

1 Isotopic Constraints on Biogeochemical Cycling of Copper in the Ocean

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3 Shotaro Takano<sup>1\*</sup>, Masaharu Tanimizu<sup>2</sup>, Takafumi Hirata<sup>3</sup>, and Yoshiki Sohrin<sup>1</sup>

4 <sup>1</sup>*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

5 <sup>2</sup>*Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and*

6 *Technology, 200 Monobe Otsu, Nankoku 783-8502, Japan*

7 <sup>3</sup>*Laboratory for Planetary Sciences, Division of Earth and Planetary Sciences, Kyoto*

8 *University, Kitashirakawa Oiwake-cho, Kyoto 606-8502, Japan*

9 **\*Corresponding author.** E-mail: shotaro@inter3.kuicr.kyoto-u.ac.jp Tel: +81 774 38

10 3098. Fax: +81 774 38 3099

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12           Trace elements and their isotopes are being actively studied as powerful  
13 tracers in the modern ocean and as proxies for the palaeocean. Although  
14 distributions and fractionations have been reported for stable isotopes of dissolved  
15 Fe, Cu, Zn, and Cd in the ocean, the data remain limited and only preliminary  
16 explanations have been given. Copper is of great interest because it is either  
17 essential or toxic to organisms and because its distribution reflects both biological  
18 recycling and scavenging. Here, we present new data of isotopic compositions of  
19 dissolved Cu ( $\delta^{65}\text{Cu}$ ) in seawater and rainwater. The Cu isotopic composition in  
20 surface seawater is explained by the mixing of rain, river, and deep water. In deep  
21 seawater,  $\delta^{65}\text{Cu}$  becomes heavier along oceanic circulation because of preferential  
22 scavenging of the lighter isotope ( $^{63}\text{Cu}$ ). Additionally, we constrain the marine  
23 biogeochemical cycling of Cu using a new box model based on Cu concentration  
24 and  $\delta^{65}\text{Cu}$ .

25

26           Copper plays an important role as a micronutrient for organisms in the ocean,  
27 but high concentrations of the free  $\text{Cu}^{2+}$  ion are toxic<sup>1</sup>. Dissolved Cu has concentrations  
28 of 0.5–6  $\text{nmol kg}^{-1}$  in seawater and mostly complexes with organic ligands, which  
29 results in very low concentrations ( $\text{fmol kg}^{-1}$  to  $\text{pmol kg}^{-1}$ ) of the free  $\text{Cu}^{2+}$  ion<sup>2</sup>.

30 Vertical distributions of dissolved Cu are of the nutrient-scavenging hybrid type<sup>3</sup>.  
31 Generally, the concentrations of nutrient-type trace metals (e.g., Zn, Ni, and Cd) are low  
32 in the surface layer of the ocean because of biological uptake. However, the  
33 concentrations increase with depth, showing a mid-depth maximum because of  
34 remineralisation from settling particles. By contrast, the concentration of dissolved Cu  
35 gradually increases with depth towards the bottom. Such distributions have been  
36 interpreted to be caused by a combination of scavenging throughout the water column  
37 and a supply from the uppermost layer of benthic sediments, where scavenged Cu is  
38 recycled to overlying seawater via early diagenesis<sup>4,5</sup>. Copper has two stable isotopes,  
39 <sup>63</sup>Cu and <sup>65</sup>Cu, and its isotopic composition is reported as  $\delta^{65}\text{Cu}(\text{‰}) =$   
40  $[(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}/(^{65}\text{Cu}/^{63}\text{Cu})_{\text{NIST SRM 976}}-1]\times 10^3$ . To date, only a few vertical profiles of  
41 dissolved  $\delta^{65}\text{Cu}$  in the ocean have been reported<sup>6, 7, 8, 9</sup>. The reported  $\delta^{65}\text{Cu}$  values  
42 (0.44–1.44‰) were substantially heavier than typical values for the solid Earth (~0‰)<sup>10</sup>.  
43 <sup>11</sup>. However, as there were relatively large uncertainties in the reported data, it has been  
44 difficult to elucidate intra-ocean distributions. This is partly due to analytical difficulties  
45 in the determination of  $\delta^{65}\text{Cu}$  caused by the interference of matrices and the  
46 inapplicability of the so-called double-spike technique.

47 Recently, we developed a simple and precise analytical method for  $\delta^{65}\text{Cu}$  based

48 on a chelating resin extraction technique<sup>12</sup>. Here, we use this method to present new  
49 data of isotopic compositions of dissolved Cu ( $\delta^{65}\text{Cu}$ ) in seawater from the North/South  
50 Atlantic, South Indian, and North Pacific. We also present new data of rainwater  
51 samples collected from urban and rural regions. Using these data, the Cu isotopic  
52 composition in surface seawater is explained in an oceanographic context. In deep  
53 seawater,  $\delta^{65}\text{Cu}$  values show a linear correlation with apparent oxygen utilisation (AOU),  
54 which suggests  $\delta^{65}\text{Cu}$  becomes heavier along oceanic circulation because of preferential  
55 scavenging of the lighter isotope (i.e.,  $^{63}\text{Cu}$ ). These are the first data showing that the  
56 stable isotopic composition of trace metals changes systematically with the age of deep  
57 water. Additionally, we propose a new box model for Cu in the ocean based on the  
58 combination of Cu concentration and  $\delta^{65}\text{Cu}$ , which successfully constrains the marine  
59 biological cycling of Cu.

60

## 61 **Results**

### 62 **Seawater analyses**

63 The observed oceanic stations are shown in Fig. 1. All seawater data are  
64 summarised in Supplementary Table 1. The vertical profiles of dissolved Cu  
65 concentration and  $\delta^{65}\text{Cu}$  for each station are presented in Supplementary Fig. 1, and

66 representative profiles are shown in Fig. 2. The Cu concentrations were in the range of  
67 0.6–4.6 nmol kg<sup>-1</sup>, and the profile at station ER10 agreed well with that determined in  
68 separate samples collected at the same station in our previous research (Supplementary  
69 Fig. 2)<sup>14</sup>. The δ<sup>65</sup>Cu values ranged from +0.41‰ to +0.85‰, which were smaller than  
70 values determined by a Mg(OH)<sub>2</sub> co-precipitation technique (+0.50–1.44‰)<sup>7, 8</sup> at other  
71 stations and similar to values determined by a solvent extraction technique  
72 (+0.44–0.78‰)<sup>6, 9</sup> at other stations (Supplementary Fig. 3). The vertical samples from  
73 BATS have been analysed using a solvent extraction technique by Thompson et al.<sup>9</sup>. The  
74 reported δ<sup>65</sup>Cu value (0.56±0.09‰) for a 2000 m depth sample was higher than our  
75 value (0.41±0.05‰). Unfortunately, we are not able to investigate the causes because  
76 the BATS samples have been exhausted. Recently, we performed intercalibration of  
77 δ<sup>65</sup>Cu with a group from ETH, Zurich (see Acknowledgements section for details) using  
78 seawater collected at a station near the Japan Trench, of which the details are described  
79 in Supplementary Methods. The ETH group used a new method based on Al(OH)<sub>3</sub>  
80 co-precipitation<sup>15</sup>, which gave results consistent to ours (Supplementary Fig. 4).

81         The vertical profiles of δ<sup>65</sup>Cu in this work showed a common feature: δ<sup>65</sup>Cu  
82 was ~0.5‰ in the surface layer and became heavier at depth. Station BD21 above the  
83 Juan de Fuca Ridge had a minimum Cu concentration at a depth of 2300 m, reflecting

84 the effect of a hydrothermal plume<sup>16</sup>. There were, however, no significant variations in  
85  $\delta^{65}\text{Cu}$ .

86

### 87 **Rainwater analyses**

88 We also determined  $\delta^{65}\text{Cu}$  in rainwater for the first time (Table 1). Rainwater  
89 was sampled from rural and urban regions in Japan. The dissolved  $\delta^{65}\text{Cu}$  values were in  
90 the narrow range of  $-0.12$ – $+0.03\%$  and did not show significant differences depending  
91 on location and time, whereas the Cu concentrations varied largely (1.1–23.5 nmol  
92  $\text{kg}^{-1}$ ), which may reflect various contributions of anthropogenic input. It has been  
93 reported that  $\delta^{65}\text{Cu}$  values were  $\sim 0\%$  for leachable fractions of marine aerosols<sup>11</sup> and  
94 bulk loess<sup>17</sup>. Rainwater would scavenge both atmospheric dusts and anthropogenic  
95 aerosols during precipitation. Therefore, it seems reasonable to presume the  $\delta^{65}\text{Cu}$  value  
96 for atmospheric input to be zero.

