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3 **Preferential preservation of pre-aged terrestrial organic carbon by**  
4 **reactive iron in estuarine particles and coastal sediments of a large**  
5 **river-dominated estuary**

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## Abstract

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27 Reactive iron ( $\text{Fe}_R$ ) plays an important role in the preservation of organic carbon (OC)  
28 in coastal sediments, yet changes in the OC bound to  $\text{Fe}_R$  (OC- $\text{Fe}_R$ ), during transport  
29 and deposition, remain poorly understood. The main goal of this work is to investigate  
30 the variation of the age and composition of OC- $\text{Fe}_R$  from estuarine suspended  
31 particulate matter (SPM) to coastal sediments, to further understand the role of  $\text{Fe}_R$  in  
32 the preservation of terrestrial OC exported from large rivers into marginal seas. We  
33 examined OC and its carbon isotopic composition ( $\Delta^{14}\text{C}_{\text{bulk}}$ ,  $\delta^{13}\text{C}_{\text{bulk}}$ ), specific surface  
34 area (SSA), grain size composition, lignin phenols,  $\text{Fe}_R$ , Mössbauer spectroscopy, and  
35 isotopic signatures of OC- $\text{Fe}_R$  ( $\Delta^{14}\text{C}_{\text{OC-Fe}_R}$ ,  $\delta^{13}\text{C}_{\text{OC-Fe}_R}$ ) in SPM and surface sediments  
36 of the Changjiang Estuary. Particulate OC (POC) and  $\text{Fe}_R$  concentrations in SPM are  
37 significantly higher than in surface sediments, with no significant differences between  
38 surface- and bottom-water SPM. This indicates that loss of OC and  $\text{Fe}_R$  largely occurs  
39 at the sediment-water interface due in part, to rapid Fe cycling. The percentage of OC-  
40  $\text{Fe}_R$  ( $f_{\text{OC-Fe}_R}$ ) in SPM ( $6.6 \pm 1.9\%$ ) is similar to that in mobile-mud sediment ( $8.8 \pm 1.8\%$ ).  
41 There are no significant differences in OC- $\text{Fe}_R$  content ( $p > 0.05$ ) from SPM to mobile-  
42 mud sediments, but non-OC- $\text{Fe}_R$  largely decreases, suggesting that terrestrial OC- $\text{Fe}_R$   
43 has greater stability compared to terrestrial non-OC- $\text{Fe}_R$ . Both  $\delta^{13}\text{C}_{\text{OC-Fe}_R}$  and  $\Delta^{14}\text{C}_{\text{OC-Fe}_R}$   
44  $\text{Fe}_R$  are lower than bulk OC, indicating that  $\text{Fe}_R$  is mainly associated with pre-aged soil  
45 OC of terrestrial plant origin, especially in estuarine SPM and mobile-mud sediments.  
46 Taken together, binding with  $\text{Fe}_R$  is a potential long-term protection mechanism for  
47 terrestrial OC. Both  $\Delta^{14}\text{C}_{\text{bulk}}$  and  $\Delta^{14}\text{C}_{\text{OC-Fe}_R}$  decrease with an increase in the ratio of  
48 hematite to (super)paramagnetic  $\text{Fe}^{3+}$ , indicating that high-crystallinity iron oxide is  
49 largely associated with pre-aged terrestrial OC, and there is a potential joint maturation  
50 mechanism between  $\text{Fe}_R$  and its associated OC. Based on literature comparisons of soils,

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51 estuarine SPM, and marine sediments, OC-Fe<sub>R</sub> associations are controlled mainly by  
52 sedimentary regimes, Fe<sub>R</sub> compositions, and OC sources. This work supports the notion  
53 that Fe<sub>R</sub> plays an important role in the stabilization and transport of river-derived  
54 terrestrial OC.

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56 **Keywords:** Changjiang Estuary; estuarine particles; mobile muds; reactive iron;  
57 organic carbon bound to reactive iron

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## 58 1. Introduction

59 Annually, global rivers transport ~170-200 Tg of particulate organic carbon (POC)  
60 to the ocean, but only ~40-75 Tg is preserved in marine sediments (Burdige, 2005;  
61 Ludwig et al. 1996; Schlünz and Schneider 2000). The fate of river-derived OC in the  
62 ocean is a key question in understanding globally important carbon sources and sinks  
63 in the coastal zone (Hedges and Keil, 1995; Blair and Aller, 2012; Bianchi et al., 2018).  
64 Organo-mineral association via mechanisms such as clay sorption and iron  
65 complexation is an important factor controlling OC preservation in marine sediments  
66 (Blattmann et al., 2019; Hemingway et al., 2019; Shields et al., 2017, 2019). Due to  
67 high specific surface area (SSA) and surface charges, reactive iron oxide ( $Fe_R$ ) is  
68 commonly associated with OC (Lalonde et al., 2012; Keil and Mayer, 2014; Shields et  
69 al. 2019). Here,  $Fe_R$  is defined as the iron phases that could be reduced by sodium  
70 dithionite, mainly including ferrihydrite, lepidocrocite, goethite, hematite, etc. (Barber  
71 et al., 2017; Lalonde et al., 2012; Poulton and Canfield, 2005; Zhao, et al., 2018a).  
72 Association between OC and  $Fe_R$  has been shown to occur via adsorption and  
73 coprecipitation (e.g., Chen et al., 2014; Eusterhues et al., 2014) and recent work shows  
74 that OC and  $Fe_R$  are associated via inner sphere complexation in coastal marine  
75 sediments (Barber et al., 2017), likely involving carboxyl ligand exchange (Chen et al.,  
76 2014; Curti et al., 2021, Zhao et al., 2022). Interestingly, recent work has shown that  
77 OC- $Fe_R$  associations persist for millennia in Arctic marine sediments (Faust et al., 2021).

78 The involvement of  $Fe_R$  in OC preservation in soils and marine sediments has been  
79 shown by many studies (Faust et al., 2021; Lalonde et al., 2012; Longman et al., 2022;  
80 Zhao et al., 2018a), but the factors controlling OC- $Fe_R$  preservation need to be better  
81 constrained. The binding capacity with OC varies among different iron oxides. For  
82 example, high SSA and low-crystallinity iron oxides (e.g., ferrihydrite) usually exhibit

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83 a higher affinity to OC, compared to high-crystallinity iron oxides, such as lepidocrocite,  
84 goethite, and hematite (Lv et al., 2016). Moreover, the OC bound to iron oxides varies  
85 in different sedimentary settings. Prior works indicate that OC-Fe<sub>R</sub> accounted for about  
86 15% to 20% of OC in soils and marine sediments (Lalonde et al., 2012; Longman et al.,  
87 2022; Wan et al., 2019; Zhao et al., 2018a). In some non-deltaic shelf and anoxic regions,  
88 more than 20% of sedimentary OC (SOC) is associated with Fe<sub>R</sub> (Ghaisas et al., 2021;  
89 Lalonde et al., 2012). However, only <10% of SOC is associated with Fe<sub>R</sub> in the sub-  
90 aqueous deltaic and mobile-muds sediments (Lalonde et al., 2012; Shields et al., 2016;  
91 Zhao et al., 2018a). Estuarine mobile muds are commonly located in the entry points of  
92 sediments to marginal seas (e.g., estuaries and inner shelves), and they are highly  
93 dynamic regions where tidal oscillations, sediment resuspension, and remobilization  
94 frequently occur, which can enhance SOC decomposition, through increased oxygen  
95 exposure time (e.g., reoxidation and repetitive redox successions) and priming effects  
96 via fresh algal OC (Aller et al., 1998; Bianchi, 2011; Blair and Aller, 2012; McKee et  
97 al., 2004). The composition of OC may also affect what types of OC-Fe<sub>R</sub> associations  
98 occur. For instance, vascular plant-derived aromatic and pyrogenic compounds appear  
99 to be preferentially bound to Fe-oxyhydroxides, in contrast to aliphatic acids (Christl  
100 and Kretzschmar, 2007; Riedel et al., 2012, 2013). The stable carbon isotopic  
101 composition of OC-Fe<sub>R</sub> ( $\delta^{13}\text{C}_{\text{OC-FeR}}$ ) is commonly higher than bulk OC over a wide  
102 range of marine sediments, indicating that Fe<sub>R</sub> is in favor of marine OC preservation  
103 (Lalonde et al., 2012). But deltaic sediments have lower  $\delta^{13}\text{C}_{\text{OC-FeR}}$  compared to  $\delta^{13}\text{C}$  of  
104 bulk OC ( $\delta^{13}\text{C}_{\text{bulk}}$ ), suggesting that Fe<sub>R</sub> in deltaic sediments is bound to more terrestrial  
105 OC (Lalonde et al., 2012; Shields et al., 2016; Sirois et al., 2018; Zhao et al., 2018a).  
106 Based on the radiocarbon age of OC-Fe<sub>R</sub> ( $\Delta^{14}\text{C}_{\text{OC-FeR}}$ ) and  $\delta^{13}\text{C}_{\text{OC-FeR}}$ , Fe<sub>R</sub> appears to  
107 protect thawed ancient terrestrial permafrost OC in the East Siberian Arctic Shelf,

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108 which weakens climate feedback - via degradation of thawed permafrost OC (Salvadó  
109 et al., 2015). Despite such efforts, the mechanisms that control the age and composition  
110 of OC-Fe<sub>R</sub> from the river to the ocean remain poorly constrained.

111 The Changjiang (Yangtze River) is the largest river in China and delivers large  
112 amounts of terrestrial-derived suspended particulate matter (SPM), rich in OC and Fe<sub>R</sub>  
113 relative to coastal sediments, to the Changjiang Estuary and adjacent East China Sea  
114 (ECS) shelf (Milliman and Farnsworth, 2011; Wang et al., 2012; Zhu et al., 2012; Zhao  
115 et al., 2021a). A previous study revealed a positive correlation between burial efficiency  
116 (percentage of OC preserved) of terrestrial OC and net sediment accumulation rate over  
117 a range of marine environments (Canfield et al., 1994). However, the preservation  
118 efficiency of terrestrial OC in the Changjiang Estuary is lower (< 30%) than other  
119 sedimentary regimes with similar high sedimentation rates, due largely to processes  
120 associated with mobile/fluidized muds (Blair and Aller, 2012; Yao et al., 2014; Zhao et  
121 al., 2021a). Terrestrial OC is continually decomposed and aged in multiple re-  
122 suspension-deposition loops during sediment mobilization in mobile muds (Bao et al.,  
123 2016, 2019a; Zhao et al., 2021a). Large inputs of Fe<sub>R</sub>, coupled with frequent physical  
124 reworking, result in rapid iron redox cycling, which is considered the primary  
125 diagenetic pathway in the Changjiang Estuary mobile muds (Zhao et al., 2017, 2018b).  
126 These mobile muds have higher OC and Fe<sub>R</sub> contents relative to the ECS shelf, but the  
127 fraction of OC-Fe<sub>R</sub> to bulk OC ( $f_{\text{OC-FeR}}$ ) is low (Zhao et al., 2018a). One possible  
128 explanation is that rapid iron redox cycling in the estuary prevents Fe<sub>R</sub> from binding  
129 with marine OC (Zhao et al., 2018a). However, it is still unclear whether the low  $f_{\text{OC-Fe}}$   
130 in estuarine sediments is because OC-Fe<sub>R</sub> is continually reduced in this highly dynamic  
131 sedimentary environment, or because the  $f_{\text{OC-FeR}}$  in estuarine SPM is inherently low. In  
132 addition, the variation of carbon isotopic composition of OC-Fe<sub>R</sub> from estuarine SPM

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133 to coastal sediments is also unknown. In this study, we analyzed  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  of OC-  
134  $\text{Fe}_\text{R}$ , as well as Fe phases, in estuarine SPM and coastal sediments of the Changjiang  
135 Estuary. Compared with previous work in this region (Ma et al., 2018; Sun et al., 2020;  
136 Wan et al., 2019; Zhao et al., 2018a), this is the first report of such data in estuarine  
137 particles. The overarching objective of this work is to build on previous studies and  
138 trace the variation of the age and composition of OC- $\text{Fe}_\text{R}$  from estuarine SPM to coastal  
139 sediments, to better understand the role of  $\text{Fe}_\text{R}$  in the preservation of terrestrial OC  
140 exported from large rivers into marginal seas. This is also the first study to examine the  
141 linkages between carbon isotopic compositions of OC- $\text{Fe}_\text{R}$  and iron phases from  
142 drainage basin soils to estuarine particles and coastal sediments, using state-of-the-art  
143 techniques for both Fe oxides and OC compositional analyses.

144

## 145 **2. Materials and Methods**

### 146 **2.1 Study area**

147 The ECS shelf is a shallow and broad epi-continental shelf (Blair and Aller, 2012).  
148 Annually, it can receive a large number of terrestrial particles from Changjiang, which  
149 is ranked as the fourth largest sediment flux in the world ( $\sim 4.8 \times 10^8$  t/year) (Milliman  
150 and Farnsworth, 2011). During river SPM transportation, coarse-grained particles  
151 preferentially are deposited in riverbeds but fine-grained particles can be transported to  
152 mobile muds and even ECS shelf regions (Guo et al., 2018; Sun et al., 2021). The bed  
153 load results in the accumulation of coarse-grained sediments in the inner estuary (Chen  
154 et al., 1999; Wu et al., 2009). Once these terrestrial particles enter the coastal ocean,  
155 most of them are “trapped” and subjected to long-term hydrodynamic sorting and  
156 reworking processes in Changjiang estuary mobile muds (CEMM) and Zhe-Min coast  
157 mobile muds (ZMMM) along the coast (Liu et al., 2006; Xu et al., 2015; Zhao et al.,

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158 2021a) (Figure 1a). The CEMM are characterized by high sedimentation rates (1-3 cm  
159 yr<sup>-1</sup>), shallow water depths, frequent physical reworking, and large terrestrial inputs (Xu  
160 et al., 2015; Yao et al., 2014; Zhao et al., 2018b). Although most of the Changjiang-  
161 derived sediment is transported to the south, a small fraction of the terrestrial SPM from  
162 the Changjiang is exported to the ECS shelf by cross-shelf transport (Iseki et al., 2003;  
163 Kao et al., 2003; Oguri et al., 2003). For the ECS shelf, sediments are dominated by  
164 relict sands, which are believed to be deposited during the Late Pleistocene when the  
165 sea level was low (Zhu et al., 2011). The ECS shelf is characterized by lower  
166 sedimentation rates (<0.5 cm/yr) and inputs of terrestrial OC compared to CEMM due  
167 to the barrier of the northward flowing Taiwan Warm Current (TWWC) (Liu et al.,  
168 2006). Nevertheless, most of the clay minerals, iron oxides, and terrestrial OC in ECS-  
169 shelf sediments are derived from Changjiang (Eisma et al., 1995; Li et al., 2014; Zhu et  
170 al., 2012).

171

## 172 2.2 Samples and data collection

173 Eleven SPM samples from the surface and bottom waters (< 2 m above the seabed)  
174 along the salinity gradient from *Xuliujing* (C1) (salinity ~0) in the inner estuary to the  
175 seaward side of the Changjiang Estuary (A6-5), were collected in July 2018 using a  
176 CTD-rosette water sampler (Seabird 911 Plus, USA) onboard the *R/V Chuangxin 2*  
177 (Figure 1b). In-situ salinity in the water column was also measured by this CTD-rosette  
178 system from C1 to A6-10 along this river-estuary shelf transect (Figure 1b). After  
179 collection, these water samples were filtered immediately through pre-combusted  
180 (550 °C for 5 h) and pre-weighed Whatman GF/F filters (0.7 µm nominal pore size),  
181 and the filters were wrapped in pre-combusted aluminum foil and stored at -20°C. Prior  
182 to chemical analyses, these filters were weighed again in the lab after freeze-drying to



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183 calculate the SPM concentrations. Eleven surface sediments (0-3 cm in depth) in the  
184 Changjiang Estuary were collected using a box core sampler during the same cruise.  
185 For avoiding disturbance, only the samples having an undisturbed sediment surface and  
186 clear overlying water were used for surface sediment sampling. All sediments were also  
187 stored frozen at -20°C prior to freeze-drying and further analyses.

