolved pool and the particulate phase. In the

837 latter scenario all particulates would be required to exhibit the same fractionation from the
838 dissolved pool. In either case, continuous reversible exchange between sinking particulates
839 and the dissolved pool, all the way down through the water column, may contribute to the
840 homogeneity of the output flux.

841

842 Unexpectedly, highly Cu enriched euxinic Black Sea sediments (with $\delta^{65}\text{Cu}_{\text{auth}}$ of +0.3‰)
843 do not record the Cu isotope signature of the open ocean (at around +0.6 to +0.9‰),
844 despite near quantitative removal of Cu from the water column. We hypothesize that this
845 signature reflects active Fe-Mn cycling at the Black Sea redoxcline, with shuttling of
846 isotopically 'bioauthigenic' Cu (i.e., at +0.3‰) to the restricted deep basin where it is
847 removed to sediment via sulphide precipitation. A similar process, albeit on a smaller
848 length-scale, likely also occurs at the sediment-water interface of suboxic to anoxic
849 continental margin sediments (e.g., San Nicolas Basin) and is also evident in the modern-
850 day near-chemocline station of the Black Sea (Station 16B). In all cases, we envisage that
851 an isotopically heavy pool of Cu is retained in the dissolved phase via complexation to
852 strong organic ligands.

853

854 Low oxygen conditions alone are not sufficient to generate strong enrichment of Cu in
855 marine sediments. Variability in the dataset presented here can be explained to first order
856 in terms of dilution of the bioauthigenic signature (at about +0.3‰) with lithogenic
857 material (at ~0‰), and the lithogenic sedimentary accumulation rate is a strong control on
858 the presence or absence of the bioauthigenic $\delta^{65}\text{Cu}$ signature in sediments.

859

860 We note that all characterised sinks for Cu in the modern ocean are isotopically light (at
861 about +0.3‰) relative to the current best estimate for the input flux (at about +0.6‰; Little
862 et al., 2014a). This disparity indicates the presence of an as yet unidentified isotopically
863 light source, of approximately lithogenic composition (~0‰; Fig. 8). Dust is one such
864 possible light source, as previously suggested by Takano et al. (2014). We suggest two
865 other possible light sources of Cu: (1) hydrothermal input, (2) partial dissolution of
866 continentally derived particulates. Distinguishing among these three possible input fluxes
867 requires future detailed research.

868

869 Finally, our findings, along with those of several previous studies, indicate that strong
870 organic ligands play a key role in the modern biogeochemical cycle of Cu and Cu isotopes.

871 This role must be fully considered in future studies seeking to apply Cu isotopes in the
872 rock record as a paleoceanographic tracer.

873

874

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876

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890

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