97

### 98 **Copper isotopes in surface seawater**

99 In Fig. 3, the  $\delta^{65}\text{Cu}$  in surface seawater is plotted against the reciprocal Cu  
100 concentration together with the ranges and averages of deep seawater, rural rainwater,  
101 and river water<sup>8</sup>. Assuming that average surface seawater is a mixture of average rural

102 rainwater, average river water, and average deep seawater, the plot would be located in  
103 the magenta triangle. Evaporation that is another important factor to control salinity; it  
104 would increase the Cu concentration but not change the  $\delta^{65}\text{Cu}$ . However, the surface  
105 water data are shifted to the right of the triangles, indicating there must be other  
106 processes that decrease the dissolved Cu concentration (up to one tenths) while keeping  
107 the  $\delta^{65}\text{Cu}$  values constant. The most likely process is phytoplankton uptake and  
108 adsorption of Cu onto the phytoplankton surface. It is well known that these processes  
109 produce biogenic sinking particles in the surface layer and they transport trace metals to  
110 the deep layer. Our data suggest that uptake and adsorption by phytoplankton in the  
111 open ocean does not cause significant fractionation of Cu isotopes. To clarify  
112 mechanisms controlling the Cu concentration and  $\delta^{65}\text{Cu}$ , it is informative to compare  
113 Cu and Cd in the ocean. For vertical profiles of dissolved Cd, the isotopic ratio ( $\epsilon^{114}\text{Cd}$ )  
114 correspondingly increases with a decrease in the concentration in the surface layer and  
115 decreases with an increase in the concentration from the surface to the intermediate  
116 layer, because biological uptake causes isotopic fractionation of Cd<sup>18, 19, 20</sup>. Therefore,  
117 the profile of  $\epsilon^{114}\text{Cd}$  from the surface to the intermediate layer becomes a mirror image  
118 of the concentration, and  $\epsilon^{114}\text{Cd}$  linearly correlates with the logarithm concentration in  
119 the surface layer because of Rayleigh fractionation during biological uptake<sup>18, 19, 20, 21</sup>.

120 However,  $\delta^{65}\text{Cu}$  does not change uniformly with respect to the Cu concentration from  
121 the surface to the intermediate layer (Fig. 2 and Supplementary Fig. 1), and does not  
122 correlate with the logarithmic concentration in the surface layer (Supplementary Fig. 5).  
123 These facts also indicate biological processes cause insignificant fractionation of the Cu  
124 isotopes.

125

### 126 **Copper isotopes in deep seawater**

127         Given that uptake and adsorption of Cu by phytoplankton does not cause  
128 fractionation of Cu isotopes, biogenic sinking particles would have the same  $\delta^{65}\text{Cu}$   
129 value as surface seawater. Copper regenerated through decomposition of the biogenic  
130 sinking particles should produce  $\delta^{65}\text{Cu}$  values in deep seawater, which are the same as  
131 those in surface seawater under this assumption. However, observed  $\delta^{65}\text{Cu}$  in deep  
132 seawater is heavier than that in surface seawater. In addition, the profiles of  $\delta^{65}\text{Cu}$  are  
133 similar to those of apparent oxygen utilisation (AOU; Fig. 2 and Supplementary Fig. 1).  
134 All  $\delta^{65}\text{Cu}$  values are plotted against AOU, revealing a positive correlation ( $R^2 = 0.60$ ,  $n$   
135  $= 77$ ; Fig. 4a). In the layer deeper than 2000 m,  $\delta^{65}\text{Cu}$  vs. AOU shows a stronger  
136 correlation ( $R^2 = 0.70$ ,  $n = 25$ ; Fig. 4b). Because AOU is a measure of the age of deep  
137 water, these data imply that  $\delta^{65}\text{Cu}$  increases through deep water circulation. When the



138 Cu concentration is plotted against AOU, there is also a weak correlation ( $R^2 = 0.31$ ,  $n =$   
139 77, Fig. 5).

140 In the case of Cd, the dissolved concentration is very low ( $\sim 0.001 \text{ nmol kg}^{-1}$ ) in  
141 the surface layer because of biological uptake, and it is high in the deep layer ( $\sim 1 \text{ nmol}$   
142  $\text{kg}^{-1}$ ) because of remineralisation from biogenic particles; it also increases along the  
143 global deep circulation<sup>3</sup>. Because there is a significant correlation between Cd and  
144 phosphate, the distribution of Cd is dominated by biogeochemical recycling. The  
145 isotopic composition of Cd is heavier in surface seawater ( $\epsilon^{114/110}\text{Cd} = 10\text{--}40$  with  
146 respect to a JMC Cd Münster solution) than in deep seawater ( $\epsilon^{114/110}\text{Cd} = \sim 3$ ) that is  
147 almost uniform in the world ocean<sup>18, 19, 20</sup>. Biological uptake depletes the Cd  
148 concentration and preferentially leaves isotopically heavy Cd in surface seawater. It is  
149 suggested that Cd in a replenished surface seawater reservoir is originally characterised  
150 by  $\epsilon^{114/110}\text{Cd} = \sim 3$  and that this Cd is almost quantitatively transported by biogenic  
151 sinking particles from the surface to depth and remineralised in deep water; thus, the Cd  
152 isotopic composition of deep water is homogeneous, whereas the Cd concentration  
153 increases along with deep water circulation.

154 The  $\delta^{65}\text{Cu}$  in deep seawater appears to be controlled by a ubiquitous effect  
155 throughout the water column and deep water pathway because  $\delta^{65}\text{Cu}$  correlates with

156 AOU. Copper is more strongly scavenged than other recycled-type trace metals such as  
157 Cd<sup>3, 5</sup>. The scavenging is likely the reason that  $\delta^{65}\text{Cu}$  is heavy in the deep layer and  
158 becomes heavier with the age of deep seawater. If this is true, <sup>63</sup>Cu would be  
159 preferentially adsorbed to sinking particles and preserved in sinks. The low linearity of  
160 Cu concentration against AOU (Fig. 5) would be due to the combination of scavenging  
161 throughout the water column and supply from sediments through decomposition of the  
162 organic fraction of sinking particles. The Cu released from sediments most likely has a  
163  $\delta^{65}\text{Cu}$  value similar to that in seawater near the bottom, resulting in the linearity of  
164  $\delta^{65}\text{Cu}$  vs. AOU.

165

#### 166 **Box model for Cu in the modern ocean**

167 We present a new box model for Cu based on both concentration and isotopic  
168 composition (Fig. 6 and Supplementary Table 2). This model assumes a steady-state for  
169 the modern ocean. In this model, the global ocean is divided simply into a euphotic  
170 layer and a deep layer at a depth of 100 m. A thin layer on the sediment surface is  
171 considered as the box of the ‘scavenged layer’, where organic matter is decomposed  
172 during early diagenesis<sup>22</sup>. In Fig. 6, the black figures are observed or previously  
173 published values, as described below. Magenta figures are values calculated using the

174 following equations<sup>11</sup>, which assumes a steady-state for each box:

175 
$$\Sigma F_{in} = \Sigma F_{out}$$

176 
$$\Sigma F_{in} \delta_{in} = \Sigma F_{out} \delta_{out}$$

177

178 where  $F_{in}$  and  $F_{out}$  represent an input and output flux for the box, and  $\delta_{in}$  and  $\delta_{out}$

179 represent  $\delta^{65}\text{Cu}$  values of  $F_{in}$  and  $F_{out}$ , respectively. Based on this work, the

180 depth-weighted averages of Cu concentration and  $\delta^{65}\text{Cu}$  are  $1.1 \text{ nmol kg}^{-1}$  and  $0.49\text{‰}$  in

181 surface seawater and  $2.5 \text{ nmol kg}^{-1}$  and  $0.60\text{‰}$  in deep seawater, respectively. The

182 water mixing rate between the upper box and lower box is assumed to be  $1.2 \times 10^{15} \text{ m}^3$