188 Previous measurements of OC,  $\delta^{13}\text{C}_{\text{bulk}}$ ,  $\text{Fe}_R$ , OC- $\text{Fe}_R$ , and  $\delta^{13}\text{C}_{\text{Fe-OC}}$  in arable soils  
189 in northern and eastern China and ZMMM sediments (Wan et al., 2019; Zhao et al.,  
190 2018a), were incorporated into our regional analyses. For soils, only sampling sites in  
191 the Changjiang basin ( $n = 7$ ) were incorporated in this study (Wan et al., 2019). In  
192 addition, a global dataset on OC- $\text{Fe}_R$  across different sedimentary regimes was also  
193 incorporated into our analyses for a better understanding of the role of  $\text{Fe}_R$  in OC  
194 preservation in both land and ocean.

195

### 196 **2.3 Specific surface area and grain size composition**

197 Both SSA and grain size composition of SPM and surface sediments in the  
198 Changjiang Estuary were determined following the method of Yao et al. (2014). Briefly,  
199 SSA was determined by a 5-point BET method using an automatic surface area analyzer  
200 (3H-2000PH4, Beishide Instrument-ST Co., China) after removing organic matter  
201 (350°C for 12 h). The relative standard deviation of the duplicate samples for SSA  
202 analyses is less than 3% ( $n = 6$ ). Grain size composition was analyzed using a laser  
203 Particle Size Analyzer (MS 2000, Malvern, UK). Particle sizes were separated into the  
204 following three groups: clay (<4  $\mu\text{m}$ ), silt (4–63  $\mu\text{m}$ ), and sand (>63  $\mu\text{m}$ ). The relative  
205 standard deviation of duplicate samples is less than 3% ( $n = 6$ ).

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## 207 **2.4 Organic carbon and its isotopic compositions ( $\delta^{13}\text{C}_{\text{bulk}}$ and $\Delta^{14}\text{C}_{\text{bulk}}$ )**

208 The OC contents and  $\delta^{13}\text{C}_{\text{bulk}}$  of SPM and surface sediments were measured using  
209 an elemental analyzer (Vario MICRO cube EA, Elementar, Germany), interfaced to a  
210 continuous flow isotope ratio mass spectrometer (Isoprime IRMS, Elementar, Germany)  
211 after removing the carbonates via acid fumigation (Wang et al., 2015). Briefly, ~30 mg  
212 of freeze-dried particles or sediments in silver capsules was acidified with a 12 M HCl  
213 vapor bath for 12 h to remove carbonates, and then dried in an oven at 60°C and crimp-  
214 sealed in tin capsules prior to analysis. The analytical precisions for OC and  $\delta^{13}\text{C}$  are  $\pm$   
215 0.02 wt% and  $\pm 0.05\%$  based on duplicate analyses ( $n = 6$ ), respectively. Selected SPM  
216 and sediment samples were oxidized using the quartz tube oxidation method for  $^{14}\text{C}$   
217 analysis (Ge et al., 2020). Radiocarbon was determined using Accelerator Mass  
218 Spectrometry (AMS) after the graphitization of  $\text{CO}_2$  at the Qingdao National  
219 Laboratory for Marine Science and Technology (QNLN) in China. Radiocarbon results  
220 are measured as fraction modern ( $F_m$ ), and the  $\Delta^{14}\text{C}$  values and conventional  
221 radiocarbon ages (years before present) are calculated based on Stuiver and Polach  
222 (1977). The analytical precision for  $\Delta^{14}\text{C}$  measurements is generally  $<5\%$ .

223

## 224 **2.5 Analyses of $\text{Fe}_R$ and OC- $\text{Fe}_R$**

225  $\text{Fe}_R$  and OC- $\text{Fe}_R$  were determined using the bicarbonate-citrate buffered dithionite  
226 (BCD) reduction method according to Lalonde et al. (2012). Briefly, sediments (~ 1g  
227 dry weight) were freeze-dried, ground, and then extracted at 80°C for 15 min. in a  
228 solution of sodium dithionite, trisodium citrate, and sodium bicarbonate. The resulting  
229 suspension was centrifuged for 10 min. at 3000 rpm after extraction and rinsed three  
230 times with artificial seawater. The supernatant and rinsed water were acidified ( $\text{pH} < 2$ )  
231 and preserved at 4°C for Fe measurement. Before measurement, these water samples

232 were centrifuged again to remove fine particles. Dissolved Fe in the supernatant and  
 233 rinsed water was measured on 1:20 diluted aliquots in nitric acid (2%) using  
 234 inductively-coupled plasma optical emission spectrometer (ICP-OES) (iCAP6300,  
 235 Thermo Fisher Scientific., USA). The reported precision for dissolved Fe in duplicate  
 236 samples was less than 2% (Zhao et al., 2017). The residual sediments were freeze-dried  
 237 before analyzing OC,  $\delta^{13}\text{C}$ , and  $\Delta^{14}\text{C}$ . A control experiment was carried out before the  
 238 extraction experiment to correct for the OC removed due to the conditions of the  
 239 extraction (e.g., pH, ionic strength, physical mixing, and heat) (OC not associated with  
 240  $\text{Fe}_R$ ) without the dithionite reducing agent. In the control experiment, all samples were  
 241 extracted under the same protocol but using sodium chloride to replace the sodium  
 242 dithionite.

243  $\text{Fe}_R$  and OC- $\text{Fe}_R$  were calculated by the following equations:

$$244 \quad \text{Fe}_R (\mu\text{mol/g}) = (\text{Fe}_{\text{extract}} - \text{Fe}_{\text{control}}) \times V/M \quad (1)$$

$$245 \quad \text{OC-Fe}_R (\text{wt}\%) = (\text{OC}_{\text{control}} - \text{OC}_{\text{extract}}) \quad (2)$$

$$246 \quad f_{\text{OC-Fe}_R} (\%) = (\text{OC}_{\text{control}} - \text{OC}_{\text{extract}}) / \text{OC}_{\text{bulk}} \quad (3)$$

247 where,  $f_{\text{OC-Fe}_R} (\%)$  is the percentage of OC bound to  $\text{Fe}_R$ ;  $\text{Fe}_{\text{control}}$  and  $\text{OC}_{\text{control}}$  are Fe  
 248 content in the supernatant and rinsed water and OC content after the control experiment,  
 249 respectively; V is the volume of the supernatant and rinsed water and M is the mass of  
 250 sample;  $\text{Fe}_{\text{extract}}$  is Fe content in the supernatant and rinsed water and  $\text{OC}_{\text{extract}}$  is OC  
 251 content after the extraction experiment;  $\text{OC}_{\text{bulk}}$  is the total OC in bulk sediment.

252 The  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  signatures of OC- $\text{Fe}_R$  ( $\delta^{13}\text{C}_{\text{Fe-OCR}}$  and  $\Delta^{14}\text{C}_{\text{Fe-OCR}}$ ) were  
 253 calculated by the following equations:

$$254 \quad \delta^{13}\text{C}_{\text{OC-Fe}_R} (\text{‰}) = (\delta^{13}\text{C}_{\text{control}} \times \text{OC}_{\text{control}} - \delta^{13}\text{C}_{\text{extract}} \times \text{OC}_{\text{extract}}) / (\text{OC}_{\text{control}} - \text{OC}_{\text{extract}}) \quad (4)$$

$$255 \quad \Delta^{14}\text{C}_{\text{OC-Fe}_R} (\text{‰}) = (\Delta^{14}\text{C}_{\text{control}} \times \text{OC}_{\text{control}} - \Delta^{14}\text{C}_{\text{extract}} \times \text{OC}_{\text{extract}}) / (\text{OC}_{\text{control}} - \text{OC}_{\text{extract}}) \quad (5)$$

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256 where  $\delta^{13}\text{C}_{\text{control}}$  and  $\Delta^{14}\text{C}_{\text{control}}$  are isotopic signatures of the OC after the control  
257 experiment;  $\delta^{13}\text{C}_{\text{extract}}$  and  $\Delta^{14}\text{C}_{\text{extract}}$  are isotopic signatures of the OC after the  
258 extraction experiment.

259

## 260 **2.6 Mössbauer spectroscopy**

261 The proportion of different iron oxides could be obtained through the subspectral  
262 area ratio in Mössbauer spectra. Selected SPM and sediment samples were analyzed for  
263 Mössbauer Spectroscopy at the Center for Advanced Mössbauer Spectroscopy at the  
264 Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Room temperature  
265 (295 K)  $^{57}\text{Fe}$  Mössbauer spectra were recorded using a proportional counter and a  
266 Mössbauer Spectrometer (MFD-500AV-02, Topologic Systems, Japan). A  $^{57}\text{Co}$  (Rh)  
267 was used as the  $\gamma$ -ray radioactive source. Spectra were calibrated against a measurement  
268 of standard  $\alpha$ -Fe foil at room temperature and evaluated using Lorentzian line profiles  
269 by the software MossWinn 3.0i. Iron oxides and other Fe-bearing mineral phases were  
270 identified on the basis of their Mössbauer parameters: isomer shift (IS), quadrupole  
271 splitting (QS), and magnetic hyperfine field (Bhf) (Dyar et al., 2006).

272

## 273 **2.7 Lignin phenols**

274 Lignin phenols are used as biomarkers for quantifying the contribution of  
275 terrigenous vascular plant tissues in bulk samples. Twelve lignin phenol oxidation  
276 products were quantified and analyzed using the alkaline CuO method, including three  
277 vanillyl phenols [V=vanillin (VAL) + acetovanillone (VON) + vanillic acid (VAD)],  
278 three syringyl phenols [S= syringaldehyde (SAL) + acetosyringone (SON) + syringic  
279 acid (SAD)], two cinnamyl phenols [C = p-coumaric acid (CAD) + ferulic acid (FAD)],  
280 three p-hydroxybenzenes [P = p-hydroxybenzaldehyde (PAL) + p-

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281 hydroxyacetophenone (PON) + p-hydroxybenzoic acid (PAD)], and 3,5-  
282 dihydroxybenzoic acid (3,5-Bd)] (Hedges and Ertel, 1982; Hedges and Mann, 1979).  
283 Briefly, powdered freeze-dried sediments containing ca. 3-5 mg OC were placed in a  
284 stainless-steel reaction vessel with  $330 \pm 4$  mg CuO and 2.5 mL of 2 M NaOH in a  
285 nitrogen glove box. Each sealed vessel was digested for 3 h at 150 °C. Then, 50  $\mu$ L of  
286 ethyl vanillin (EVAL) was added to each reaction vessel as an internal standard before  
287 the aqueous reaction products were separated from the sediments by centrifugation. The  
288 supernatant was acidified with HCl to pH < 2, extracted using ethyl acetate 3 times, and  
289 dried under a gentle N<sub>2</sub> stream. The oxidation products were derivatized with N, O-Bis-  
290 (trimethylsilyl)-trifluoroacetamide (BSTFA) for 1 h, and then, the derivatives were  
291 measured using an Agilent 7890A gas chromatography-flame ionization detector (GC-  
292 FID). The identification and quantification of lignin phenols were based on the recovery  
293 of an internal standard (EVAL) and an absolute recovery (methyl 3,4-  
294 dimethoxybenzoate), and a mixture of lignin-phenol standards containing known  
295 amounts of compounds of interest.  $\Sigma_8$  (mg/g dry sediment) and  $\Lambda_8$  (mg/100 mg OC) are  
296 used as indicators of lignin concentrations, which is the total weight of the 8 lignin  
297 phenols (V+S+C) normalized to 1 g dry sediment and 100 mg OC, respectively. The  
298 acid-to-aldehyde ratios of V and S [(Ad/Al)<sub>v</sub> and (Ad/Al)<sub>s</sub>] phenols are used as  
299 indicators for lignin oxidative degradation (Hedges et al., 1988). The P/(S + V) ratio is  
300 used as a specific indicator of the degradation state of lignin side chains by brown-rot  
301 fungi (Dittmar and Lara, 2001). The 3,5-Bd/V ratio is considered to be an indicator of  
302 OC oxidation in soils (Houel et al., 2006). Higher values of these indicators suggest  
303 stronger oxidative degradation of lignin phenols (Dittmar and Lara, 2001; Hedges et al.,  
304 1988; Houel et al., 2006).

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## 306 **2.8 Statistical analyses**

307 Statistical analyses in this study were performed using SPSS 22 software.  
308 Correlations between the measured parameters were determined by Pearson correlation  
309 analysis with a two-tailed test. Significant statistical differences, based on 95%  
310 confidence intervals, were examined using a one-way analysis of variance (ANOVA)  
311 and *t*-test. The K-means Clustering Analysis can divide a given data set into a set of *k*  
312 groups (i.e. *k* clusters) in which each observation belongs to the cluster with the nearest  
313 mean, and is used to divide surface sediments into the different sedimentary regimes.

314

## 315 **3. Results**

### 316 **3.1 Hydrological characteristics and different sedimentary regimes**

317 The salinity increases from 0 at C1 in the inner estuary to 34.5 at A6-10 in the ECS  
318 shelf, with a rapid increase in the estuarine mixing zone from C7 to A6-2 ([Figure S1](#)).  
319 At most sampling sites, the salinity in the bottom water is higher than that in surface  
320 water ([Figure S1](#)). The SPM concentration ranges from 47.6 to 248 mg/L with the  
321 highest SPM concentration (>200 mg/L) at A6-1, ~120km away from the estuary  
322 ([Figure S1](#)). In the estuarine mixing zone (from C7 to A6-2), the SPM concentration in  
323 bottom waters is higher than that in surface waters ([Figure S1](#)). The SSA values range  
324 from 16.2 at A6-5S to 25.6 m<sup>2</sup>/g at C8B in SPM samples (here S and B represent SPM  
325 samples in surface water and bottom water, respectively) ([Figure 2a](#)). In surface  
326 sediments, the SSA values largely range from 2.3 to 24.0 m<sup>2</sup>/g, with the highest and  
327 lowest values in estuarine mobile muds and ECS shelf sediments, respectively ([Figure](#)  
328 [2a and Table S2](#)). The median grain size (MGS) in SPM samples varies from 6.37 μm  
329 to 15.4 μm with an average of 7.96 ± 2.71 μm, which is similar to mobile-mud  
330 sediments but lower than that in the inner estuary and ECS shelf ([Tables S1 and S2](#)).

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331 Clays and silts are the dominant size fractions (> 70 wt%) in SPM samples and estuarine  
332 mud sediments, while sands are dominant in ECS-shelf and inner-estuary sediments (>  
333 65 wt%) (Figure 2b and Table S1).

334 The surface sediments are categorized into the following three sedimentary  
335 regimes based on different sedimentary environments and bulk properties: inner estuary  
336 (C1, C2, and A6-1), mobile muds (A6-2, A6-3, A6-5, and A6-6), and ECS shelf (A6-7,  
337 A6-8, A6-9, and A6-10). These three different sedimentary regimes are supported by  
338 K-means Clustering Analysis based on water depth, salinity, SSA, and grain size  
339 composition. The water salinity of the inner estuary is typically less than 10, and the  
340 MGS of the sediments is usually higher than 100  $\mu\text{m}$  (Figure S1 and Table S1). The  
341 water salinity of the mobile mud is in the range of 10-30, and the MGS of the mobile-  
342 mud sediment is less than 10  $\mu\text{m}$  (Figure S1 and Table S2). The water salinity of the  
343 ECS shelf is higher than 30, and the MGS of the ECS-shelf sediment is also higher than  
344 100  $\mu\text{m}$  (Figure S1 and Table S2). The water depth in the inner estuary and mobile mud  
345 (< 25 m) is lower than that in the ECS shelf (> 45 m) (Table S2).

346

### 347 **3.2 Bulk organic carbon and its carbon isotopic composition of SPM and surface** 348 **sediments**

349 The POC contents in SPM are significantly higher than SOC in sediments ( $0.87 \pm$   
350  $0.19$  wt% vs.  $0.34 \pm 0.19$  wt%) ( $p < 0.05$ ) (Figure 2c and Table S1). Mobile-mud  
351 sediments have higher SOC content relative to sediments in the inner estuary and ECS  
352 shelf (Figure 2c and Table S2). The average OC/SSA ratio ( $0.28 \pm 0.04$  mg OC/m<sup>2</sup>) in  
353 mobile-mud sediments is significantly lower than those of SPM ( $0.41 \pm 0.11$  mg  
354 OC/m<sup>2</sup>), the inner-estuary ( $0.45 \pm 0.20$  mg OC/m<sup>2</sup>) and ECS-shelf sediments ( $0.67 \pm$   
355  $0.16$  mg OC/m<sup>2</sup>). SOC has a significantly higher average  $\delta^{13}\text{C}$  value ( $-22.4 \pm 1.2$  ‰)

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356 ( $p < 0.05$ ) than POC ( $-24.2 \pm 1.2 \text{ ‰}$ ) (Figure 2e). There are no significant differences  
357 ( $p > 0.05$ ) in grain size, SSA, OC content, OC/SSA ratio, and  $\delta^{13}\text{C}$  between surface and  
358 bottom SPM samples, and only  $\Delta^{14}\text{C}$  values for surface SPM samples are determined  
359 (Figure 3). The  $\Delta^{14}\text{C}$  values of POC increase with salinity and ranged from  $-360\text{‰}$  to -  
360  $246\text{‰}$ , with an average radiocarbon age of  $2950 \pm 470 \text{ yr}$  (Figure 3f and Table S1). The  
361  $\Delta^{14}\text{C}$  values of SOC range from  $-816\text{‰}$  to  $-312\text{‰}$  and the average radiocarbon age in  
362 SOC in the inner estuary ( $9610 \pm 3480 \text{ yr}$ ) is older than those in mobile muds ( $3260 \pm$   
363  $350 \text{ yr}$ ) and the ECS shelf ( $3350 \text{ yr}$ ) (Figure 2f and Table S2).

364

### 365 **3.3 OC-Fe<sub>R</sub> associations in SPM and surface sediments**

366  $\text{Fe}_R$ , OC- $\text{Fe}_R$  content, non-OC- $\text{Fe}_R$  content,  $f_{\text{OC-Fe}_R}$ , OC- $\text{Fe}_R/\text{Fe}_R$  ratios,  $\delta^{13}\text{C}_{\text{OC-Fe}_R}$ ,  
367 and  $\Delta^{14}\text{C}_{\text{OC-Fe}_R}$  values in SPM samples and surface sediments of the Changjiang Estuary  
368 are shown in Table S3. The  $\text{Fe}_R$  contents in surface sediments are significantly lower  
369 than those in SPM samples ( $p < 0.01$ ), ranging from  $28.0$  to  $162.7 \text{ } \mu\text{mol/g sed.}$ , with  
370 higher values in mobile muds and lower values in the inner estuary and ECS shelf  
371 (Figure 3a). The OC- $\text{Fe}_R$  content in SPM samples ranges from  $0.03$  to  $0.08 \text{ wt\%}$ , which  
372 is very close to that in mobile-mud sediments ( $0.05 \pm 0.01 \text{ wt\%}$ ) but generally higher  
373 than those in inner-estuary ( $0.02 \pm 0.01 \text{ wt\%}$ ) and ECS-shelf sediments ( $0.04 \pm 0.01$   
374  $\text{wt\%}$ ) ( $p < 0.05$ ) (Table S3). The non-OC- $\text{Fe}_R$  content in SPM samples ranges from  $0.64$   
375 to  $1.19 \text{ wt\%}$ , which is significantly higher than those in mobile-mud ( $0.51 \pm 0.04 \text{ wt\%}$ ),  
376 inner-estuary ( $0.10 \pm 0.06 \text{ wt\%}$ ) and ECS-shelf sediments ( $0.24 \pm 0.04 \text{ wt\%}$ ) ( $p < 0.05$ )  
377 (Table S3). Fractions of OC- $\text{Fe}_R$  in bulk OC ( $f_{\text{OC-Fe}_R}$ ) in SPM samples ( $6.6 \pm 1.9\%$ ) are  
378 similar to those in mobile-mud sediments ( $8.8 \pm 1.8\%$ ) but significantly lower than  
379 inner-estuary ( $20.0 \pm 5.0\%$ ) and ECS-shelf sediments ( $14.1 \pm 3.3\%$ ) ( $p < 0.05$ ) (Figure  
380 3c and Table S3). Molar ratios of OC- $\text{Fe}_R$  to total  $\text{Fe}_R$  (OC- $\text{Fe}_R/\text{Fe}_R$ ) are generally low



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381 in SPM samples ( $0.20 \pm 0.06$ ), inner-estuary sediment ( $0.23 \pm 0.08$ ), and mobile-mud  
382 sediment ( $0.30 \pm 0.10$ ), but higher values in ECS-shelf sediment ( $0.79 \pm 0.39$ ) (Figure  
383 3d).

384 The  $\delta^{13}\text{C}_{\text{OC-FeR}}$  values show an increasing trend from  $-34.9\%$  at C1B in the inner  
385 estuary to  $-24.7\%$  at A6-5S in mobile muds with the increase of salinity in SPM samples  
386 (Figures S1 and 3e). A lower  $\delta^{13}\text{C}_{\text{OC-FeR}}$  value of surface sediments is observed in  
387 mobile muds ( $-27.6 \pm 3.7\%$ ) but a higher  $\delta^{13}\text{C}_{\text{OC-FeR}}$  value is observed in ECS shelf  
388 samples ( $-22.3 \pm 2.1\%$ ) (Figure 3e). The  $\Delta^{14}\text{C}_{\text{OC-FeR}}$  values range from  $-637\%$  to  $-143\%$   
389 in SPM samples, with low values in the estuarine mixing zone (from C7S to A6-1S)  
390 (Figure 3f). Similarly, low  $\Delta^{14}\text{C}_{\text{OC-FeR}}$  values are mostly observed in sediments in the  
391 estuarine mixing zone with the oldest radiocarbon age of  $\sim 15800$  yr at A6-1 (Figure 3f).  
392 Like bulk properties, there are no significant differences ( $p > 0.05$ ) in OC-FeR  
393 associations between SPM samples in surface- and bottom-waters (Figure 3).

394

### 395 3.4 Mössbauer Spectroscopy

396 Mössbauer spectra are obtained for selected samples (Figure S2). Iron is present as  
397  $\text{Fe}^{2+}$  in octahedral coordination and  $\text{Fe}^{3+}$  distributed between (super)paramagnetic  
398 phases and magnetic phases (Table S4). The isomer shift (IS) and quadrupole splitting  
399 (QS) values of octahedral  $\text{Fe}^{2+}$  indicate that the ferrous phase could be a clay mineral  
400 or other silicate phase, like chlorite (IS = 1.09-1.14, QS = 2.59-2.66) and illite (IS =  
401 1.12, QS = 2.61) (Dyar et al., 2006) (Table S4). The (super)paramagnetic  $\text{Fe}^{3+}$  fraction  
402 may include any combination of iron (oxyhydr)oxides, such as ferrihydrite, akaganéite,  
403 lepidocrocite, or (super)paramagnetic goethite and nanoparticulate ( $< 30$  nm) or low-  
404 crystalline fraction of hematite, which are expected to be proportional to  $\text{Fe}_R$  (Zhao et  
405 al., 2018a). This is supported by a significant positive relationship between  $\text{Fe}_R$

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406 concentration and the fraction of (super)paramagnetic  $\text{Fe}^{3+}$  (Figure S3). The magnetic  
407  $\text{Fe}^{3+}$  phase mainly occurred as hematite ( $\text{IS} = 0.37$ ,  $\text{OS} = -0.20$ ,  $\text{Bhf} = 51.8$ ) at most  
408 sampling sites (Table S4) (Dyar et al., 2006). The (super)paramagnetic  $\text{Fe}^{3+}$  fraction is  
409 dominant ( $> 40\%$ ) in all samples, with higher abundances in SPM and mobile-mud  
410 sediments than in inner-estuary and ECS-shelf sediments (Figure S3). In contrast, the  
411 fraction of octahedral  $\text{Fe}^{2+}$  is higher in inner-estuary and ECS-shelf sediments  
412 compared to SPM samples and mobile-mud sediments (Figure S3). The fraction of  $\text{Fe}^{3+}$   
413 in the magnetic phase is the lowest in all sampling sites (Figure S3). This is also  
414 reflected by no significant positive relationships between  $\text{Fe}_R$  concentration and  
415 magnetic  $\text{Fe}^{3+}$  fractions ( $p > 0.05$ ), although hematite is also extracted by the BCD  
416 method (Figure S3).

417

### 418 **3.5 Lignin phenols**

419 The lignin phenols and related parameters in SPM samples and surface sediments  
420 are shown in Table S5. The  $\Sigma_8$  of SPM samples range from 0.82 to 2.02 mg/g dry  
421 sediment and decrease with an increase in salinity (Figure S5). For surface sediments,  
422 higher  $\Sigma_8$  is observed in mobile muds relative to the inner estuary and ECS shelf (Figure  
423 S5). The  $\Lambda_8$  in SPM samples varies from 0.05 to 0.11 mg/100mg OC with  
424 no obvious variation trends (Figure S5). Similar to the distribution of  $\Sigma_8$ , high  $\Lambda_8$  is  
425 found in estuarine sediments (e.g., A6-1 and A6-3) and low  $\Lambda_8$  was found in the inner-  
426 estuary and ECS-shelf sediments (Figure S5). Lignin degradation indices, such as  
427  $(\text{Ad}/\text{Al})_v$ ,  $(\text{Ad}/\text{Al})_s$ ,  $\text{P}/(\text{S}+\text{V})$ , and  $3,5\text{-Bd}/\text{V}$ , all show similar distribution patterns, with  
428 higher values in the inner-estuary and ECS-shelf sediments, but lower values in SPM  
429 samples and mobile-mud sediments (Figure S5).

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## 431 **4. Discussion**

### 432 **4.1 OC, Fe<sub>R</sub>, and OC-Fe<sub>R</sub> associations from river-estuarine particles to coastal** 433 **sediments**

434 The overall compositional differences between SPM and surface sediments  
435 suggest that the majority of Changjiang-derived particles, containing mostly terrestrial  
436 OC, are deposited in the estuarine mobile muds, where significant losses of OC  
437 occurred. There are no significant differences in grain size composition and SSA values  
438 between SPM and mobile-mud sediments ( $p > 0.05$ ), indicating that most of the estuarine  
439 fine-grained SPM is deposited in the mobile mud region of the Changjiang Estuary  
440 (Figures 2a and 2b). High sedimentation rates partly result in higher OC content in  
441 mobile-mud sediments relative to inner-estuary and ECS-shelf sediments (Figure 2c)  
442 (Zhao et al., 2021a). Similarly, higher lignin concentrations ( $\Sigma_8$  and  $\Lambda_8$ ) in mobile-mud  
443 sediments also suggest greater deposition of terrestrial plant-derived OC relative to the  
444 inner-estuary and ECS-shelf sediments (Figure S5). This can be attributed to coastal  
445 currents and the limitation of cross-shelf sediment transport by TWWC (Liu et al.,  
446 2007).

447 However, this deposited terrestrial OC may not be well preserved because of  
448 frequent resuspension and redeposition of mobile muds (Bao et al., 2016; Yao et al.,  
449 2014, 2015; Zhao et al., 2018b). The OC/SSA ratio in SPM samples is significantly ( $p$   
450  $< 0.05$ ) higher than that in mobile-mud sediments, with no significant differences ( $p >$   
451  $0.05$ ) between surface- and bottom-water SPM, indicating that loss of OC mainly occurs  
452 in sediments or at the sediment-water interface (Figure 2d). Similarly, the Fe<sub>R</sub> in SPM  
453 is also significantly higher than that in mobile-mud sediments ( $p < 0.05$ ) (Figure 3a).  
454 Surface fine-grained sediments can be resuspended into bottom-waters and involved in  
455 resuspension-redeposition loops in the Changjiang Estuary (Bao et al., 2019b; Guo et

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456 al., 2003), which is partly supported by higher SPM concentrations in bottom-waters  
457 compared to surface-waters in the estuarine mixing zone (Figure S1). At the same time,  
458 sediment in the mobile muds is well mixed because of frequent physical reworking (Xu  
459 et al., 2015), likely resulting in surface sediment with high OC and  $Fe_R$  contents mixed  
460 with deep sediment with low OC and  $Fe_R$  contents. Hence, higher OC and  $Fe_R$  content  
461 in bottom-water SPM compared to surface sediments indicates that most OC and  $Fe_R$   
462 removal occurs in the sediments and/or at the sediment-water interface (Figures 2c and  
463 3a). This is also supported by a higher fraction of (super)paramagnetic  $Fe^{3+}$  in SPM  
464 relative to surface sediments, reflective of the loss of highly reactive  
465 (super)paramagnetic  $Fe^{3+}$  (Figure S4). In the case of estuarine particles, OC and  $Fe_R$  are  
466 largely, although not exclusively, associated with particle surfaces (Blair and Aller,  
467 2012; Mayer 1994; Poulton and Raiswell, 2005). Here SSA is considered to be  
468 primarily influenced by physical sorting processes (Blair and Aller et al., 2012; Mayer,  
469 1994; Keil et al., 1997). Therefore, normalization of OC or  $Fe_R$  to SSA provides a way  
470 to examine net reaction or supply processes in particle populations independently of  
471 physical sorting (Blair and Aller et al., 2012; Poulton and Raiswell, 2005; Sun et al.,  
472 2021). Due to similar grain size composition and SSA values, the decrease of OC and  
473  $Fe_R$  contents from estuarine SPM to mobile-mud sediment reflects net loss during  
474 sediment deposition rather than other physical processes (Figure 2c).

475 Simultaneous decreases of  $Fe_R$  and OC from estuarine SPM to mobile-mud  
476 sediments indicated that iron redox cycling may be partly responsible for the loss of  
477 OC in mobile-mud sediments (Figure S6). Previous work has indicated that iron  
478 reduction is an important early diagenetic pathway for OC remineralization in the  
479 CEMM (Zhao et al., 2017, 2018b). Results of whole-core incubation experiments  
480 showed that both dissolved inorganic carbon and  $Fe^{2+}$  concentrations increase in pore-

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481 water with incubation time in the CEMM, demonstrating that iron reduction is largely  
482 responsible for OC remineralization (Zhao et al., 2018b). Nevertheless, the role of Fe  
483 reduction is clearly underestimated in this incubation experiment due to the absence of  
484 physical mixing (Zhao et al., 2018b). Xu et al. (2015) found the depth of reworked mud  
485 is more than 20 cm in the CEMM, where high disturbance events usually occur over  
486 very short time intervals, e.g., days to weeks, based on multi-radiotracer techniques (Xu  
487 et al., 2015). However, despite frequent physical reworking in the CEMM, the oxygen  
488 penetration depth is ~1-3 mm at different seasons, reflective of anoxic or sub-oxic  
489 conditions (Song et al., 2020), which indicates that redox conditions in sediments may  
490 change quickly. In fact, anoxic or sub-oxic conditions coupled with physical reworking  
491 in mobile muds could enhance Fe reduction and OC remineralization because metal  
492 oxides help to shuttle electrons between O<sub>2</sub> and OC (Aller, 2004; Burdige, 1993;  
493 Canfield et al., 1993; Fu et al., 2019). Thus, iron reduction resulting in the loss of bulk  
494 OC and Fe<sub>R</sub> in the CEMM is expected.