183  $\text{year}^{-1}$ , which has been determined from  $^{14}\text{C}$  data<sup>23</sup>. We assumed that the main inputs of

184 dissolved Cu to the ocean are riverine and atmospheric inputs. The reported riverine

185 input of dissolved Cu to the ocean among four studies<sup>4, 8, 24, 25</sup> was in the range of

186  $6\text{--}9 \times 10^8 \text{ mol year}^{-1}$ , and the average value of  $7.6 \times 10^8 \text{ mol year}^{-1}$  was applied to our

187 model. The removal rate of dissolved Cu from the ocean was estimated to be  $\sim 4.0 \text{ nmol}$

188  $\text{kg}^{-1} \text{ year}^{-1}$  by using a vertical advection diffusion model<sup>4, 5</sup>. By multiplying this value

189 by the total ocean volume ( $1.35 \times 10^{21} \text{ kg}$ ), the scavenging flux of Cu in the ocean was

190 estimated to be  $5.4 \times 10^9 \text{ mol year}^{-1}$ . Riverine input  $\delta^{65}\text{Cu}$  was determined in rivers

191 worldwide; the rivers account for approximately one-quarter of all riverine discharge to

192 the ocean<sup>8</sup>. The discharge-weighted average of  $0.68\text{‰}$  of these rivers was used in our

193 model. The  $\delta^{65}\text{Cu}$  of atmospheric input was assumed to be 0‰ because  $\delta^{65}\text{Cu}$  values are  
194 ~0‰ for rainwater, leachable fractions of marine aerosols<sup>11</sup>, and loess<sup>17</sup>. It was assumed  
195 that the  $\delta^{65}\text{Cu}$  of sinking particles (of mainly biogenic origin) from surface water was  
196 the same as the  $\delta^{65}\text{Cu}$  of ambient surface seawater (i.e., 0.49‰), because isotopic  
197 fractionation during phytoplankton uptake and adsorption onto phytoplankton surface is  
198 expected to be insignificant, as described above. The  $\delta^{65}\text{Cu}$  of the benthic flux from the  
199 scavenged layer to deep seawater was assumed to be the global average of 0.58‰. This  
200 value is the average of  $\delta^{65}\text{Cu}$  in seawater samples nearest the bottom of the ocean. The  
201 unknown Cu fluxes that were calculated by this model are those of supply from the  
202 atmosphere, transport by sinking particles from the surface, preservation in sediments,  
203 and return from the scavenged layer to deep water. The unknown  $\delta^{65}\text{Cu}$  values  
204 calculated by this model are those of the transporting flux by sinking particles in deep  
205 water and the preserved flux into sediments.

206

## 207 **Discussion**

208 From our data we infer that the  $\delta^{65}\text{Cu}$  values in surface seawater are mainly  
209 controlled by supply from rivers, atmosphere, and deep seawater. Biological uptake  
210 does not cause significant isotopic fractionation of Cu in the open ocean.  $\delta^{65}\text{Cu}$  values

211 in deep seawater are heavier than those in surface seawater and become heavier with the  
212 age of deep seawater because of preferential scavenging for the light isotope ( $^{63}\text{Cu}$ ).

213 Biological fractionation of Cu isotopes has not yet been sufficiently clarified in  
214 the literature. There are only a few studies concerning isotopic fractionation of Cu by  
215 phytoplankton. Laboratory experiments have shown that uptake by several diatoms  
216 caused no significant fractionation or slight enrichment of the heavy Cu isotope ( $^{65}\text{Cu}$ )  
217 when the initial Cu concentration was  $\sim 200 \text{ nmol L}^{-1}$  (ref. 26). However, a geochemical  
218 study in the Garonne River suggested that diatom species prefer the light Cu isotope  
219 ( $^{63}\text{Cu}$ )<sup>27</sup>. Thus, it is necessary to determine the  $\delta^{65}\text{Cu}$  of natural phytoplankton in the  
220 open ocean in future work.

221 We suggest that Fe-Mn oxides may be a major sink of Cu in the oxic ocean.  
222  $\delta^{65}\text{Cu}$  values of Fe-Mn nodules are  $0.33 \pm 0.23\text{‰}$  (ave $\pm$ 2-sd,  $n = 14$ ) in the Pacific,  
223  $0.25 \pm 0.26\text{‰}$  ( $n = 8$ ) in the Atlantic, and  $0.31 \pm 0.23\text{‰}$  ( $n = 31$ ) in the world ocean<sup>10</sup>; the  
224  $\delta^{65}\text{Cu}$  values of Fe-Mn crusts are  $0.54 \pm 0.07\text{‰}$  ( $n = 8$ ) in the Pacific,  $0.33 \pm 0.15\text{‰}$  ( $n =$   
225  $8$ ) in the Atlantic, and  $0.44 \pm 0.23\text{‰}$  ( $n = 16$ ) in the world ocean<sup>11</sup>. Thus,  $\delta^{65}\text{Cu}$  of Fe-Mn  
226 crusts and nodules is lighter than that of dissolved Cu in the ocean. Furthermore, the  
227  $\delta^{65}\text{Cu}$  of Fe-Mn crusts is significantly heavier in the Pacific than in the Atlantic ( $p =$   
228  $0.01$ ). These data are consistent with preferential scavenging of  $^{63}\text{Cu}$  and gradual

229 accumulation of  $^{65}\text{Cu}$  in seawater through the global ocean circulation. This view,  
230 however, seems contrary to experimental results on adsorption of Cu isotopes on Fe  
231 oxyhydroxides<sup>26, 28</sup>, which indicate enrichment of the heavy Cu isotope onto oxide  
232 surfaces in  $\text{NaNO}_3$  solutions or mixtures of acidic drainage and river water. The  
233 discrepancy may be caused by differences in conditions, such as pH, Cu concentration,  
234 and organic ligands concentration, between experimental solutions and natural seawater.  
235 Additionally, it was found that Cu is associated with Mn and not Fe in Fe-Mn crusts<sup>29</sup>.  
236 Isotopic fractionation between free Cu and organic ligand-bound Cu would also be  
237 important for Cu isotopes in seawater, because Cu is mostly complexed with organic  
238 ligands. In a laboratory experiment, humic acid preferentially complexes with the heavy  
239 Cu isotope<sup>30</sup>. Therefore, it is likely that the complexation of Cu with dissolved organic  
240 ligands in seawater also causes mass fractionation of Cu, because the organic ligands  
241 and humic acid most likely have the same functional groups. Furthermore, Cu is  
242 contained not only in the Fe-Mn oxide fraction but also in the organic fraction of  
243 sinking particles<sup>31, 32</sup>. Thus, understanding isotopic fractionation during scavenging of  
244 dissolved Cu from seawater is not straightforward. It was originally proposed in a  
245 previous field study of rivers and oceans that there is equilibrium partitioning of  
246 isotopes between heavy Cu bound to organic ligands in the dissolved phase and light Cu

247 adsorbed to particles<sup>8</sup>. This hypothesis is consistent with our explanation of light Cu  
248 scavenging.

249 In the box model using both the Cu concentration and  $\delta^{65}\text{Cu}$  (Fig. 6), we  
250 constrained the transporting flux of Cu from surface to deep water by sinking particles  
251 to be  $3.4 \times 10^9 \text{ mol year}^{-1}$ . The residence time for dissolved Cu in surface water (<100 m)  
252 is ~9 years, which is consistent with previous estimates of 3.2–11.7 years<sup>5, 33</sup>. The  
253 calculated preservation flux of Cu into sediments is  $1.7 \times 10^8 \text{ mol year}^{-1}$ . The overall  
254 residence time of Cu in the ocean is calculated by dividing the average concentration by  
255 the preservation flux. Our estimate of the overall residence time of Cu is 2000 years,  
256 which is within the range of literature values (1700–6400 years)<sup>4, 11</sup>. The calculated  
257  $\delta^{65}\text{Cu}$  of preserved Cu in sediments is +0.30‰, which is quite similar to the averages  
258 reported for Fe-Mn oxides<sup>10, 11</sup>.