495 From estuarine particles to mobile-mud sediments, there are no significant  
496 differences in OC-Fe<sub>R</sub> content ( $p > 0.05$ ), but OC not bound to Fe<sub>R</sub> (non-OC-Fe<sub>R</sub> = bulk  
497 OC - OC-Fe<sub>R</sub>) largely decreases from estuarine particles to mobile-mud sediments,  
498 indicating that OC-Fe<sub>R</sub> is preserved better than non-OC-Fe<sub>R</sub> (Figure 3b and Table S3).  
499 This also demonstrates that Fe<sub>R</sub> can protect OC even in estuarine mobile muds with  
500 intense iron reduction. The  $f_{\text{OC-FeR}}$  values in estuarine SPM ( $f_{\text{OC-FeR}} = 6.6 \pm 1.9\%$ ) and  
501 mobile-mud sediments ( $f_{\text{OC-FeR}} = 8.8 \pm 1.8\%$ ) are lower than those in inner-estuary ( $f_{\text{OC-FeR}}$   
502  $= 20.0 \pm 5.0\%$ ) and ECS-shelf ( $f_{\text{OC-FeR}} = 14.1 \pm 3.3\%$ ) sediments, showing Fe<sub>R</sub> may  
503 play a more important role in OC preservation in sandy sediments (Figure 3c). Higher  
504 Fe<sub>R</sub> and OC contents but lower  $f_{\text{OC-FeR}}$  in estuarine SPM and mobile-mud sediments  
505 relative to inner-estuary and ECS-shelf sediment suggest that OC-Fe<sub>R</sub> associations are

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506 not generally controlled by  $\text{Fe}_R$  and OC availability (Faust et al., 2021; Longman et al.,  
507 2021). These low  $f_{\text{OC-Fe}_R}$  values in estuarine SPM samples and mobile-mud sediments  
508 are close to those in other deltaic sediments (e.g., ~7.6% in Mackenzie River Delta, and  
509 ~8.1% in the youngest subaerial region of Wax Lake Delta) (Lalonde et al., 2012;  
510 Shields et al., 2016). The  $f_{\text{OC-Fe}_R}$  in the inner-estuary and ECS-shelf sediments is in the  
511 range of previous results of typical oxic or sub-oxic marine sediments, and close to the  
512 global average ( $f_{\text{OC-Fe}_R} = 21.5 \pm 8.6\%$ ) (Lalonde et al., 2012). The fraction of fine-  
513 grained sediment (Clay+Silt%) has a negative relationship with  $f_{\text{OC-Fe}_R}$ , suggesting that  
514 sediment type is likely responsible for the interaction between OC and  $\text{Fe}_R$ , with high  
515  $f_{\text{OC-Fe}_R}$  in coarse-grained sediments (inner-estuary and ECS-shelf sediments) but low  
516  $f_{\text{OC-Fe}_R}$  in fine-grained sediments (SPM and mobile-mud sediments) (Figure 4a). This is  
517 possible because sandy sediments provide less surface area to adsorb OC, and thus  
518 binding with  $\text{Fe}_R$  becomes more important for OC preservation (Figure 4b). In addition,  
519 earlier work indicated that low  $\text{Fe}_R$  concentrations and less resuspension in the ECS  
520 shelf and inner estuary likely diminish the role of iron redox cycling, thus contributing  
521 to the greater proportion of OC bound to  $\text{Fe}_R$  (Figure 4c) (Zhao et al., 2018a). This is  
522 also supported by the negative correlation between  $f_{\text{OC-Fe}_R}$  and the fraction of  
523 (super)paramagnetic  $\text{Fe}^{3+}$ , which suggests that  $\text{Fe}_R$  binds with more OC in the case of  
524 low fractions of reactive ferric oxide phases in ECS-shelf and inner-estuary sediments  
525 (Figure S4). As a result, binding with  $\text{Fe}_R$  not only protects OC in mobile-muds but is  
526 also likely a complementary mechanism for OC preservation when sediments lack fine-  
527 grained components. Clearly, a direct comparison of OC bound to clay mineral and OC-  
528  $\text{Fe}_R$  is needed in future studies.

529 There is no significant change of OC- $\text{Fe}_R$  from SPM to mobile-mud sediments,  
530 suggesting that OC- $\text{Fe}_R$  associations are not broken up during sediment deposition

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531 ( $p > 0.05$ ) (Figure 3b). However, a large amount of  $Fe_R$  is removed as discussed before,  
532 which indicates that the greatest loss of  $Fe_R$  occurs with OC-free  $Fe_R$  (Figure 3a). Barber  
533 et al. (2017) pointed out that a quantitatively important fraction of  $Fe_R$  extracted by the  
534 BCD method is not directly associated with OC. In fact, OC- $Fe_R$  associations not only  
535 protect OC from microbial degradation but also are considered to stabilize  $Fe_R$  (van der  
536 Zee et al., 2003; Schröder et al., 2016; Zhao et al., 2022). The OC-free  $Fe_R$  may be  
537 subjected to more intense reduction than OC-associated  $Fe_R$ , also leading to a higher  
538 OC- $Fe_R/Fe_R$  ratio in mobile-mud sediments relative to SPM (Figure 3d). Therefore, a  
539 mutual protection mechanism of  $Fe_R$  and its associated OC likely contributes to the  
540 stability of OC- $Fe_R$  associations in CEMM.

541

#### 542 **4.2 Association with $Fe_R$ as a potential mechanism for long-term preservation of** 543 **terrestrial OC in estuarine sediments**

544 The variation of isotopic compositions ( $\delta^{13}C_{bulk}$  and  $\Delta^{14}C_{bulk}$ ) of OC from estuarine  
545 particles to ECS shelf sediments suggests dynamic addition and removal of OC from  
546 different sources (Figures 2e and 2f). Marine OC usually has higher  $\delta^{13}C$  ( $-20 \pm 1\%$ )  
547 and  $\Delta^{14}C$  values ( $\sim 0\%$ ) relative to typical terrestrial OC in the Changjiang Estuary and  
548 ECS shelf ( $\delta^{13}C = -25.7 \pm 1\%$  and  $\Delta^{14}C = -255 \pm 26\%$ ) (Wu et al., 2013; Zhao et al.,  
549 2021b). However, isotopic compositions of OC from different terrestrial sources in the  
550 Changjiang sedimentary system vary largely (Galy et al., 2007; Wu et al., 2018; Yu et  
551 al., 2007) (Figure 5). For example, the  $\delta^{13}C$  value for higher plants ranged from  $-26.5\%$   
552 to  $-33.7\%$ , but the  $\delta^{13}C$  values for soil-derived OC ( $-23 \pm 2\%$ ) and rock-derived OC ( $-$   
553  $20.3 \pm 1.5\%$ ) are relatively high (Galy et al., 2008; Wu et al., 2018). The  $\Delta^{14}C$  values  
554 for higher plants are very close to marine OC ( $0 \pm 50\%$ ) (Wu et al., 2018). However,  
555 the  $\Delta^{14}C$  values for soil-derived OC and rock-derived OC are  $-276 \pm 30\%$  and  $-950 \pm$

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556 50‰, respectively (Galy et al., 2008; Wu et al., 2018). Increases in  $\delta^{13}\text{C}_{\text{bulk}}$  and  $\Delta^{14}\text{C}_{\text{bulk}}$   
557 values of POC from the inner estuary with low salinity (e.g., C1 and C7) to mobile  
558 muds with high salinity (e.g., A6-5) indicate the addition of modern marine OC to the  
559 estuarine SPM (Figures 2e and 2f). This supports previous work that showed the  
560 replacement of terrestrial OC by marine OC on fine soil-derived particulates from rivers  
561 with increasing salinities in coastal margins (Keil et al., 1994, 1997; Prahl et al., 1994).  
562  $\delta^{13}\text{C}$  values of SOC also increase from the inner estuary to the ECS shelf, revealing the  
563 addition of marine OC to the sediments (Figure 2e). Increased  $\delta^{13}\text{C}$  values may also  
564 occur with the addition of  $\text{C}_4$  plant-derived OC with high  $\delta^{13}\text{C}$  values (-9‰ to -16‰)  
565 (Pancost and Boot, 2004). However, as the POC of Changjiang is dominated by  $\text{C}_3$   
566 plants, the  $\text{C}_4$  plant-derived OC contribution to OC in the Changjiang Estuary should  
567 be minimal (Wu et al., 2007). Even with the addition of marine OC, the OC/SSA ratios  
568 largely decrease from SPM to mobile-mud sediments, indicating that terrestrial OC  
569 must be decomposed and/or desorbed before final burial. No significant change of  $\Delta^{14}\text{C}$   
570 values of bulk OC between SPM and mobile-mud sediments ( $p>0.05$ ) also indicates  
571 that the simultaneous addition of modern marine OC and loss of young terrestrial OC  
572 balance the  $\Delta^{14}\text{C}_{\text{bulk}}$  value during sediment deposition (Figure 3f). This result supports  
573 previous work which showed that frequent physical reworking activities in the  
574 Changjiang Estuary mobile muds enhance the remineralization of young terrestrial OC  
575 via increased oxygen-exposure time (OET) (Zhao et al., 2021a). Clearly, the effect of  
576 young terrestrial OC loss on  $\Delta^{14}\text{C}_{\text{bulk}}$  is balanced by the addition of modern marine OC,  
577 and thus the  $\Delta^{14}\text{C}$  value of the remaining terrestrial OC is relatively low. Results from  
578 ramped pyrolysis-oxidation (RPO) analysis also suggest that the younger part of  
579 terrestrial OC could be selectively removed, resulting in aging terrestrial OC from  
580 Changjiang SPM to mobile-mud sediments (Bao et al., 2019b). Both the  $\delta^{13}\text{C}_{\text{bulk}}$  value



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581 and OC/SSA ratio increase from mobile-mud to ECS-shelf sediments, but the  $\Delta^{14}\text{C}_{\text{bulk}}$   
582 value stays constant, further demonstrating the balance between marine OC addition  
583 and young terrestrial OC decomposition, desorption, and/or aging during cross-shelf  
584 transport (Figures 3e and 3f). The lowest  $\Delta^{14}\text{C}$  values are observed in inner-estuary  
585 sediments (Figure 3f), which are likely affected by hydrodynamic sorting in the  
586 Changjiang Estuary. Petrogenic and aged plant-derived OC associated with coarse-  
587 sized particles are preferentially deposited and accumulated in the inner estuary, but  
588 relatively young soil-derived OC and/or plant-derived OC associated with fine-grained  
589 particles are transported to the mobile muds and even to the ECS shelf (Sun et al., 2021;  
590 Zhao et al., 2021a).

591 Associations with  $\text{Fe}_R$  allow for the long-term preservation of terrestrial OC in  
592 marine environments (Faust et al., 2021). Here we used  $\Delta\delta^{13}\text{C}$  ( $\delta^{13}\text{C}_{\text{bulk}} - \delta^{13}\text{C}_{\text{OC-FeR}}$ ) and  
593  $\Delta\Delta^{14}\text{C}$  ( $\Delta\delta^{14}\text{C}_{\text{bulk}} - \Delta\delta^{14}\text{C}_{\text{OC-FeR}}$ ) to determine the difference in carbon isotopes between  
594 bulk OC and OC- $\text{Fe}_R$  where positive values indicate lower isotopic values in OC- $\text{Fe}_R$   
595 relative to bulk OC (Figures 3g and 3h). Similar to bulk OC,  $\delta^{13}\text{C}_{\text{OC-FeR}}$  and  $\Delta^{14}\text{C}_{\text{OC-FeR}}$   
596 gradually increase from estuarine SPM to the mobile-mud sediments and then to the  
597 ECS shelf, suggesting the addition of marine OC to  $\text{Fe}_R$  (Figures 3e and 3f). This  
598 distribution trend of  $\delta^{13}\text{C}_{\text{OC-FeR}}$  from the estuary to the shelf agrees well with previous  
599 results that OC- $\text{Fe}_R$  is largely related to bulk OC sources (Salvadó et al., 2015; Shields  
600 et al., 2016; Zhao et al., 2018a). For example, Salvadó et al. (2015) found that OC- $\text{Fe}_R$   
601 is substantially older and more terrestrial than the bulk sediment OC in the Laptev Sea  
602 but younger and more dominated by marine plankton sources in the East Siberian Sea,  
603 mainly depending on the different biogeochemical characteristics of these shelf regimes.  
604 However, positive  $\Delta\Delta^{14}\text{C}_{\text{OC-FeR}}$  and  $\Delta\delta^{13}\text{C}_{\text{OC-FeR}}$  values in SPM and sediments at  
605 most sampling sites indicate that  $\text{Fe}_R$  helps to retain pre-aged soil OC of plant origin in

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606 the Changjiang Estuary (Figures 3g, 3h, and 5). Previous work also showed a more  
607 depleted  $^{13}\text{C}_{\text{OC-FeR}}$  for deltaic sediments, which have higher terrestrially derived inputs  
608 (e.g., Mackenzie River Delta and Wax Lake Delta) than other coastal sediments with  
609 high marine inputs (Lalonde et al., 2012; Shields et al., 2016). In particular, higher  
610  $\Delta\Delta^{14}\text{C}_{\text{OC-FeR}}$  values and  $\Delta\delta^{13}\text{C}_{\text{OC-FeR}}$  are observed in SPM and sediments in the estuarine  
611 mixing zone (from C7 to A6-2), which is partly due to estuarine flocculation (Figures  
612 3g and 3h). Recent work showed that a substantial fraction of particulate Fe and  
613 colloidal Fe can be removed in the estuarine mixing zone through flocculation and  
614 sedimentation (Conrad et al., 2019). During flocculation processes, terrestrial OC-FeR  
615 also prefers sedimentation in the estuarine mixing zone rather than being transported to  
616 mid/outer shelf regions (Conrad et al., 2019; Jilbert et al., 2018). Estuarine flocculation  
617 can be demonstrated by higher SPM concentrations in the estuarine mixing zone  
618 relative to other regions (Figure S1). However, lower  $\Delta\Delta^{14}\text{C}_{\text{OC-FeR}}$  and  $\Delta\delta^{13}\text{C}_{\text{OC-FeR}}$   
619 values in SPM relative to sediments at most sampling sites suggest that marine OC-FeR  
620 may be decomposed and/or desorbed during sediment deposition, but pre-aged soil OC  
621 of plant origin could be retained by FeR (Figures 3g and 3h). Pre-aged soil-derived OC  
622 develops from long-term residence times in the watersheds (Blair et al., 2010; Drenzek  
623 et al., 2009). A series of studies show that FeR preferentially binds with terrestrial plant-  
624 derived compounds, like lipids, cellulose, and lignins (Christl and Kretzschmar, 2007;  
625 Shields et al., 2016; Riedel et al., 2013; Zhao et al., 2018a). This is also supported by a  
626 positive relationship between FeR and  $\Sigma_8$  ( $p < 0.01$ ) (Figure S7). Some terrestrial lipids  
627 in coastal regions like  $\text{C}_{22}$  *n*-alkane and  $\text{C}_{25}$  *n*-alkane may have very low  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$   
628 values ( $\delta^{13}\text{C} < -30\text{‰}$  and  $\Delta^{14}\text{C} < -600\text{‰}$ ) (Feng et al., 2013), which is consistent with  
629  $\delta^{13}\text{C}_{\text{OC-FeR}}$  and  $\Delta^{14}\text{C}_{\text{OC-FeR}}$  values in estuarine SPM and mobile-mud sediments (Figure  
630 5). FeR decreases with increases in lignin-related degradation indices, suggesting that

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631 the remaining OC-associated Fe<sub>R</sub> is mainly bound with degraded plant-derived OC  
632 (Figure S7). Common lignin-related degradation parameters are the ratios of acidic  
633 lignin phenols (e.g., SAD, VAD, CAD, and 3, 5-Bd) with carboxylic functional groups  
634 to others (e.g., (Ad/Al)<sub>v</sub> and P/(S + V)) (Figure S7). Previous work showed that lignin-  
635 related degradation parameters decreased after Fe<sub>R</sub> extraction in deltaic sediments,  
636 indicating selective adsorption of acidic lignin phenols by Fe<sub>R</sub> (Shields et al., 2016 Zhao  
637 et al., 2018a). Lignin-derived carboxylic compounds are preferentially adsorbed to Fe<sub>R</sub>  
638 due to ligand exchange between carboxyl functional groups and Fe<sub>R</sub> (Chen et al., 2014;  
639 Linkhorst et al., 2017; Lv et al., 2016), which likely increases OC sequestration and  
640 stabilization (Curti et al., 2021). The  $\Delta\delta^{13}\text{C}_{\text{OC-Fe}_R}$  value is equal to ~0 in the ECS shelf  
641 (e.g., A6-8, A6-9, and A6-10) suggesting that both bulk OC and OC-Fe<sub>R</sub> are from the  
642 same marine source (Figure 3g). This is partly because of high primary production and  
643 relatively stable sedimentary environments in the ECS shelf, which can contribute Fe<sub>R</sub>  
644 to binding with more marine OC (Zhao et al., 2018a). Interestingly, although Fe<sub>R</sub> can  
645 bind with modern marine OC, the radiocarbon age of OC-Fe<sub>R</sub> is ~1000 years older than  
646 bulk OC in ECS-shelf sediments (~4360 yr for OC-Fe<sub>R</sub> vs. ~3350 yr for bulk OC),  
647 further indicating that Fe<sub>R</sub> still protects a part of pre-aged terrestrial OC in these  
648 sediments (Figure 3h).

649 Aging of terrestrial OC is common in passive continental margins where adequate  
650 accommodation space allows for extensive hydrodynamically-driven  
651 deposition/resuspension events (Bao et al., 2018; Blair and Aller, 2012; Chu et al.,  
652 2022). Recent studies have demonstrated that protection by fine-grained minerals (silt  
653 fraction) is an important mechanism for OC aging (Ausín et al., 2021; Bao et al., 2016;  
654 Hemingway et al., 2019; Keil and Mayer, 2014). Our results showed that binding with  
655 Fe<sub>R</sub> may be an important way of preserving old terrestrial OC on particles and slowing

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656 or even precluding the replacement of terrestrial OC by marine OC (e.g., Keil et al.,  
657 1997; Blair and Aller, 2012), allowing for persistence of terrestrial OC-Fe<sub>R</sub> in the  
658 marine environment. Because most river-derived OC deposits in deltaic and mobile  
659 muds, these carbon isotopic results further support the hypothesis that OC-Fe<sub>R</sub>  
660 associations play an important role in the stabilization of terrestrial OC in estuarine  
661 regions (Shields et al., 2016; Sirois et al., 2018; Zhao et al., 2018a).

662 Iron oxides could transform with time to more stable forms by increased  
663 crystallinity, aggregation, and growth (Raiswell et al., 2011). In general, hematite is  
664 mainly formed in soils and is a more stable, mature, and higher density mineral,  
665 compared to those more commonly precipitated in the redox interface by co-  
666 precipitation, such as ferrihydrite (Jaynes and Bigham, 1986; Raiswell, 2011). Here we  
667 define the ratios of hematite to (super)paramagnetic Fe<sup>3+</sup> (H/P ratio) to show the  
668 crystallinity of iron oxides, with a higher H/P ratio representing higher crystallinity of  
669 iron oxides. Higher H/P ratios are observed in inner-estuary sediments relative to  
670 mobile-mud and ECS-shelf sediments, suggesting higher crystallinity of iron oxides  
671 there (Figure S4). Hydrodynamic sorting of riverine-derived sediments may lead to the  
672 preferential deposition of high-density, crystalline phases such as hematite in the inner  
673 estuary, while the low-density, poorly crystalline (super)paramagnetic Fe<sup>3+</sup> such as  
674 ferrihydrite is transported to mobile muds and the ECS shelf (Figure S4) (Zhao et al.,  
675 2018a). Both  $\Delta^{14}\text{C}_{\text{bulk}}$  and  $\Delta^{14}\text{C}_{\text{OC-Fe}_R}$  decrease with the increase in H/P ratio (Figure 6a  
676 and 6b), demonstrating that high-crystallinity iron oxide is mainly associated with old  
677 terrestrial OC and accumulated in the inner estuary, and low-crystallinity iron oxide is  
678 associated with relatively young terrestrial OC and transported to mobile muds and ECS  
679 shelf. <sup>14</sup>C-derived carbon residence time is positively correlated to Fe phase  
680 crystallinity in soils (Hall et al., 2018), suggesting that OC-associated Fe<sub>R</sub> may mature

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681 along with the aging of OC-Fe<sub>R</sub>. The higher ratio of H/P ratio in the mobile muds  
682 relative to the ECS shelf could be due to the increase in the maturation of Fe oxides  
683 after experiencing long-term resuspension and re-deposition cycles before eventual  
684 burial (Figure S4) (Zhao et al., 2018a). Soil incubation experiments showed that while  
685 a substantial portion of the co-precipitated OC is lost during repeated redox fluctuations  
686 due to low crystallinity, a core OC-Fe<sub>R</sub> structure could still remain (Chen et al., 2020).  
687 Thus low-crystallinity iron oxides and their associated marine OC would not be well  
688 preserved in estuarine mobile-mud sediments (Figures 3e and S4). For ECS shelf  
689 sediments, a relatively quiescent sedimentary regime weakens iron redox cycling and  
690 contributes to the preservation of low-crystallinity iron oxides and their associated  
691 marine OC (e.g., A6-9) (Figures 3e and S4). It is worth noting that the  $\delta^{13}\text{C}_{\text{bulk}}$  and  
692  $\delta^{13}\text{C}_{\text{OC-FeR}}$  did not show any significant relationships with H/P ratios (Figure S8). This  
693 is partly because H/P ratios are largely influenced by hydrodynamic sorting and  
694 maturation processes, but both  $\delta^{13}\text{C}_{\text{bulk}}$  and  $\delta^{13}\text{C}_{\text{OC-FeR}}$  are largely related to bulk OC  
695 sources. For example, inner-estuary sediments have higher H/P ratios because of  
696 hydrodynamic sorting (Figure S4), but ECS-shelf sediments have higher  $\delta^{13}\text{C}_{\text{bulk}}$  and  
697  $\delta^{13}\text{C}_{\text{OC-FeR}}$  values relative to other regions due to marine OC input (Figures 2e and 3e).  
698 A key question that remains is how important the role of OC-Fe<sub>R</sub> associations is in  
699 determining the fate of terrestrially-derived OC in regions with low riverine inputs of  
700 Fe<sub>R</sub>.

701

### 702 **4.3 Variation of OC-Fe<sub>R</sub> associations from land to ocean**

703 The land-to-ocean aquatic continuum (LOAC) is a ‘river pipeline’ of OC transport  
704 from upland soils to the ocean, playing an important role in controlling atmospheric  
705 CO<sub>2</sub> on annual to centennial timescales (Regnier et al., 2022). Here, for a better

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706 understanding of the preservation mechanism of OC by Fe<sub>R</sub> in a typical LOAC, the  
707 variation of OC-Fe<sub>R</sub> associations from land to ocean in the Changjiang sedimentary  
708 system is investigated by incorporating our data with results from previous work on  
709 soils in the Changjiang basin and sediments in ZMMM (Wan et al., 2019; Zhao et al.,  
710 2018a). This is because most of Changjiang estuarine SPM is derived from the  
711 Changjiang basin soils, firstly deposited in CEMM and then transported to the south  
712 (ZMMM) along the coast by currents (Liu et al., 2006; Wu et al., 2007). These soil  
713 sampling sites cover the main soil types in the Changjiang basin soils (Wan et al., 2019;  
714 Yu et al., 2007). Furthermore, data on OC-Fe<sub>R</sub> associations in global soils and different  
715 marine environments are also collected for providing additional information on the role  
716 of Fe<sub>R</sub> in protecting OC from land to ocean.

717 OC-Fe<sub>R</sub> associations vary significantly from soils to estuarine SPM in the  
718 Changjiang sedimentary system. Terrestrial OC in estuarine particles is derived from  
719 the Changjiang drainage basin soils (Wu et al., 2018). Although OC and Fe<sub>R</sub> contents  
720 vary across different soils, there are no significant differences in OC and Fe<sub>R</sub> contents  
721 in soils and estuarine SPM (p>0.05) (Figures 7a and 7b). However,  $f_{OC-FeR}$  and OC-  
722 Fe<sub>R</sub>/Fe<sub>R</sub> ratios largely decrease from soils ( $f_{OC-FeR} = 17.8 \pm 9.2\%$ , OC-Fe<sub>R</sub>/Fe<sub>R</sub>  
723 ratio =  $1.21 \pm 1.15$ ) to estuarine SPM ( $f_{OC-FeR} = 6.6 \pm 1.9\%$ , OC-Fe<sub>R</sub>/Fe<sub>R</sub> ratio =  $0.20 \pm$   
724  $0.06$ ) (Figures 7c and 7d). Similarly, high  $f_{OC-FeR}$  values are found in permafrost soils  
725 ( $f_{OC-FeR} = 19.5 \pm 12.3\%$ ) and alpine grasslands soils of the Qinghai-Tibetan Plateau ( $f_{OC-}$   
726  $FeR} = 15.8 \pm 12\%$ ), where the Changjiang originates (Fang et al., 2019; Mu et al., 2016).  
727 One possible reason for the decrease in  $f_{OC-FeR}$  and OC-Fe<sub>R</sub>/Fe<sub>R</sub> ratios is that a fraction  
728 of OC is decomposed during sediment transport in Changjiang. Although soils and  
729 estuarine SPM have similar  $\delta^{13}C_{bulk}$ , the  $\delta^{13}C_{OC-FeR}$  values in estuarine SPM are lower  
730 than those in soils, indicating selective protection of specific plant-derived compounds

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731 by  $\text{Fe}_R$  during river sediment transport (Figures 7e and 7f). For example, plant-derived  
732 lignin usually has a lower  $\delta^{13}\text{C}$  value compared to plant-derived polysaccharides, such  
733 as cellulose (Loader et al., 2003). Synchrotron Radiation-based Fourier Transform  
734 Infrared (SR-FTIR) microspectroscopy analysis shows that more plant-derived  
735 polysaccharides and aliphatic compounds than carboxylic acids and lignin derivatives  
736 are bound with iron oxides in soils of the Changjiang drainage basin (Wan et al., 2019).  
737 However, the sorption of the more labile polysaccharide-derived OC on iron oxides is  
738 weaker than recalcitrant lignin-derived OC (Kaiser et al., 2000). Thus, the greater loss  
739 of  $\text{Fe}_R$ -associated polysaccharides, relative to  $\text{Fe}_R$ -associated lignin during transport  
740 along the Changjiang, may explain the lower  $\delta^{13}\text{C}_{\text{OC-Fe}_R}$  values in estuarine SPM  
741 compared to soils. Another possible reason is the selective transport of fine-grained  
742 soils with low  $f_{\text{OC-Fe}_R}$  to estuarine regions. In fact, soils in the lower reaches of the  
743 Changjiang have a lower clay fraction relative to estuarine SPM (mean of 17.4% vs.  
744 27.3%, respectively) (Wu et al., 2020) (Table S1), indicating that more fine-grained  
745 soils are transported to the estuarine region by the river, and fine-grained estuarine  
746 particles and sediments have low  $f_{\text{OC-Fe}_R}$  values (Figure 4a). There still remains limited  
747 knowledge on the controls and variability of OC- $\text{Fe}_R$  associations in riverine particles  
748 during transport along the main channel of the Changjiang, and most other large rivers.  
749 As discussed before, although OC and  $\text{Fe}_R$  largely decrease from estuarine SPM to  
750 CEMM,  $f_{\text{OC-Fe}_R}$  and  $\delta^{13}\text{C}_{\text{OC-Fe}_R}$  keep constant, indicating that  $\text{Fe}_R$  plays an important role  
751 in protecting terrestrial OC in estuarine mobile muds (Figure 7). Similarly, there are no  
752 significant differences in OC,  $\text{Fe}_R$ ,  $f_{\text{OC-Fe}_R}$ ,  $\text{OC-Fe}_R/\text{Fe}_R$ , and  $\delta^{13}\text{C}_{\text{OC-Fe}_R}$  between CEMM  
753 and ZMMM sediments, but the  $\delta^{13}\text{C}_{\text{bulk}}$  value significantly increases from CEMM to  
754 ZMMM ( $p < 0.05$ ) (Figure 7). This indicated that frequent physical reworking in mobile  
755 muds may inhibit  $\text{Fe}_R$  from binding with more marine OC, but the  $\text{Fe}_R$  still protects

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756 terrestrial OC. The  $f_{\text{OC-Fe}_R}$ ,  $\text{OC-Fe}_R/\text{Fe}_R$ , and  $\delta^{13}\text{C}_{\text{OC-Fe}_R}$  all increase from estuarine SPM  
757 and mobile-mud sediments to ECS-shelf sediments, indicating that  $\text{Fe}_R$  binds more  
758 marine OC during cross-shelf sediment transport (Figure 7). This is partly due to less  
759 re-suspension in the ECS shelf relative to mobile muds in the ECS inner shelf during  
760 this prolonged lateral transport (Bao et al., 2019b). At the same time, estuarine  
761 flocculation likely leads to a large fraction of terrestrial  $\text{OC-Fe}_R$  that is deposited in  
762 mobile muds rather than being transported to ECS shelf regions. It is worth noting that  
763  $\text{Fe}_R$  content in surface sediments in the Okinawa Trough is very low ( $0.40 \pm 0.05$  mg/g),  
764 partly due to less terrestrial input, but  $\text{OC-Fe}_R/\text{Fe}_R$  ratio is high ( $>10$ ), demonstrating  
765 that  $\text{Fe}_R$  binds with more OC in this deep-sea region (Sun et al., 2020).