259 We also constrained the atmospheric input of dissolved Cu to be  $9.6 \times 10^8 \text{ mol}$   
260  $\text{year}^{-1}$ . Our model suggests that the present atmospheric input of Cu is comparable to  
261 the riverine input. A significant correlation was found between Cu and  $^{210}\text{Pb}$  in surface  
262 seawater, implying a strong atmospheric supply of Cu because  $^{210}\text{Pb}$  is a tracer for  
263 atmospheric input<sup>4</sup>. These authors estimated both the atmospheric and riverine Cu input  
264 to be  $6.0 \times 10^8 \text{ mol year}^{-1}$ , which is similar to our results. However, our value is

265 significantly larger than the natural atmospheric input previously estimated at  $5.4 \times 10^7$   
266 mol year<sup>-1</sup>, which was obtained by multiplying the total dust flux by the mean crustal  
267 Cu concentration and solubility<sup>11</sup>.

268           Two possible explanations are given to rationalise this difference. First, it is  
269 possible that the Cu concentration and solubility in marine aerosols would be different  
270 from those in the continental crust. The enrichment factor of Cu relative to Al in marine  
271 aerosols varies over a large range of 1–200 compared with the continental crust<sup>25</sup>. The  
272 solubility of Cu in aerosols has a wide range of 15–86%<sup>34</sup>. It was suggested that the  
273 enriched and soluble Cu in aerosols is from anthropogenic sources<sup>34, 35, 36</sup>. However,  
274 Maring et al. evaluated the source of Cu enrichment in aerosols near Enewetak in the  
275 North Pacific, suggesting that atmospheric soluble Cu is from primary natural origins  
276 and that soil organic matter enriched in Cu could be a significant source of soluble Cu<sup>37</sup>.  
277 If anthropogenic Cu has significantly affected atmospheric input as we estimated, then  
278 the steady-state assumption is imperfect for the modern ocean, because anthropogenic  
279 inputs would have substantially increased in the recent ~100 years, whereas the overall  
280 oceanic residence time of Cu is approximately 1000 years. Second, other fluxes to open  
281 ocean surface may be suggested. One possible flux is from the continental shelf  
282 sediment, where a portion of Cu is derived from the reduction of primary terrigenous



283 metal oxides<sup>38</sup>. The  $\delta^{65}\text{Cu}$  value of this flux would also be close to the crustal value  
284 (‰) and lighter than that of surface seawater. If these fluxes are included in our box  
285 model, then our estimate of atmospheric input may decrease. As described above, some  
286 uncertainties remain in our box model. Our results, however, confirm possibilities of  
287 this new box model based on both concentration and isotopic composition of trace  
288 metals.

289

## 290 **Methods**

### 291 **Seawater samples**

292         The South Indian and North Pacific seawater samples were collected during the  
293 R/V *Hakuho-maru* voyages KH 09-4, KH 10-2, KH 11-7, and KH 12-4 using a clean  
294 sampling system<sup>14</sup>. In a clean booth, seawater was filtered through a 0.2  $\mu\text{m}$  cartridge  
295 (Acro pak, Poll), acidified with HCl to pH 1.7–2.2, and stored in 2 L or 4 L LDPE  
296 bottles (Nalge Nunc) or 6 L LDPE cubic bags (Lontainer, Sekisui Seikei), which were  
297 pre-cleaned by overnight treatment with 4 M HCl followed by rinsing with deionised  
298 water. The North Atlantic sample was a GEOTRACES reference material collected at  
299 BATS during the US-GEOTRACES KN193-5 voyage of the R/V *Knorr*. The South  
300 Atlantic sample was collected at Station 3 during the UK-GEOTRACES D357 voyage

301 of the RSS *Discovery*.

302

### 303 **Rainwater samples**

304 Rainwater was collected from two sites using pre-cleaned polyethylene funnels  
305 and cubic bags (Lontainer) or 2 L LDPE bottles. One site was on the roof of the main  
306 building of the Institute for Chemical Research, which is located in an urban area of the  
307 Main Island, Japan. The other site was on top of Mt. Kajigamori, which is located in a  
308 rural area of Sikoku Island. Rainwater samples were filtered through a 0.22  $\mu\text{m}$  filter  
309 (Millipore) and acidified with HCl to pH 1.7–2.1.

310

### 311 **Analytical procedure of $\delta^{65}\text{Cu}$ and Cu**

312 Copper concentration and isotopic composition were determined as described  
313 in a previous paper<sup>12</sup>. Briefly, Cu in seawater or rainwater was collected using a column  
314 of Nobias chelate PA-1 resin (Hitachi High Technologies) followed by elution with 1 M  
315  $\text{HNO}_3$ . The eluate was evaporated to dryness, and the residue was re-dissolved with 10  
316 M HCl. The sample was passed through a column of anion exchange resin (AG MP-1,  
317 Bio-Rad); additional 10 M HCl was then passed through the column to remove  
318 co-existing elements, followed by the elution of Cu with 5 M HCl. This eluate was

319 evaporated to dryness and the residue was re-dissolved with 1 M HNO<sub>3</sub>. Finally, the 1  
320 M HNO<sub>3</sub> solution was re-evaporated and the residue was re-dissolved with 0.4 M HNO<sub>3</sub>,  
321 yielding the pre-concentrated sample. One hundred micrograms of the pre-concentrated  
322 sample was diluted with 0.4 M HNO<sub>3</sub> by a factor of ~10 and used for measurement of  
323 Cu concentration. Co-existing Na, Mg, Ba, Ni, Zn, Cr, and Ti were also measured to  
324 ascertain whether these interfering elements possessed concentrations sufficiently low  
325 to permit accurate Cu isotopic measurements. When the Na (ppb)/Cu (ppb) ratio in the  
326 pre-concentrated sample was higher than 1, the solution was not used for discussion.  
327 For the Cu isotopic measurement, which used a multicollector ICP-MS (Thermo  
328 Finnigan Neptune or Neptune Plus), the final solution was diluted to adjust the Cu  
329 concentration to 50 ppb and Zn was added to give a solution of 100 ppb for external  
330 normalisation. The precision of this method was evaluated previously by repeated  
331 analyses of coastal seawater to be  $\pm 0.07\text{‰}$  ( $\pm 2\text{-sd}$ ,  $n = 6$ )<sup>12</sup>. In this study, 34 samples  
332 were each divided into two aliquots and analysed in duplicate, resulting in an average  
333 2-sd of 0.045 ‰ ( $n = 34$ ) for  $\delta^{65}\text{Cu}$  and 0.11 nmol kg<sup>-1</sup> ( $n = 34$ ) for Cu concentration.  
334 These values are shown as error bars in the figures.

335

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476 cadmium in the surface waters of the North Atlantic and North Pacific Ocean. *J.*  
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478

479

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490

#### 491 **Author contributions**

492 S.T. and Y.S. designed the research. S.T. determined the concentration of Cu and  $\delta^{65}\text{Cu}$ .  
493 M.T. contributed to measurements with MC-ICP-MS. T.H helped with the development  
494 of the analytical method and supplied the standard reference material of Cu (NIST SRM  
495 976). All authors contributed to the interpretation of the data and preparation of the  
496 manuscript.

497

#### 498 **Competing financial interests**

499 The authors declare no competing financial interests.

500

501

## 502 **Figure legends**

503

504 Figure 1 Station locations. Samples for the analysis of  $\delta^{65}\text{Cu}$  were collected at these  
505 stations during R/V *Hakuho-maru* voyages. The numbers of samples are 10 at TR7, 10  
506 at TR15, 10 at CR27, 14 at BD17, 12 at BD21, and 18 at ER10. This figure was  
507 produced with Ocean Data View<sup>13</sup>.

508

509 Figure 2 Representative vertical profiles of the concentration and isotopic composition  
510 of Cu. Magenta triangles indicate Cu concentration. Blue squares and black circles  
511 indicate  $\delta^{65}\text{Cu}$  and apparent oxygen utilisation (AOU), respectively. Black diamonds  
512 indicate fluorescence or chlorophyll a (Chl. a). The error bars are 2-sd of  $\pm 0.045\%$  for  
513  $\delta^{65}\text{Cu}$  and  $\pm 0.11 \text{ nmol kg}^{-1}$  for Cu concentration, as described in the Methods section.  
514 The vertical profiles at all stations are shown in Supplementary Fig. 1.

515

516 Figure 3  $\delta^{65}\text{Cu}$  versus reciprocal Cu concentration for surface seawater (<100 m). The  
517 error bars of the magenta circles are 2-sd of  $\pm 0.045\%$ . The blue, black, and orange

518 shaded areas indicate the ranges of the data for deep seawater, river water, and rural rain,  
519 respectively. The magenta triangle indicates the possible range of mixtures of average  
520 deep seawater, river water, and rainwater. The surface water data shifted to the right of  
521 the triangle indicate that other processes decrease the dissolved Cu concentration in the  
522 surface seawater.

523

524 Figure 4  $\delta^{65}\text{Cu}$  versus AOU for seawater. The error bars for  $\delta^{65}\text{Cu}$  are 2-sd of  $\pm 0.045\%$ .

525 (a) All  $\delta^{65}\text{Cu}$  values were plotted against AOU. The solid line was determined by a

526 regression analysis of all plots:  $\delta^{65}\text{Cu} = 0.00067 \times \text{AOU} + 0.50$ ,  $R^2 = 0.60$ ,  $n = 77$ ,  $p <$

527  $0.001$ . (b)  $\delta^{65}\text{Cu}$  values were plotted against AOU in deep seawater ( $>2000$  m). The

528 solid line was determined by a regression analysis of all plots:  $\delta^{65}\text{Cu} = 0.0016 \times \text{AOU} +$

529  $0.32$ ,  $R^2 = 0.70$ ,  $n = 25$ ,  $p < 0.001$ .

530

531 Figure 5 Cu concentration versus AOU in the ocean. The error bars are 2-sd of  $\pm 0.11$

532  $\text{nmol kg}^{-1}$ . The solid line was defined as:  $[\text{Cu}] = 0.0046 \times \text{AOU} + 1.5$ ,  $R^2 = 0.31$ ,  $n = 77$ ,

533  $p < 0.001$ .

534

535 Figure 6 Box model for Cu cycling in the ocean based on both elemental concentration  
536 and isotopic ratio. The Roman and italic values below the process names represent Cu  
537 flux in units of  $10^9 \text{ mol year}^{-1}$  and  $\delta^{65}\text{Cu}$  values, respectively. Black figures indicate  
538 observed values and magenta figures indicate values calculated based on mass balance.

539 **Table**

540

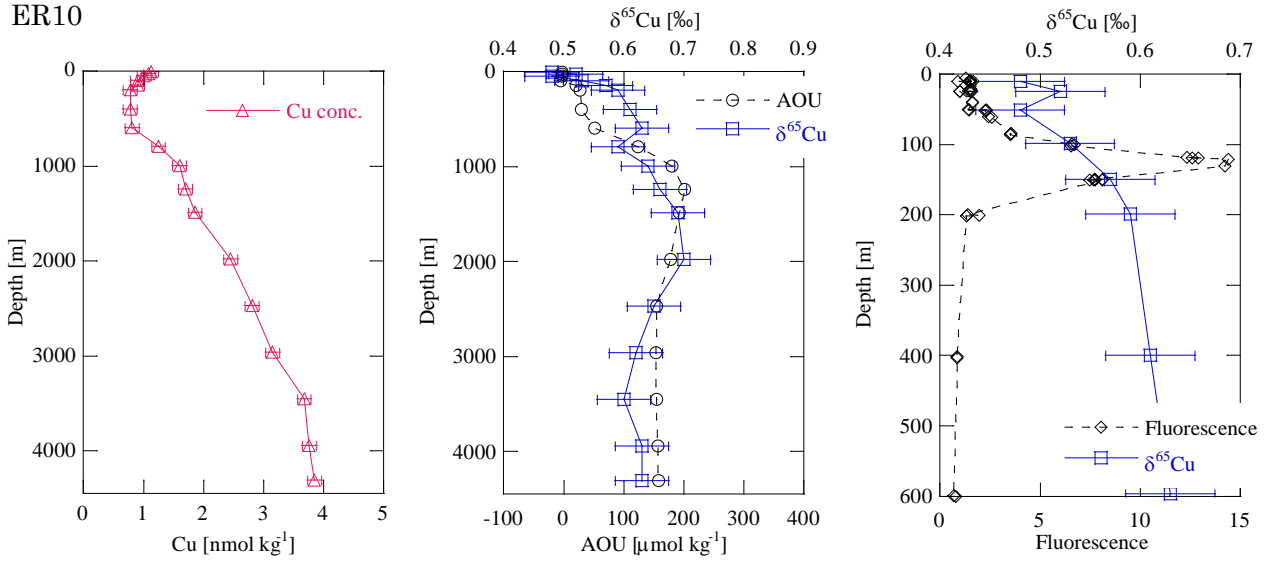
541 **Table 1** Rainwater analysis results

Sample <sup>a</sup>	Date	Cu [nmol kg <sup>-1</sup> ]	$\delta^{65}\text{Cu}$
Urban-1	3 Jul 2013	23.46	-0.12
Urban-2	20 Jun 2013	1.51	-0.08
Urban-3	26 Jun 2013	1.84	0.03
Rural-1	16 Jun 2013	1.12	-0.03
Rural-1	16 Jun 2013	1.14	-0.01
Rural-2	8 Jul 2013	2.60	0.03

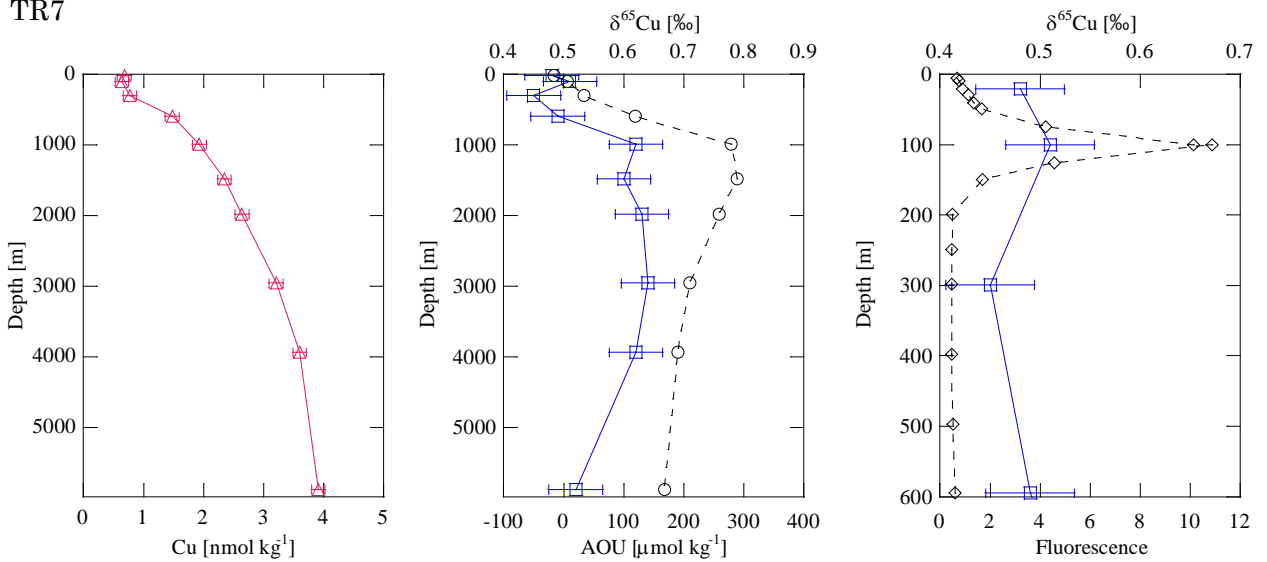
542 <sup>a</sup>‘Urban’ samples were collected on the roof of the main building on the Uji campus  
543 on Main Island, Japan. ‘Rural’ samples were collected at the top of Mt. Kajigamori  
544 on Sikoku Island, Japan.