766 The distribution of  $f_{\text{OC-Fe}_R}$  is investigated in soils and marine sediments on a global  
767 scale for a better understanding of the role of  $\text{Fe}_R$  in OC protection in both land and  
768 ocean settings (Figure 8a). Overall, the  $f_{\text{OC-Fe}_R}$  values in estuarine SPM and deltaic  
769 regions are lower than those in soils and marine sediments in continental margins,  
770 anoxic and sulphidic, and deep-sea regions (Figure 8b). The  $f_{\text{OC-Fe}_R}$  has no significant  
771 relationship with OC and  $\text{Fe}_R$  contents, further supporting that availability of OC and  
772  $\text{Fe}_R$  is not the exclusive controlling factor for  $\text{OC-Fe}_R$  associations both in soils and  
773 marine sediments (Figures 8c and 8d). Many factors like iron oxide type, OC  
774 composition, and environmental conditions (e.g., sedimentation rate, mixing dynamics,  
775 and redox conditions) likely greatly influence  $\text{OC-Fe}_R$  associations (Chen et al., 2020;  
776 Faust et al., 2021; Zhao et al., 2018a; Zhao et al., 2022). For example, in sediments with  
777 abundant  $\text{Fe}_R$  content, the dominant Fe oxides are more crystalline iron like hematite  
778 and goethite, which have relatively low reactivity and cannot provide enough surface  
779 area to stabilize OC (Faust et al., 2021). In addition, sedimentary conditions like  
780 estuarine physical reworking likely prevent  $\text{Fe}_R$  from binding with more OC (Zhao et



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781 [al., 2018a](#)). Our integrated dataset shows an average of  $16.7 \pm 13.7\%$  of bulk OC is  
782 bound to  $\text{Fe}_R$  in different soil types (e.g., forest, crop, and grassland) ([Figure 8b](#)) ([Ye et](#)  
783 [al., 2022 and references therein](#)). Meanwhile, there are no significant differences  
784 between  $\delta^{13}\text{C}_{\text{bulk}}$  and  $\delta^{13}\text{C}_{\text{OC-Fe}_R}$  in soils, demonstrating relative consistency of OC  
785 source for bulk OC and OC- $\text{Fe}_R$  ([Figure 8e](#)). However, from soils to estuarine SPM and  
786 deltaic sediments,  $f_{\text{OC-Fe}_R}$ , bulk OC, and  $\text{Fe}_R$  contents all largely decrease ( $p < 0.05$ ),  
787 reflective of decomposition or selective transport of OC- $\text{Fe}_R$  associations as discussed  
788 above ([Figures 8c and 8d](#)). At the same time, lower  $\delta^{13}\text{C}_{\text{OC-Fe}_R}$  relative to  $\delta^{13}\text{C}_{\text{bulk}}$  in  
789 estuarine SPM and deltaic sediments further supports the importance of  $\text{Fe}_R$  in the  
790 protection of plant-derived OC during sediment transport in the river ([Figure 8e](#)).  
791 However, continental margins, coastal and freshwater wetlands, anoxic/sulphidic, and  
792 deep-sea sediments have higher  $f_{\text{OC-Fe}_R}$  and  $\delta^{13}\text{C}_{\text{OC-Fe}_R}$ , demonstrating that more  
793 marine/algal OC is bound to  $\text{Fe}_R$  in marine settings ([Figures 8c and 8e](#)). The variations  
794 of these global data on OC- $\text{Fe}_R$  associations from land to ocean further demonstrate that  
795 OC- $\text{Fe}_R$  associations are largely related to different sedimentary regimes, such as OC  
796 sources,  $\text{Fe}_R$  compositions, and sedimentary dynamics.

797 The Changjiang sedimentary system is a typical LOAC, with a large river and a  
798 highly dynamic estuary, like the Mississippi and Amazon river sedimentary systems  
799 ([Blair and Aller, 2012; Nittrouer et al., 2021](#)). It is worth noting that each of these river  
800 systems is characterized by high  $\text{Fe}_R$  and plant-derived OC concentrations in river  
801 particles, rapid Fe redox cycling in estuarine mobile muds, and selective retention of  
802 older terrestrially-derived OC during lateral sediment transport ([Aller et al., 2004; Blair](#)  
803 [and Aller, 2012; Poulton and Raiswell, 2002; Zhao et al., 2021a](#)). Protection of OC  
804 during the lateral transfer from land to ocean is a key process controlling the release of  
805 carbon back into the atmosphere in these LOAC systems ([Regnier et al., 2022](#)). Here,

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806 we propose that in addition to other forms of mineral protection (i.e. clay sorption), OC-  
807 Fe<sub>R</sub> association is a significant variable regarding the fate of pre-aged terrestrial OC in  
808 the coastal ocean. Clearly, this mechanism of OC stabilization and aging needs to be  
809 further verified in other large river sedimentary systems. In addition, for a global  
810 assessment of the role of Fe<sub>R</sub> in OC preservation, the variation of OC-Fe<sub>R</sub> associations  
811 from land to ocean in small mountain river sedimentary systems also needs to be further  
812 studied.

813

## 814 **5. Conclusion**

815 OC-Fe<sub>R</sub> associations in the Changjiang sedimentary system vary dynamically  
816 from soils in drainage basins to estuarine SPM and to estuarine and ECS shelf sediments,  
817 which are controlled mainly by sedimentary regimes, OC sources, and Fe<sub>R</sub>  
818 compositions. The formation of OC-Fe<sub>R</sub> associations occur initially in soils, and then a  
819 large part of OC-Fe<sub>R</sub> is decomposed and/or desorbed from iron oxides during long-  
820 distance sediment transport in the river basin. Some plant-derived OC is selectively  
821 protected by Fe<sub>R</sub> during sediment transport in the river. When the river-derived particles  
822 and associated OC reach the estuary, frequent physical reworking coupled with rapid  
823 Fe redox cycling in mobile muds leads to the remineralization of non-OC-Fe<sub>R</sub> and loss  
824 of OC-free Fe<sub>R</sub>. The OC-Fe<sub>R</sub> in mobile muds is composed of mostly pre-aged soil OC  
825 of terrestrial plant origin, and preserved better than non-OC-Fe<sub>R</sub> from this process,  
826 indicating that association with Fe<sub>R</sub> is an important mechanism for old terrestrial OC  
827 preservation in estuarine sediments. Complex and intense hydrodynamic and  
828 sedimentary dynamic processes in estuarine regions also greatly influence the  
829 distribution of iron oxides and their associated OC. The high-crystallinity iron oxides  
830 are largely associated with pre-aged terrestrial OC and preferentially deposited in inner-

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831 estuary sediments, but low-crystallinity iron oxides are associated with relatively young  
832 terrestrial OC and transported to mobile muds and ECS shelf. In the ECS shelf, low  $Fe_R$   
833 concentrations coupled with less resuspension weaken iron reduction, which  
834 contributes to  $Fe_R$  binding with more marine OC. Our global dataset on OC- $Fe_R$   
835 associations in land and ocean coupled well with the results in the Changjiang  
836 sedimentary system, further showing that the OC- $Fe_R$  associations are largely related to  
837 sedimentary regimes. Our work supports that  $Fe_R$  plays an important role in the  
838 stabilization and transport of pre-aged terrestrial OC from land to the ocean.

839

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## 854 **Appendix A. Supplementary Material**

855 The supplementary materials contain supplemental figures (Figures S1-S8) in a PDF  
856 file and research data associated with this study (Tables S1-S5) in an Excel file.  
857 Supplemental figures include distributions of salinity and suspended particulate matter  
858 concentration (Figure S1), Mössbauer spectra (Figure S2), correlations of the reactive  
859 iron and different iron phases (Figure S3), distributions of different iron phases (Figure  
860 S4), distributions of lignin phenols and lignin degradation indices (Figure S5),  
861 correlation of organic carbon versus reactive iron (Figure S6), correlations of the  
862 reactive iron with lignin degradation indices (Figure S7) and correlations of the ratio of  
863 hematite to (super) paramagnetic  $\text{Fe}^{3+}$  versus  $\Delta^{13}\text{C}_{\text{bulk}}$  and  $\Delta^{13}\text{C}_{\text{OC-FeR}}$  (Figure S8).  
864 Supplemental tables include bulk parameters (Tables S1 and S2), parameters of OC-  
865  $\text{FeR}$  (Table S3), Mössbauer parameters (Table S4), and lignin phenols and related  
866 parameters (Table S5).

867

## 868 **References**

- 869 Aller R. C. (1998) Mobile deltaic and continental shelf muds as suboxic, fluidized bed  
870 reactors. *Mar. Chem.* 61(3–4), 143–155.
- 871 Aller R. C. (2004) Conceptual models of early diagenetic processes: the muddy seafloor  
872 as an unsteady, batch reactor. *J. Mar. Res.* 62, 815–835.
- 873 Ausín B., Bruni E., Haghypour N., Welte C., Eglinton T. I. (2021) Controls on the  
874 abundance, provenance and age of organic carbon buried in continental margin  
875 sediments. *Earth Planet. Sci. Lett.* 558, 116759.
- 876 Bai J., Luo M., Yang Y., Xiao S., Zhai Z., and Huang J. (2021) Iron-bound carbon  
877 increases along a freshwater- oligohaline gradient in a subtropical tidal wetland. *Soil*  
878 *Biol. Biochem.* 154, 108128.
- 879 Bao R., McIntyre C., Zhao M., Zhu C., Kao S. J., and Eglinton T. I. (2016) Widespread  
880 dispersal and aging of organic carbon in shallow marginal seas. *Geology* 44, 37941–  
881 37948.

---

882 Bao R., Van der Voort T. S., Zhao M., Guo X., Montluçon D. B., McIntyre C., and  
883 Eglinton T. I. (2018) Influence of hydrodynamic processes on the fate of sedimentary  
884 organic matter on continental margins. *Global Biogeochem. Cycles* 32, 1420–1432.

885 Bao R., Zhao M., McNichol A., Galy V., McIntyre C., Haghypour N. and Eglinton T. I.  
886 (2019a) Temporal constraints on lateral organic matter transport along a coastal mud  
887 belt. *Org. Geochem.* 128, 86–93.

888 Bao R., Zhao M., McNichol A., Wu Y., Guo X., Haghypour N., and Eglinton T. I. (2019b)  
889 On the origin of aged sedimentary organic matter along a river-shelf-deep ocean  
890 transect. *J. Geophys. Res. Biogeosci.* 124(8), 2582–2594.

891 Barber A., Brandes J., Leri A., Lalonde K., Balind K., Wirick S., Wang J., and Gélina  
892 Y. (2017) Preservation of organic matter in marine sediments by inner-sphere  
893 interactions with reactive iron. *Sci. Rep.* 7(1), 366.

894 Bianchi T. S., Blair N., Burdige D., Eglinton T. I., Galy V. (2018) Centers of organic  
895 carbon burial at the land-ocean interface. *Org. Geochem.* 115, 138–155.

896 Bianchi T.S. (2011) The role of terrestrially derived organic carbon in the coastal ocean:  
897 A changing paradigm and the priming effect. *Proc. Nat. Acad. Sci.* 108(49), 473–  
898 481.

899 Blair N. E., Leithold E. L., Brackley H., Trustrum N., Page, M., Childress L. (2010)  
900 Terrestrial sources and export of particulate organic carbon in the Waipaoa  
901 sedimentary system: problems, progress and processes. *Mar. Geol.* 270(1–4), 108–  
902 118.

903 Blair N. E., and Aller R. C. (2012) The fate of terrestrial organic carbon in the marine  
904 environment. *Annu. Rev. Mar. Sci.* 4, 401–423.

905 Blattmann T. M., Liu Z., Zhang Y., Zhao Y., and Eglinton T. I. (2019) Mineralogical  
906 control on the fate of continentally derived organic matter in the ocean. *Science* 366,  
907 742–745.

908 Burdige D. J. (1993) The biogeochemistry of manganese and iron reduction in marine  
909 sediments. *Earth-Sci. Revi.* 35, 249–284.

910 Burdige D. J. (2005) Burial of terrestrial organic matter in marine sediments: A re-  
911 assessment. *Global Biogeochem. Cycles* 19, GB4011.

912 Canfield D. E. (1994) Factors influencing organic carbon preservation in marine  
913 sediments. *Chem. Geol.* 114(3–4), 315–329.

---

914 Canfield D. E., Thamdrup B., and Hansen J. W. (1993) The anaerobic degradation of  
915 organic matter in Danish coastal sediments: Iron reduction, manganese reduction,  
916 and sulfate reduction. *Geochim. Cosmochim. Acta* 57(16), 3867–3883.

917 Chen C., Dynes J. J., Wang J., and Sparks D. L. (2014) Properties of Fe-organic matter  
918 associations via coprecipitation versus Adsorption. *Environ. Sci. Technol.* 48,  
919 13751–13759.

920 Chen C., Hall S. J., Coward E., and Thompson A. (2020) Iron-mediated organic matter  
921 decomposition in humid soils can counteract protection. *Nat. Commun.* 11, 2255.

922 Chen J., Li D., Chen B., Hu F., Zhu H., and Liu C. (1999) The processes of dynamic  
923 sedimentation in the Changjiang Estuary. *J. Sea Res.* 41, 129-140.

924 Christl I., and Kretzschmar R. (2007) C-1s NEXAFS spectroscopy reveals chemical  
925 fractionation of humic acid by cation-induced coagulation. *Environ. Sci. Technol.*  
926 41(6), 1915–1920.

927 Chu M., Zhao M., Eglinton T. I., and Bao R. (2022) Differentiating the causes of aged  
928 organic carbon in marine sediments. *Geophys. Res. Lett.* 49, e2021GL096912.

929 Conrad S., Ingri J., Gelting J., Nordblad F., Engström E., Rodushkin I., Andersson P. S.,  
930 Porcelli D., Gustafsson Ö., Semiletov I. and Öhlander B., (2019) Distribution of Fe  
931 isotopes in particles and colloids in the salinity gradient along the Lena River plume,  
932 Laptev Sea. *Biogeosciences*, 16(6), 1305–1319.

933 Curti L., Moore O. W., Babakhani P., Xiao K-Q., Woulds C., Bray A. W., Fisher B. J.,  
934 Kazemian M., Kaulich B., Peacock C. L. (2021) Carboxyl-richness controls organic  
935 carbon preservation during coprecipitation with iron (oxyhydr)oxides in the natural  
936 environment. *Commun. Earth Environ.* 2, 229.

937 Dicen G. P., Navarrete I. A., Rallos R. V., Salmo III S. G., Garcia M. C. A. (2019) The  
938 role of reactive iron in long-term carbon sequestration in mangrove sediments.

939 Dittmar T., and Lara R. J., (2001) Molecular evidence for lignin degradation in sulfate-  
940 reducing mangrove sediments (Amazônia, Brazil). *Geochim. Cosmochim. Acta* 65,  
941 1417–1428.

942 Drenzek N. J., Huguen K. A., Montluçon D. B., Southon J. R., dos Santos G. M., Druffel  
943 E. R. M., Giosan L., and Eglinton T. I. (2009) A new look at old carbon in active  
944 margin sediments. *Geology* 37(3), 239-242.

945 Dyar M. D., Agresti D. G., Schaefer, M. W., Grant C. A., and Sklute E. C. (2006)  
946 Mössbauer spectroscopy of earth and planetary materials. *Annu. Rev. Earth Pl. Sci.*  
947 34(1), 83–125.

- 
- 948 Eisma D., Ji Z., Chen S., Chen M., and Van der Gaast S. J. (1995). Clay mineral  
949 composition of recent sediments along the China coast. *Nederlands Instituut voor*  
950 *Onderzoek der Zee (report)* 4, 1–13.
- 951 Eusterhues K., Hädrich A., Neidhardt J., Küsel K., Keller T. F., Jandt K. D., and Totsche,  
952 K. U. (2014) Reduction of ferrihydrite with adsorbed and coprecipitated organic  
953 matter: Microbial reduction by *Geobacter bremensis* vs. abiotic reduction by Na-  
954 dithionite. *Biogeosciences* 11(4), 6039–6067.
- 955 Fang K., Qin S., Chen L., Zhang Q., Yang Y. (2019) Al/Fe mineral controls on soil  
956 organic carbon stock across Tibetan alpine grasslands. *J. Geophys. Res. Biogeosci.*  
957 124, 247–259.
- 958 Faust J. C., Stevenson M. A., Abbott G. D., Knies J., Tessin A., Mannion I., Ford A.,  
959 Hilton R., Peakall J., März C. (2020) Does Arctic warming reduce preservation of  
960 organic matter in Barents Sea sediments? *Philos. Trans. A Math. Phys. Eng. Sci.* 378,  
961 20190364.
- 962 Faust J. C., Tessin A., Fisher B. J., Zindorf M., Papadaki S., Hendry K. R., Doyle K. A.,  
963 and März Z. (2021) Millennial scale persistence of organic carbon bound to iron in  
964 Arctic marine sediments. *Nat. Commun.* 12, 275.
- 965 Feng X., Benitez-Nelson B. C., Montluçon D. B., Prah F. G., McNichol A. P., Xu L.,  
966 Repeta D. J., and Eglinton T. I. (2013) <sup>14</sup>C and <sup>13</sup>C characteristics of higher plant  
967 biomarkers in Washington margin surface sediments. *Geochim. Cosmochim. Acta*  
968 105, 14–30.
- 969 Fu L., Zhou T., Wang J., You L., Lu Y., Yu L., Zhou S. (2019) NanoFe<sub>3</sub>O<sub>4</sub> as solid  
970 electron shuttles to accelerate acetotrophic methanogenesis by *methanosarcina*  
971 *barkeri*. *Front. Microbiol.* 10, 388.
- 972 Galy V., France-Lanord C., Beyssac O., Faure P., Kudrass H., Palhol F. (2007) Efficient  
973 organic carbon burial in the Bengal fan sustained by the Himalayan erosional system.  
974 *Nature.* 450, 407–10.
- 975 Galy V., Beyssac O., France-Lanord C., and Eglinton, T. (2008) Recycling of graphite  
976 during Himalayan erosion: A geological stabilization of carbon in the crust. *Science*  
977 322, 943–945.
- 978 Ge T., Xue Y., Jiang X., Zou L., and Wang X. (2020) Sources and radiocarbon ages of  
979 organic carbon in different grain size fractions of Yellow River-transported particles  
980 and coastal sediments. *Chem. Geol.* 534, 119452.
- 981 Ghaisas N. A., Maiti K., and Roy A. (2021) Iron-mediated organic matter preservation

---

982 in the Mississippi River-influenced shelf sediments. *J. Geophys. Res. Biogeosci.*  
983 126(4), e2020JG006089.