ER10

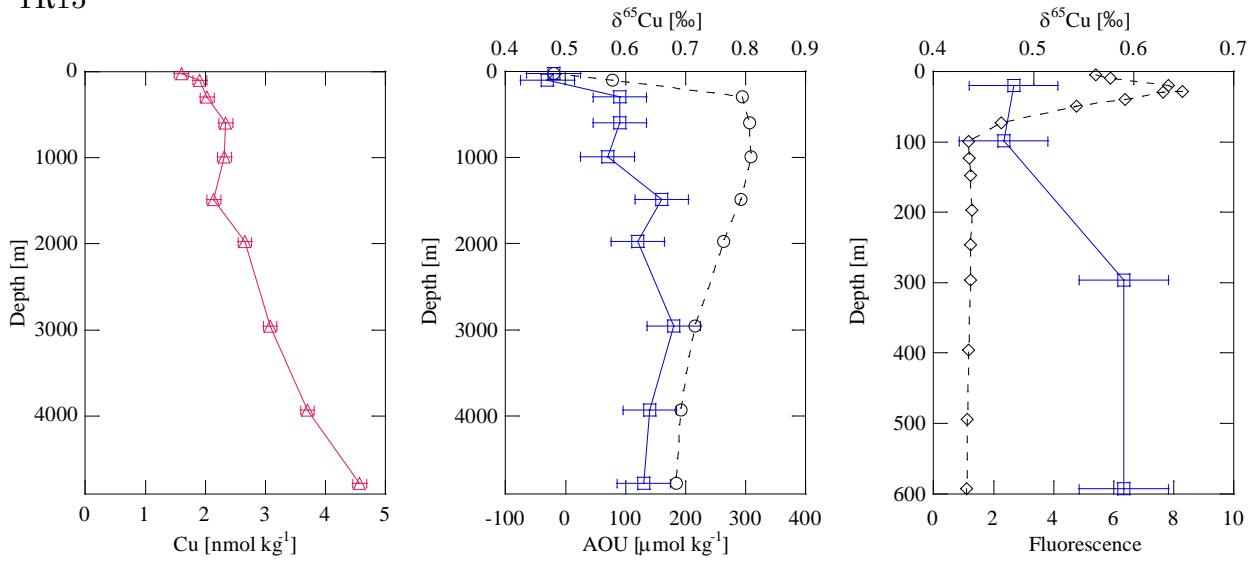


TR7

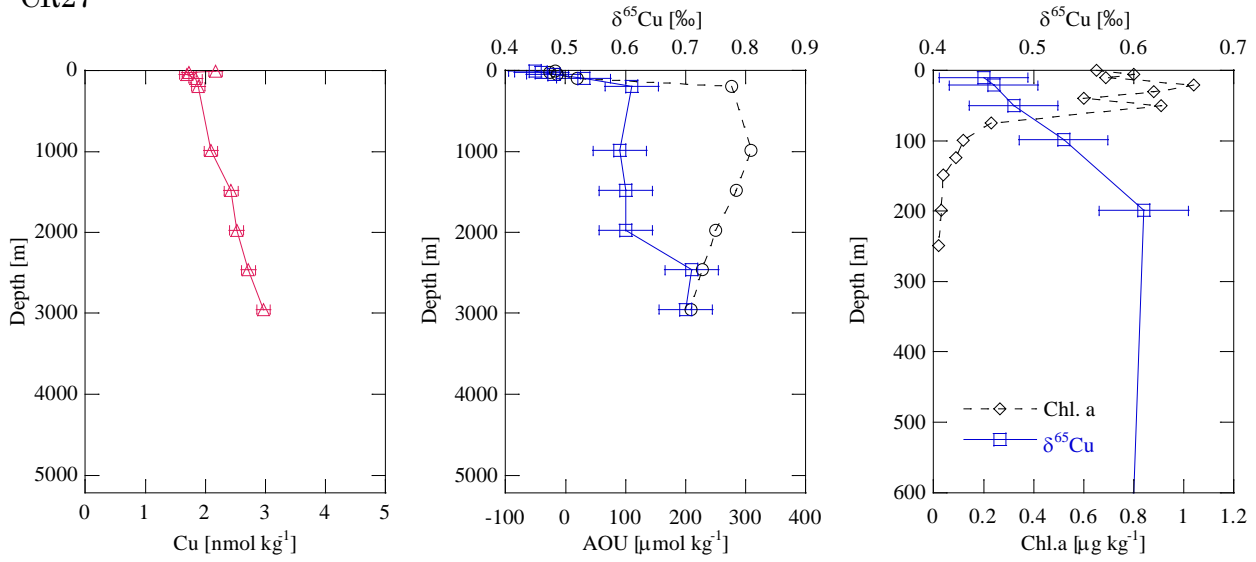


Supplementary Figure 1 Vertical profiles of Cu concentration,  $\delta^{65}\text{Cu}$ , apparent oxygen utilisation (AOU), and fluorescence or chlorophyll a (Chl. a) in the ocean. Magenta triangles indicate Cu concentration. Blue squares and black circles indicate  $\delta^{65}\text{Cu}$  and AOU, respectively. Black diamonds indicate Chl. a or fluorescence.

TR15

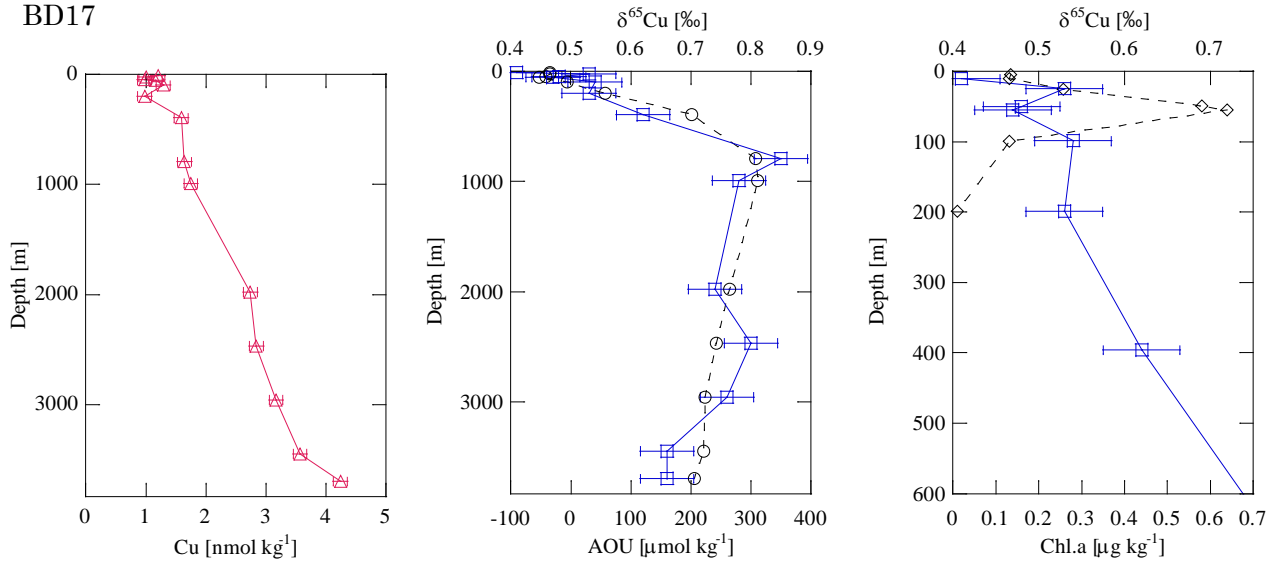


CR27

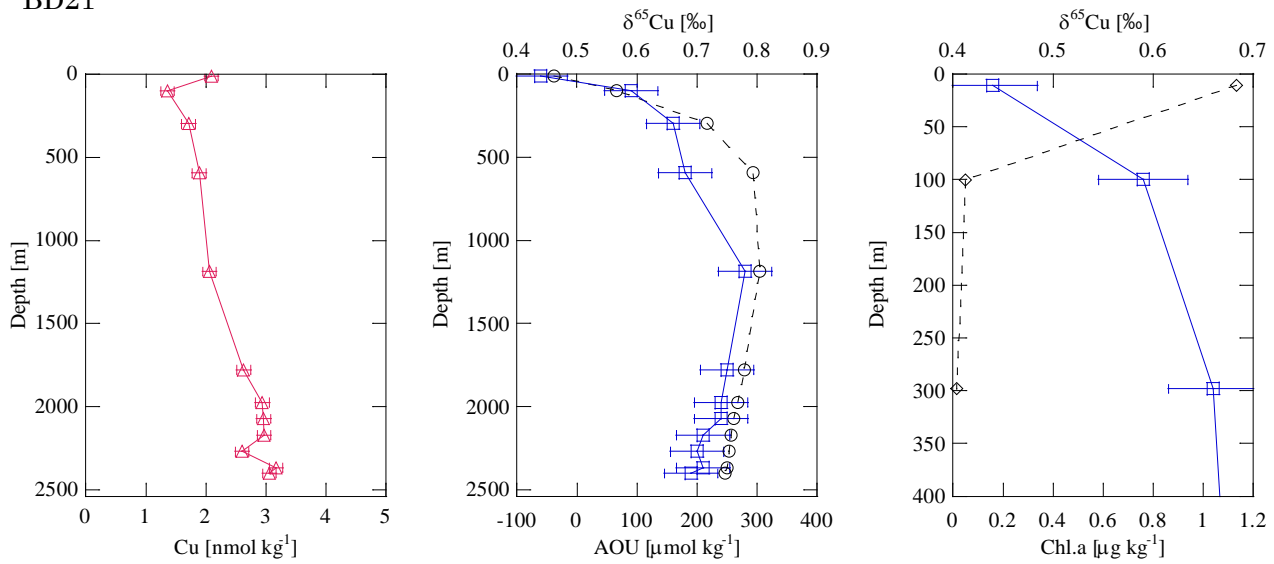


Supplementary Figure 1 (continued)

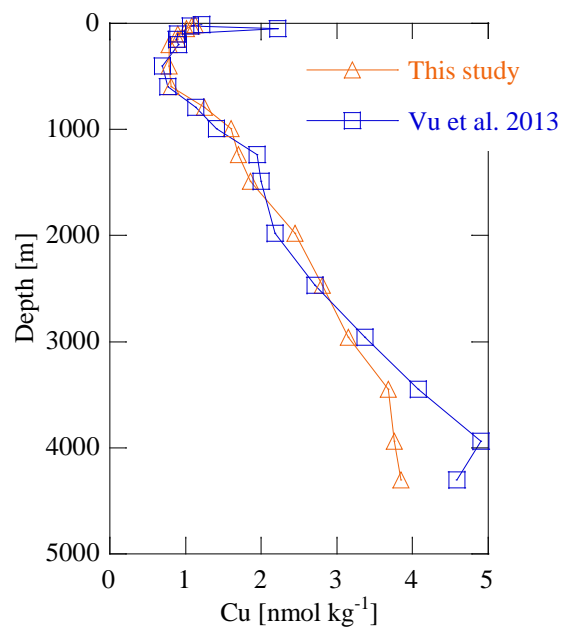
BD17



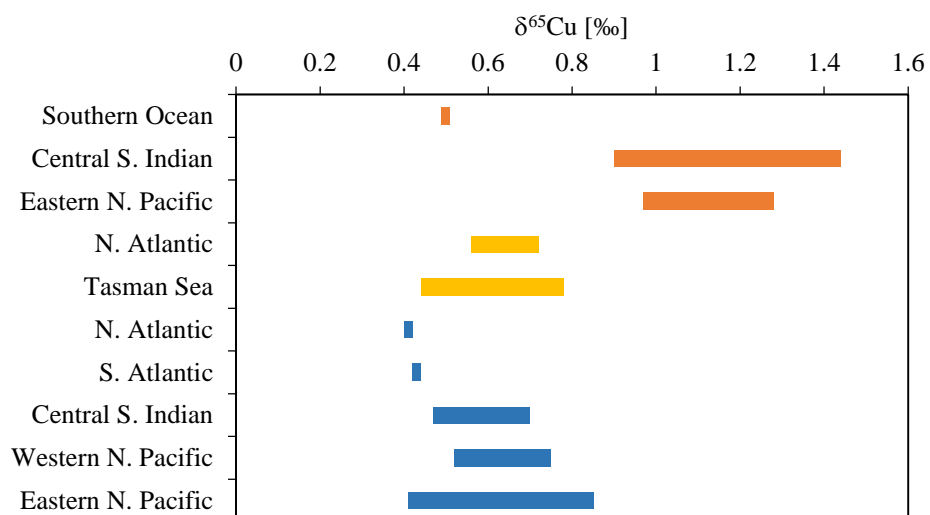
BD21



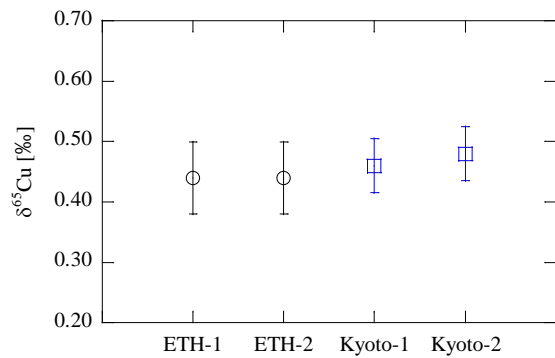
Supplementary Figure 1 (continued)



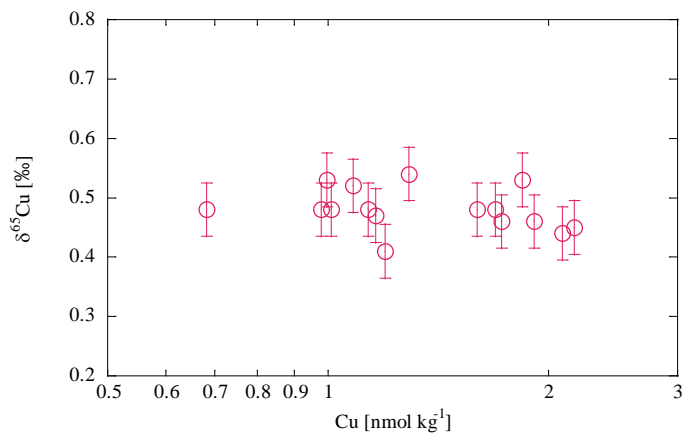
Supplementary Figure 2 Comparison of Cu concentration profiles at ER10 from a previous paper<sup>1</sup> and from this work. Blue squares and orange triangles represent data in the previous and present study, respectively.



Supplementary Figure 3 Comparison of dissolved  $\delta^{65}\text{Cu}$  ranges in seawater. Orange and yellow bars indicate the ranges reported by British (ETH at present)<sup>2,3</sup> and Australian groups<sup>4,5</sup>, respectively. Blue bars indicate those in this study.



Supplementary Figure 4 Intercalibration of  $\delta^{65}\text{Cu}$  in seawater between the method of the ETH group (black circles) and our method (blue squares). Uncertainties for the ETH methodology are based on repeated ( $n = 29$ ) analyses of a secondary Cu standard over a period of 6 months. The seawater sample collected at a 7145 m depth near the Japan Trench was divided into 4 aliquots and analysed in duplicate with each method. The results were found to be consistent within uncertainties.



Supplementary Figure 5 The correlation between  $\delta^{65}\text{Cu}$  and Cu concentration in the surface seawater (<100 m). Note that the horizontal axis is a logarithmic scale.

Supplementary Table 1 Seawater analysis results.

Depth [m]	First analysis		Second analysis		Average		2 s.d.	
	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg <sup>-1</sup> ]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg <sup>-1</sup> ]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg <sup>-1</sup> ]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg <sup>-1</sup> ]
<i>KH 11-7, TR7, 29.99N, 165.01E, depth 5883 m, 19 June 2011</i>								
21	0.48	0.68			0.48	0.68		
100	0.49	0.63	0.53	0.66	0.51	0.64	0.05	0.04
299	0.48	0.77	0.43	0.77	0.45	0.77	0.07	0.00
595	0.48	1.47	0.51	1.50	0.49	1.48	0.03	0.05
991	0.67	1.94	0.58	1.92	0.62	1.93	0.12	0.02
1484	0.60	2.35			0.60	2.35		
1979	0.63	2.68	0.62	2.59	0.63	2.64	0.02	0.12
2958	0.67	3.19	0.61	3.22	0.64	3.21	0.09	0.05
3938	0.62	3.66	0.61	3.54	0.62	3.60	0.01	0.18
5882	0.54	3.95	0.50	3.87	0.52	3.91	0.06	0.11
<i>KH11-7, TR15, 165.01°E, 51.00°N, depth 4802 m, 27 June 2011</i>								
20	0.46	1.59	0.50	1.61	0.48	1.60	0.06	0.03
99	0.46	1.90	0.46	1.93	0.46	1.91	0.00	0.04
296	0.61	2.03			0.61	2.03		
593	0.62	2.24	0.60	2.43	0.61	2.34	0.03	0.27
989	0.62	2.27	0.54	2.37	0.58	2.32	0.11	0.15
1482	0.70	2.25	0.62	2.02	0.66	2.14	0.12	0.32
1974	0.62	2.67			0.62	2.67		
2953	0.70	3.06	0.69	3.11	0.70	3.08	0.02	0.07
3929	0.65	3.51	0.67	3.90	0.66	3.70	0.04	0.54
4781	0.62	4.31	0.64	4.83	0.63	4.57	0.03	0.74
<i>KH11-7, TR17, 143.87°E, 37.81°N, depth 7150 m, 30 June 2011</i>								
7145	0.49	4.22	0.46	4.20	0.48	4.21	0.04	0.03