984 Guo Y., Yang S., Su N., Li C., Yin P., and Wang Z. (2018) Revisiting the effects of  
985 hydrodynamic sorting and sedimentary recycling on chemical weathering  
986 indices. *Geochim. Cosmochim. Acta* 227, 48–63.

987 Guo Z. G., Yang Z. S., Fan D. D., Pan Y. J., (2003) Seasonal variation of sedimentation  
988 in the Changjiang Estuary mud area. *J. Geogr. Sci.* 13, 348–354.

989 Hall S. J., Berhe A. A., and Thompson A. (2018) Order from disorder: do soil organic  
990 matter composition and turnover co-vary with iron phase crystallinity?.  
991 *Biogeochemistry* 140, 93–110

992 Hedges J. I., and Ertel J. R. (1982) Characterization of lignin by gas capillary  
993 chromatography of cupric oxide oxidation products. *Anal. Chem.* 54 (2), 174–178.

994 Hedges J. I., and Mann D. C. (1979). The characterization of plant tissues by their lignin  
995 oxidation products. *Geochim. Cosmochim. Acta* 43 (11), 1803–1807.

996 Hedges J. I., and Keil R. G. (1995) Sedimentary organic matter preservation: an  
997 assessment and speculative synthesis. *Mar. Chem.* 49, 123–126.

998 Hedges J. I., Blanchette R. A., Weliky K., Devol A. H. (1988) Effects of fungal  
999 degradation on the CuO oxidation products of lignin: a controlled laboratory study.  
1000 *Geochim. Cosmochim. Acta* 52 (11), 2717–2726.

1001 Hemingway J. D., Rothman D. H., Grant K. E., Rosengard S. Z., Eglinton T. I., Derry  
1002 L. A., and Galy V. (2019) Mineral protection regulates long-term global preservation  
1003 of natural organic carbon. *Nature* 570, 228–231.

1004 Houel S., Louchouart P., Lucotte M., Canuel R., Ghaleb B. (2006) Translocation of soil  
1005 organic matter following reservoir impoundment in boreal systems: implications for  
1006 in situ productivity. *Limnol. Oceanogr.* 51 (3), 1497–1513.

1007 Iseki K., Okamura K., Kiyomoto Y. (2003) Seasonality and composition of downward  
1008 particulate fluxes at the continental shelf and Okinawa Trough in the East China Sea.  
1009 *Deep Sea Res. Pt. II* 50, 457–473.

1010 Jaynes W. F., and Bigham J. M. (1986) Concentration of iron oxides from soil clays by  
1011 density gradient centrifugation. *Soil Sci. Soc. Am. J.* 50(6), 1633–1639.

1012 Jia, W., and Peng, P. (2005) Molecular structure of kerogens from source rocks of the  
1013 Tarim Basin: a study by Py-GC-MS and methylation-Py-GC-MS. *Sci. China, Ser. D,*  
1014 *Earth Sci.* 48, 313–325.



---

1015 Jilbert T., Asmala E., Schröder C., Tiihonen R., Myllykangas J. P., Virtasalo J. J.,  
1016 Kotilainen A., Peltola P., Ekholm P., Hietanen S., (2018) Impacts of flocculation on  
1017 the distribution and diagenesis of iron in boreal estuarine sediments. *Biogeosciences*,  
1018 12, 1519–1522.

1019 Kao S., Lin F., and Liu K. (2003) Organic carbon and nitrogen contents and their  
1020 isotopic compositions in surficial sediments from the East China Sea shelf and the  
1021 southern Okinawa Trough. *Deep Sea Res. Pt II* 50(6-7), 1203–1217.

1022 Kaiser K., and Guggenberger G. (2000) The role of DOM sorption to mineral surfaces  
1023 in the preservation of organic matter in soils. *Org. Geochem.* 31(7-8), 711–725.

1024 Keil, R. G., Tsamakis, E., Fuh, C. B., Giddings, J. C., and Hedges, J. I. (1994)  
1025 Mineralogical and textural controls on the organic composition of coastal marine  
1026 sediments: Hydrodynamic separation using SPLITT-fractionation. *Geochim.*  
1027 *Cosmochim. Acta* 58(2), 879-893.

1028 Keil R. G., Mayer L. M., Quay P. D., Richey J. E., and Hedges J. I. (1997) Loss of  
1029 organic matter from riverine particles in deltas. *Geochim. Cosmochim. Acta* 61(7),  
1030 1507-1511.

1031 Keil R. G., and Mayer L. M. (2014) Mineral matrices and organic matter. *Treatise on*  
1032 *Geochemistry.* 76, 337–359.

1033 Lalonde K., Mucci A., Ouellet A., and Gélinas Y. (2012) Preservation of organic matter  
1034 in sediments promoted by iron. *Nature.* 483(7388), 198–200.

1035 Loader N. J., Robertsonab I., and McCarrolla D. (2003) Comparison of stable carbon  
1036 isotope ratios in the whole wood, cellulose and lignin of oak tree-rings. *Palaeogeogr.*  
1037 *Palaeocl.* 196(3–4), 395–407.

1038 Li D., Yao P., Bianchi T. S., Zhang T., Zhao B., Pan H., Wang J., and Yu Z. (2014)  
1039 Organic carbon cycling in sediments of the Changjiang Estuary and adjacent shelf:  
1040 Implication for the influence of three Gorges Dam. *J. Mar. Syst.* 139, 409–419.

1041 Linkhorst A., Dittmar T., and Waska, H. (2017) Molecular fractionation of dissolved  
1042 organic matter in a shallow subterranean estuary: The role of the iron curtain.  
1043 *Environ. Sci. Technol.* 51(3), 1312–1320.

1044 Liu J. P., Li A. C., Xu K. H., Velozzi D. M., Yang Z. S., Milliman J. D., and DeMaster  
1045 D. J. (2006) Sedimentary features of the Yangtze river-derived along-shelf clinoform  
1046 deposit in the East China Sea. *Cont. Shelf Res.* 26, 2141–2156.

1047 Liu J. P., Xu K. H., Li A. C., Milliman J. D., Velozzi D. M., Xiao S. B., and Yang Z. S.

---

1048 (2007) Flux and fate of Yangtze River sediment delivered to the East China Sea.  
1049 *Geomorphology* 85, 208–224.

1050 Longman J., Gernon T. M., Palmer M. R., and Manners H. R. (2021) Tephra deposition  
1051 and bonding with reactive oxides enhances burial of organic carbon in the Bering  
1052 Sea. *Global Biogeochem. Cycles* 35, e2021GB007140.

1053 Longman, J., Faust, J. C., Bryce, C., Homoky, W. B., and März, C. (2022) Organic  
1054 carbon burial with reactive iron across global environments. *Global Biogeochem.*  
1055 *Cycles* 36, e2022GB007447.

1056 Ludwig W., Amiotte-Suchet P., and Probst J L. (1996) River discharges of carbon to the  
1057 world's oceans: determining local inputs of alkalinity and of dissolved and  
1058 particulate organic carbon. *Global Biogeochem. Cycles* 10, 23–41.

1059 Lv J., Zhang S., Wang S., Luo L., Cao D., and Christie P. (2016) Molecular-scale  
1060 investigation with ESI-FT-ICR-MS on fractionation of dissolved organic matter  
1061 induced by adsorption on iron oxyhydroxides. *Environ. Sci. Technol.* 50(5), 2328–  
1062 2336.

1063 Ma W. W., Zhu M. X., Yang G. P., Li T. (2018). Iron geochemistry and organic carbon  
1064 preservation by iron (oxyhydr)oxides in surface sediments of the East China Sea and  
1065 the south Yellow Sea. *J. Mar. Syst.* 178, 62–74.

1066 Mayer L. M. (1994) Relationships between mineral surfaces and organic carbon  
1067 concentrations in soils and sediments. *Chem. Geol.* 114, 347–363.

1068 McKee B.A., Aller R. C., Allison M. A., Bianchi, T. S., and Kineke G. C. (2004)  
1069 Transport and transformation of dissolved and particulate materials on continental  
1070 margins influenced by major rivers: benthic boundary layer and seabed  
1071 processes. *Cont. Shelf Res.* 24(7–8), 899–926.

1072 Milliman J. D., and Farnsworth K. L. (2011) River discharge to the coastal ocean—a  
1073 global synthesis. Cambridge: Cambridge University Press.

1074 Mu C. C., Zhang T. J., Zhao Q., Guo H., Zhong W., Su H., and Wu Q. B. (2016) Soil  
1075 organic carbon stabilization by iron in permafrost regions of the Qinghai-Tibet  
1076 Plateau. *Geophys. Res. Lett.* 43, 10286–10294.

1077 Nittrouer C. A., Demaster D. J., Kuehl S. A., Figueiredo Jr A. G., Sternberg R. W., Faria  
1078 E. C., Silveira R. W., Allison M. A., Kineke G. C., Ogston, A. S., Souza Filho P. W.  
1079 M., Asp N. E., Nowacki D. J., and Fricke, A. T. (2021) Amazon sediment transport  
1080 and accumulation along the continuum of mixed fluvial and marine processes. *Annu.*

---

1081 *Rev. Mar. Sci.* 13(1), 501-536.

1082 Oguri K., Matsumoto E., Yamada M., Saito Y., and Iseki K. (2003) Sediment  
1083 accumulation rates and budgets of depositing particles of the East China Sea. *Deep*  
1084 *Sea. Res. Pt. II* 50, 513–528.

1085 Pancost R. D., and Boot C. S., (2004) The palaeoclimatic utility of terrestrial  
1086 biomarkers in marine sediments. *Mar. Chem.* 92(1–4), 239–261.

1087 Prahl F. G., Ertel, J. R., Goni, M. A., Sparrow, M. A., and Eversmeyer, B. (1994)  
1088 Terrestrial organic carbon contributions to sediments on the Washington  
1089 margin. *Geochim. Cosmochim. Acta* 58(14), 3035–3048.

1090 Poulton S. W., and Canfield D. E. (2005) Development of a sequential extraction  
1091 procedure for iron: implications for iron partitioning in continentally derived  
1092 particulates. *Chem. Geol.* 214, 209–221.

1093 Poulton S. W., and Raiswell R. (2002) The low-temperature geochemical cycle of iron:  
1094 from continental fluxes to marine sediment deposition. *Am. J. Sci.* 302(9), 774–805.

1095 Raiswell R. (2011) Iron transport from the continents to the open ocean: The aging-  
1096 rejuvenation cycle. *Elements* 7(2), 101–106.

1097 Regnier P., Resplandy L., Najjar R. G., and Ciais P. (2022) The land-to-ocean loops of  
1098 the global carbon cycle. *Nature* 603, 401-410.

1099 Riedel T., Biester H., and Dittmar T. (2012) Molecular fractionation of dissolved  
1100 organic matter with metal salts. *Environ. Sci. Technol.* 46(8), 4419–4426.

1101 Riedel T., Zak D., Biester H., and Dittmar T. (2013) Iron traps terrestrially derived  
1102 dissolved organic matter at redox interfaces. *Proc. Natl. Acad. Sci. U. S. A.* 110(25),  
1103 10,101–10,105.

1104 Salvadó J. A., Tesi T., Andersson A., Ingri J., Dudarev O. V., Semiletov I. P., and  
1105 Gustafsson Ö. (2015) Organic carbon remobilized from thawing permafrost is  
1106 resequenced by reactive iron on the Eurasian Arctic shelf. *Geophys. Res. Lett.* 42,  
1107 8122–8130.

1108 Schlünz B., and Schneider R. R. (2000) Transport of terrestrial organic carbon to the  
1109 oceans by rivers: Re-estimating flux- and burial rates. *Int. J. Earth Sci.* 88, 599–606.

1110 Schröder C., Köhler I., Muller F. L. L., Chumakov A. I., Kuppenko I., Ruffer R., and  
1111 Kappler A. (2016) The biogeochemical iron cycle and astrobiology. *Hyperfine*  
1112 *Interact.* 237, 85.

1113 Shields M. R., Bianchi T. S., Gélinas Y., Allison M. A., and Twilley R. R. (2016)

---

1114 Enhanced terrestrial carbon preservation promoted by reactive iron in deltaic  
1115 sediments. *Geophys. Res. Lett.* 43, 1149–1157.

1116 Shields M. R., Bianchi T. S., Mohrig D., Hutchings J. A., Kenney W. H., Kolker A. S.,  
1117 and Curtis J. S. (2017). Ecosystem Engineering Builds Coastline and Stores Blue  
1118 Carbon in the Mississippi River Delta Complex. *Nat. Geosci.* 10, 846-851.

1119 Shields M. R., Bianchi T. S., Kolker A. S., Kenney W. F., Mohrig D., Osborne T. Z., and  
1120 Curtis J. H. (2019) Biogeochemical proxies resolve the sources and diagenetic state  
1121 of sedimentary organic carbon in Wax Lake Delta, Louisiana (USA). *J. Geophys.*  
1122 *Res. Biogeosci.* 124, 1115–1131.

1123 Sirois M., Couturier M., Barber A., G elinas Y., and Chaillou G. (2018) Interactions  
1124 between iron and organic carbon in a sandy beach subterranean estuary. *Mar. Chem.*  
1125 202, 86–96.

1126 Stuiver M., Polach H. A., (1977) Discussion: Reporting of <sup>14</sup>C data. *Radiocarbon* 19,  
1127 355–363.

1128 Song G., Liu S., Zhang J., Zhu Z., Zhang G., Marchant H. K., Kuypers M. M. M. Lavik  
1129 G. (2020) Response of benthic nitrogen cycling to estuarine hypoxia. *Limnol.*  
1130 *Oceanogr.* 9999, 1–15.

1131 Sun C. H., Zhu M. X., Ma, W. W., Sun Z. L., Zhang X. R., Ding K. Y., and Liu S. H.  
1132 (2020) Examining bulk and iron-associated organic carbon through depth in margin  
1133 sea sediments (China) under contrasting depositional settings: Chemical and  
1134 NEXAFS spectral characterization. *J. Mar. Syst.* 207, 103344.

1135 Sun X., Fan D., Cheng P., Hu L., Sun X., and Guo Z. (2021) Source, transport and fate  
1136 of terrestrial organic carbon from Yangtze River during a large flood event: Insights  
1137 from multiple-isotopes ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ,  $\Delta^{14}\text{C}$ ) and geochemical tracers. *Geochim.*  
1138 *Cosmochim. Acta* 308, 217–236.