Supplementary Table 1 (continued)

Depth [m]	First analysis		Second analysis		Average		2 s.d.	
	$\delta^{65}\text{Cu}$	Cu	$\delta^{65}\text{Cu}$	Cu	$\delta^{65}\text{Cu}$	Cu	$\delta^{65}\text{Cu}$	Cu
	[‰]	[nmol kg <sup>-1</sup> ]	[‰]	[nmol kg <sup>-1</sup> ]	[‰]	[nmol kg <sup>-1</sup> ]	[‰]	[nmol kg <sup>-1</sup> ]
<i>KH-10-2, CR27, 159.99°E, 46.97°N, depth 5114 m, 29 June 2010</i>								
10	0.46	2.21	0.45	2.13	0.45	2.17	0.00	0.11
21	0.45	1.78	0.47	1.68	0.46	1.73	0.03	0.15
50	0.46	1.71	0.50	1.68	0.48	1.69	0.05	0.04
99	0.52	1.92	0.54	1.77	0.53	1.84	0.04	0.21
199	0.63	1.90	0.59	1.87	0.61	1.88	0.05	0.05
990	0.60	2.10	0.58	2.09	0.59	2.09	0.03	0.02
1483	0.62	2.41	0.58	2.46	0.60	2.43	0.06	0.07
1974	0.60	2.57	0.60	2.48	0.60	2.52	0.01	0.12
2464	0.70	2.72	0.71	2.72	0.71	2.72	0.01	0.01
2954	0.72	2.99	0.68	2.95	0.70	2.97	0.07	0.06
<i>KH-12-4, BD17, 132.40°W, 43.00°N, depth 3732 m, 27–28 September 2012</i>								
11	0.41	1.20			0.41	1.20		
25	0.53	1.00			0.53	1.00		
50	0.48	0.98			0.48	0.98		
55	0.47	1.16			0.47	1.16		
99	0.54	1.29			0.54	1.29		
199	0.53	0.98			0.53	0.98		
396	0.62	1.59			0.62	1.59		
792	0.85	1.64			0.85	1.64		
989	0.78	1.75			0.78	1.75		
1975	0.74	2.74			0.74	2.74		
2466	0.80	2.84			0.80	2.84		
2956	0.76	3.17			0.76	3.17		
3445	0.66	3.57			0.66	3.57		
3695	0.66	4.24			0.66	4.24		

Supplementary Table 1 (continued)

Depth [m]	First analysis		Second analysis		Average		2 s.d.	
	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg <sup>-1</sup> ]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg <sup>-1</sup> ]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg <sup>-1</sup> ]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg <sup>-1</sup> ]
<i>KH-12-4, BD21, 128.43°W, 48.45°N, depth 2438 m, 30 September–1 October</i>								
11	0.44	2.09			0.44	2.09		
100	0.59	1.36			0.59	1.36		
298	0.66	1.71			0.66	1.71		
594	0.68	1.89			0.68	1.89		
1186	0.78	2.06			0.78	2.06		
1777	0.75	2.63			0.75	2.63		
1974	0.74	2.94			0.74	2.94		
2071	0.74	2.96			0.74	2.96		
2170	0.71	2.97			0.71	2.97		
2268	0.70	2.60			0.70	2.60		
2366	0.71	3.17			0.71	3.17		
2399	0.69	3.06			0.69	3.06		

Supplementary Table 1 (continued)

Depth [m]	First analysis		Second analysis		Average		2 s.d.	
	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg <sup>-1</sup> ]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg <sup>-1</sup> ]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg <sup>-1</sup> ]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg <sup>-1</sup> ]
<i>KH-09-5, ER10, 72.55°E, 20.00°S, depth 4343 m, 11 December 2009</i>								
11	0.48	1.13	0.48	1.14	0.48	1.13	0.01	0.02
25	0.51	1.07	0.52	1.09	0.52	1.08	0.02	0.03
51	0.50	1.01	0.46	1.01	0.48	1.01	0.05	0.01
99	0.50	0.90	0.55	0.90	0.53	0.90	0.07	0.01
150	0.58	0.90	0.55	0.89	0.57	0.90	0.05	0.01
199	0.61	0.79	0.57	0.77	0.59	0.78	0.06	0.02
400	0.61	0.78			0.61	0.78		
597	0.63	0.81			0.63	0.81		
795	0.59	1.25			0.59	1.25		
993	0.64	1.60			0.64	1.60		
1240	0.66	1.70			0.66	1.70		
1486	0.69	1.86			0.69	1.86		
1979	0.70	2.45			0.70	2.45		
2470	0.65	2.81			0.65	2.81		
2962	0.62	3.15			0.62	3.15		
3452	0.60	3.68			0.60	3.68		
3941	0.63	3.76			0.63	3.76		
4306	0.63	3.85			0.63	3.85		
<i>BATS, 64.10°E, 31.40°N, depth 4500 m</i>								
2000	0.41	1.70			0.41	1.59		
<i>D357, #163, 13.39°E, 36.46°S, depth 4894 m</i>								
4723	0.44	2.87	0.42	2.89	0.43	2.88	0.03	0.01
Average					0.60	2.20	0.045	0.11
<i>n</i>					77	77	34	34

Supplementary Table 2 Box model for Cu cycling in the ocean<sup>a</sup>

			$\delta^{65}\text{Cu}$	Cu flux [ $10^9 \text{ mol y}^{-1}$ ]	
Surface seawater	Input	Atmospheric	0.00	0.96	
		Riverine	0.68	0.76	
		Upwelling	0.60	3.0	
[Cu] = 1.1 nmol kg <sup>-1</sup>					
$\delta^{65}\text{Cu} = 0.49$	Output	Downwelling	0.49	1.3	
		Particulate	0.49	3.4	
Deep seawater	Input	Downwelling	0.49	1.3	
		Benthic	0.58	3.7	
		Particulate	0.49	3.4	
[Cu] = 2.5 nmol kg <sup>-1</sup>					
$\delta^{65}\text{Cu} = 0.60$	Output	Upwelling	0.60	3.0	
		Particulate	0.49	5.4	
Scavenged Layer	Input	Particulate	0.49	5.4	
		Output	Benthic	0.58	3.7
			Preserved	0.30	1.7

<sup>a</sup> Black and magenta figures are the observed and calculated values, respectively.

## Supplementary Methods

### Intercalibration of seawater $\delta^{65}\text{Cu}$

We performed the intercalibration of  $\delta^{65}\text{Cu}$  with the ETH group using a seawater sample collected at a depth of 7145 m near the Japan Trench (TR17, 143.87°E, 37.81°N, bottom depth 7150 m). This sample was divided into 4 aliquots and analysed twice with both the methodology of the ETH group and our method. The obtained  $\delta^{65}\text{Cu}$  values were consistent between the ETH group and us, as shown in Supplementary Fig. 4.

The ETH group pre-concentrated Cu from seawater using a co-precipitation technique with  $\text{Al}(\text{OH})_3$ . The detail of this technique is described in Zhao et al. (2014)<sup>6</sup>. The pre-concentrated metal fraction was purified twice using anion exchange chromatography, as described in Archer and Vance (2004)<sup>7</sup>. The purified sample was oxidised by refluxing in  $\text{HNO}_3+\text{H}_2\text{O}_2$  (ref. 8). After evaporating the sample to dryness, the residue was re-dissolved with 2% nitric acid for isotopic measurements on a multi-collector ICP-MS. The setting of the multi-collector ICP-MS is detailed in Little et al. (2014)<sup>8</sup>.

## Supplementary References

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