1139 van der Zee C., Roberts D. R., Rancourt D. G., and Slomp C. P. (2003) Nanogoethite is  
1140 the dominant reactive oxyhydroxide phase in lake and marine  
1141 sediments. *Geology* 31(11), 993-996.

1142 Wagai R., and Mayer L. M. (2007) Sorptive stabilization of organic matter in soils by  
1143 hydrous iron oxides. *Geochim. Cosmochim. Acta* 71, 25–35.

1144 Wan D., Ye T., Lu Y., Chen W., and Huang Q. (2019) Iron oxides selectively stabilize  
1145 plant-derived polysaccharides and aliphatic compounds in agricultural soils. *Eur. J.*  
1146 *Soil Sci.* 70(6), 1153–1163.

- 
- 1147 Wang D., Zhu M., Yang G., and Ma W. W., (2018) Reactive iron and iron-bound organic  
1148 carbon in surface sediments of the river-dominated Bohai Sea (China) versus the  
1149 Southern Yellow Sea. *J. Geophys. Res. Biogeosci.* 124, 79–98.
- 1150 Wang J., Yao P., Bianchi T. S., Li D., Zhao B., and Cui X. Q., Pan H. H., Zhang T. T.,  
1151 and Yu Z. G. (2015) The effect of particle density on the sources, distribution, and  
1152 degradation of sedimentary organic carbon in the Changjiang Estuary and adjacent  
1153 shelf. *Chem. Geol.* 402, 52–67.
- 1154 Wang X., Ma H., Li R., Song Z., and Wu J. (2012) Seasonal fluxes and source variation  
1155 of organic carbon transported by two major Chinese Rivers: The Yellow River and  
1156 Changjiang (Yangtze) River. *Global Biogeochem. Cycles* 26, GB2025.
- 1157 Wu C, Qian P, Zheng X, Zhou L, Wang H, Xu H. (2020) Quartz grain characteristics of  
1158 the late Pleistocene hard clay in the Yangtze River delta and implications for  
1159 sedimentary environment and provenance. *Quaternary Res.* 1–17.
- 1160 Wu J., Wang Y., and Cheng H. (2009) Bedforms and bed material transport pathways  
1161 in the Changjiang (Yangtze) Estuary. *Geomorphology* 104(3–4), 175–184.
- 1162 Wu Y., Eglinton T., Yang L., Deng B., Montluçon D., and Zhang J. (2013) Spatial  
1163 variability in the abundance, composition, and age of organic matter in surficial  
1164 sediments of the East China Sea. *J. Geophys. Res. Biogeosci.* 118, 1495–1507.
- 1165 Wu Y., Eglinton T. I., Zhang J., and Montluçon D. B. (2018) Spatiotemporal variation  
1166 of the quality, origin, and age of particulate organic matter transported by the Yangtze  
1167 River (Changjiang). *J. Geophys. Res. Biogeosci.* 123, 2908–2921.
- 1168 Wu Y., Zhang J., Liu S. M., Zhang Z. F., Yao Q. Z., Hong G. H., Cooper L. (2007).  
1169 Sources and distribution of carbon within the Yangtze River system. *Estuar. Coast  
1170 shelf S.* 71(1–2), 13–25.
- 1171 Xu B. C., Bianchi T. S., Allison M. A., Dimova, N. T., Wang H. J., Zhang L. J., Diao S.  
1172 B., Jiang X. Y., Zhen Y., Yao P., Chen H. T., Yao Q. Z., Dong W. H., Sui J. J., and Yu  
1173 Z. G. (2015) Using multi-radiotracer techniques to better understand sedimentary  
1174 dynamics of reworked muds in the Changjiang River Estuary and inner shelf of East  
1175 China Sea. *Mar. Geol.* 370, 76–86.
- 1176 Yao P., Zhao B., Bianchi T. S., Guo Z., Zhao M., Li D., Pan H. H., Wang J., Zhang T.  
1177 T., and Yu Z. G. (2014) Remineralization of sedimentary organic carbon in mud  
1178 deposits of the Changjiang Estuary and adjacent shelf: Implications for carbon  
1179 preservation and authigenic mineral formation. *Cont. Shelf Res.* 91, 1–11.

- 
- 1180 Yao P., Yu Z. G., Bianchi T. S., Guo Z. G., Zhao M. X., Knappy C. S., Keely B. J., Zhao  
1181 B., Zhang T. T., Pan H. H., Wang J. P., and Li D. (2015) A multiproxy analysis of  
1182 sedimentary organic carbon in the Changjiang Estuary and adjacent shelf. *J.*  
1183 *Geophys. Res. Biogeosci.* 120, 1407–1429.
- 1184 Ye C., Huang W., Hall S. J., and Hu S., (2022) Association of organic carbon with  
1185 reactive iron oxides driven by soil pH at the global scale. *Global Biogeochem. Cycles*  
1186 36, e2021GB007128.
- 1187 Yu H., Wu Y., Zhang J., Yao Q. Z., and Zhu Z. Y. (2007) The characteristics of lignin of  
1188 plants and soil samples in the Yangtze River (Changjiang) drainage basin. *Acta Sci.*  
1189 *Circumst.* 27, 817–823 (in Chinese with English abstract).
- 1190 Zhang J., Wu Y., Jennerjahn T. C., Ittekkot V., and He Q. (2007) Distribution of organic  
1191 matter in the Changjiang (Yangtze River) Estuary and their stable carbon and  
1192 nitrogen isotopic ratios: Implications for source discrimination and sedimentary  
1193 dynamics. *Mar. Chem.* 106, 111–126.
- 1194 Zhao B., Yao P., Bianchi T. S., Xu Y. H., Liu H., Zhang X. H., Liu J. W., Yu Z. G. (2017)  
1195 Early diagenesis and authigenic mineral formation in mobile-muds of the  
1196 Changjiang Estuary and adjacent shelf. *J. Mar. Syst.* 172, 64–74.
- 1197 Zhao B., Yao P., Bianchi T. S., Shields M. R., Cui X. Q., Zhang X. W., Huang X. Y.,  
1198 Schröder C., Zhao J., and Yu Z. G. (2018a) The role of reactive iron in the  
1199 preservation of terrestrial organic carbon in estuarine sediments. *J. Geophys. Res.*  
1200 *Biogeosci.* 123, 3556–3569.
- 1201 Zhao B., Yao P., Bianchi T. S., Arellano A. R., Wang X. C., Yang J. B., Su R., Wang J.,  
1202 Xu Y., Huang X., Chen L., Ye J., and Yu Z. (2018b) The remineralization of  
1203 sedimentary organic carbon in different sedimentary regimes of the Yellow and East  
1204 China Seas. *Chem. Geol.* 495, 104–117.
- 1205 Zhao B., Yao P., Bianchi T. S., and Yu Z. G. (2021a) Controls on organic carbon burial  
1206 in the Eastern China Marginal Seas: A regional synthesis. *Global Biogeochem.*  
1207 *Cycles* 35, e2020GB006608.
- 1208 Zhao B., Yao P., Li D., and Yu Z. (2021b) Effects of river damming and delta erosion  
1209 on organic carbon burial in the Changjiang Estuary and adjacent East China Sea  
1210 inner shelf. *Sci Total Environ.* 793, 148610.
- 1211 Zhao Y., Moore O. W., Xiao K. Q., Curti L., Fariña A. O., Banwart S. A., Peacock C. L.  
1212 (2022) The role and fate of organic carbon during aging of ferrihydrite. *Geochim.*

- 
- 1213 *Cosmochim. Acta* 335, 339-355.
- 1214 Zhu, C., Weijers, J., Wagner, T., Pan, J. M., and Pancost, R. D. (2011) Sources and  
1215 distributions of tetraether lipids in surface sediments across a large river-dominated  
1216 continental margin. *Org. Geochem.* 42(4), 376-386.
- 1217 Zhu M. X., Hao X. C., Shi X. N., Yang G. P., and Li T. (2012) Speciation and spatial  
1218 distribution of solid-phase iron in surface sediments of the East China Sea  
1219 continental shelf. *Appl. Geochem.* 27(4), 892–905.
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1221 **Figure Captions**

1222 **Figure 1.** (a) The map of the Changjiang, and the Eastern China Marginal Seas (ECMS)  
1223 (Including the Bohai Sea (BS), Yellow Sea (YS), and East China Sea (ECS)). Blue dots  
1224 denote sampling sites for surface sediments in this study. Red circles denote sampling  
1225 sites for suspended particulate matter (SPM) in this study. Brown dots denote sites for  
1226 surface soils in the Changjiang basin in Wan et al. (2019). Green dots denote sites for  
1227 surface sediments (0-3 cm) in the Zhe-Min coastal mobile muds (ZMMM) in Zhao et  
1228 al. (2018a). The dashed box represents the study area. (b) Sampling sites. Red circles  
1229 denote sites for SPM, and blue dots denote sites for surface sediments. The yellow  
1230 region denotes the Changjiang Estuary mobile muds (CEMM) and ZMMM. Pink  
1231 arrows denote the direction of currents (Liu et al., 2007). ZMCC: Zhe-Min Coastal  
1232 Current; YSCC: Yellow Sea Coastal Current; YSMW: Yellow Sea Mixing Water;  
1233 TWWC: Taiwan Warm Current.

1234  
1235 **Figure 2.** Distributions of SSA ( $\text{m}^2/\text{g}$ ) (a), Clay (%) (b), OC (%) (c), OC/SSA ( $\text{mg}$   
1236  $\text{OC}/\text{m}^2$ ) (d),  $\delta^{13}\text{C}$  (‰) (e) and  $\Delta^{14}\text{C}$  (‰) (f) in the suspended particulate matter (SPM)  
1237 and surface sediments in the Changjiang Estuary and adjacent East China Sea (ECS)  
1238 shelf.

1239  
1240 **Figure 3.** Distributions of reactive iron ( $\mu\text{mol}/\text{g}$ ) (a), OC-Fe<sub>R</sub> (wt%) (b),  $f_{\text{OC-FeR}}$  (%) (c),  
1241 OC-Fe<sub>R</sub>/Fe<sub>R</sub> (mol/mol) (d),  $\delta^{13}\text{C}_{\text{OC-FeR}}$  (‰) (e),  $\Delta^{14}\text{C}_{\text{OC-FeR}}$  (‰) (f),  $\Delta\delta^{13}\text{C}_{\text{OC-FeR}}$  (g), and  
1242  $\Delta\Delta^{14}\text{C}_{\text{OC-FeR}}$  of the suspended particulate matter (SPM) and surface sediments in the  
1243 Changjiang Estuary and adjacent East China Sea (ECS) shelf. Yellow shadow denotes  
1244 the estuarine mixing zone.

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1246 **Figure 4.** Correlations of  $f_{\text{OC-FeR}}$  with the fraction of fine-grained sediment (Clay+Silt %)   
1247 (a), SSA ( $\text{m}^2/\text{g}$ ) (b),  $\text{Fe}_R$  ( $\mu\text{mol}/\text{g}$ ) (c), and the fraction of (super)paramagnetic  $\text{Fe}^{3+}$  (d)   
1248 in the suspended particulate matter (SPM) and surface sediments in the Changjiang   
1249 Estuary and adjacent East China Sea (ECS) shelf.

1250

1251 **Figure 5.** Relationships of  $\Delta^{14}\text{C}$  versus  $\delta^{13}\text{C}$  in the suspended particulate matter (SPM)   
1252 and surface sediments in the Changjiang Estuary and adjacent East China Sea (ECS)   
1253 shelf. The  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values of  $\text{C}_3$  plants in the Changjiang basin were from Yu et   
1254 al. (2007) and Wu et al. (2018). The  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values of the Changjiang river basin   
1255 soils were from Wu et al. (2018). The  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values of Himalayan rock are from   
1256 Galy et al. (2008). The  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values of kerogen are from Jia et al. (2005). The   
1257  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values of East China Sea marine phytoplankton were from Zhang et al.   
1258 (2007). The  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values of Changjiang delta sediments were from Wu et al.   
1259 (2013).

1260

1261 **Figure 6.** Ratio of hematite to (super) paramagnetic  $\text{Fe}^{3+}$  versus  $\Delta^{14}\text{C}_{\text{bulk}}$  (b), and   
1262  $\Delta^{14}\text{C}_{\text{OC-FeR}}$  (c) in the suspended particulate matter (SPM) and surface sediments in the   
1263 Changjiang Estuary and adjacent East China Sea (ECS) shelf.

1264

1265 **Figure 7.** Box and whisker plots of OC (wt%) (a),  $\text{Fe}_R$  ( $\mu\text{mol}/\text{g}$ ) (b),  $f_{\text{OC-FeR}}$  (%) (c), OC-   
1266  $\text{Fe}_R/\text{Fe}_R$  ratio (d),  $\delta^{13}\text{C}_{\text{bulk}}$  (‰) (e),  $\delta^{13}\text{C}_{\text{OC-FeR}}$  (‰) (f) and schematic overview of the   
1267 OC- $\text{Fe}_R$  associations in the Changjiang Estuary and adjacent East China Sea (ECS)   
1268 shelf (g). The green dots represent marine OC, the black dots represent terrestrial OC,   
1269 and the dark yellow ellipses represent reactive iron. CEMM: Changjiang Estuary   
1270 mobile-muds; ZMMM: Zhe-Min coast mobile-muds; OT: Okinawa Trough. The brown

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1271 arrows denote the Changjiang major sediment dispersal pathways. Data in soils are  
1272 from Wan et al. (2019). Data in ZMMM are from Zhao et al. (2018a). Data in OT are  
1273 from Sun et al. (2020).

1274

1275 **Figure 8.** Distribution of  $f_{OC-FeR}$  in soils and marine sediments on a global scale (a). The  
1276 average  $f_{OC-FeR}$  in different sedimentary regimes in land and ocean (b). Correlations of  
1277  $f_{OC-FeR}$  versus OC (c),  $f_{OC-FeR}$  versus  $Fe_R$  (d), and  $\delta^{13}C_{bulk}$  versus  $\delta^{13}C_{OC-FeR}$  (e) in soils  
1278 and marine sediments on a global scale. Data on soils are from Ye et al. (2022) and  
1279 references therein. Estuarine suspended particulate matter (SPM) includes the  
1280 Changjiang SPM (this study). Deltaic and mobile-mud sediments include the  
1281 Changjiang estuary mobile muds, Zhe-Min coast mobile muds, Makenzie River delta,  
1282 Quebec beach subterranean Estuary, and Wax Lake Delta (Lalonde et al., 2012; Shields  
1283 et al., 2016; Sirois et al., 2018; Sun et al., 2020; Zhao et al., 2018a and this study).  
1284 Continental margin sediments include the Mexican Margin, St-Lawrence Gulf, Madeira  
1285 turbidite, Washington Coast, Arabian Sea, Barents Sea shelf, Eurasian Arctic Shelf,  
1286 Gulf of Mexico, the middle and outer shelf of the East China Sea, Bohai, and South  
1287 Yellow Sea (Faust et al., 2020; Ghaisas et al., 2021; Lalonde et al., 2012; Longman et  
1288 a., 2021; Ma et al., 2018; Salvado et al., 2015; Wang et al., 2018; Zhao et al., 2018a and  
1289 this study). Coastal and freshwater wetlands include tidal wetlands of the Min River  
1290 estuary and mangrove areas across the Philippines (Bai et al., 2021; Dicen et al., 2019).  
1291 Anoxic and sulphidic sediments include the Black Sea, Mexican Margin, Indian Margin,  
1292 Lake Brock, and Arabian Sea (Lalonde et al., 2012). Deep-sea sediments include the  
1293 Southern Ocean, Equatorial Pacific, station M and the Okinawa Trough (Lalonde et al.,  
1294 2012; Sun et al., 2020).