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

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Abstract

Reactive iron (Fe_R) plays an important role in the preservation of organic carbon (OC) in coastal sediments, yet changes in the OC bound to Fe_R (OC-Fe_R), during transport and deposition, remain poorly understood. The main goal of this work is to investigate the variation of the age and composition of OC-Fe_R from estuarine suspended particulate matter (SPM) to coastal sediments, to further understand the role of Fe_R in the preservation of terrestrial OC exported from large rivers into marginal seas. We examined OC and its carbon isotopic composition ($\Delta^{14}C_{bulk}$, $\delta^{13}C_{bulk}$), specific surface area (SSA), grain size composition, lignin phenols, Fe_R, Mössbauer spectroscopy, and isotopic signatures of OC-Fe_R ($\Delta^{14}C_{OC\text{-}FeR}$, $\delta^{13}C_{OC\text{-}FeR}$) in SPM and surface sediments of the Changjiang Estuary. Particulate OC (POC) and Fe_R concentrations in SPM are significantly higher than in surface sediments, with no significant differences between surface- and bottom-water SPM. This indicates that loss of OC and Fe_R largely occurs at the sediment-water interface due in part, to rapid Fe cycling. The percentage of OC-Fe_R ($f_{OC\text{-}FeR}$) in SPM (6.6 ± 1.9%) is similar to that in mobile-mud sediment (8.8 ± 1.8%). There are no significant differences in OC-Fe_R content ($p>0.05$) from SPM to mobile-mud sediments, but non-OC-Fe_R largely decreases, suggesting that terrestrial OC-Fe_R has greater stability compared to terrestrial non-OC-Fe_R. Both $\delta^{13}C_{OC\text{-}FeR}$ and $\Delta^{14}C_{OC\text{-}FeR}$ are lower than bulk OC, indicating that Fe_R is mainly associated with pre-aged soil OC of terrestrial plant origin, especially in estuarine SPM and mobile-mud sediments. Taken together, binding with Fe_R is a potential long-term protection mechanism for terrestrial OC. Both $\Delta^{14}C_{bulk}$ and $\Delta^{14}C_{OC\text{-}FeR}$ decrease with an increase in the ratio of hematite to (super)paramagnetic Fe^{3+}, indicating that high-crystallinity iron oxide is largely associated with pre-aged terrestrial OC, and there is a potential joint maturation mechanism between Fe_R and its associated OC. Based on literature comparisons of soils, estuarine SPM, and marine sediments, OC-Fe_R associations are controlled mainly by sedimentary regimes, Fe_R compositions, and OC sources. This work supports the notion that Fe_R plays an important role in the stabilization and transport of river-derived terrestrial OC.

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

1. Introduction

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

The involvement of Fe_R in OC preservation in soils and marine sediments has been shown by many studies (Faust et al., 2021; Lalonde et al., 2012; Longman et al., 2022; Zhao et al., 2018a), but the factors controlling OC-Fe_R preservation need to be better constrained. The binding capacity with OC varies among different iron oxides. For example, high SSA and low-crystallinity iron oxides (e.g., ferrihydrite) usually exhibit a higher affinity to OC, compared to high-crystallinity iron oxides, such as lepidocrocite, goethite, and hematite (Lv et al., 2016). Moreover, the OC bound to iron oxides varies in different sedimentary settings. Prior works indicate that OC-Fe$_R$ accounted for about 15% to 20% of OC in soils and marine sediments (Lalonde et al., 2012; Longman et al., 2022; Wan et al., 2019; Zhao et al., 2018a). In some non-deltaic shelf and anoxic regions, more than 20% of sedimentary OC (SOC) is associated with Fe$_R$ (Ghaisas et al., 2021; Lalonde et al., 2012). However, only <10% of SOC is associated with Fe$_R$ in the sub-aqueous deltaic and mobile-muds sediments (Lalonde et al., 2012; Shields et al., 2016; Zhao et al., 2018a). Estuarine mobile muds are commonly located in the entry points of sediments to marginal seas (e.g., estuaries and inner shelves), and they are highly dynamic regions where tidal oscillations, sediment resuspension, and remobilization frequently occur, which can enhance SOC decomposition, through increased oxygen exposure time (e.g., reoxidation and repetitive redox successions) and priming effects via fresh algal OC (Aller et al., 1998; Bianchi, 2011; Blair and Aller, 2012; McKee et al., 2004). The composition of OC may also affect what types of OC-Fe$_R$ associations occur. For instance, vascular plant-derived aromatic and pyrogenic compounds appear to be preferentially bound to Fe-oxyhydroxides, in contrast to aliphatic acids (Christl and Kretzschmar, 2007; Riedel et al., 2012, 2013). The stable carbon isotopic composition of OC-Fe$_R$ ($\delta^{13}C_{OC\text{-}FeR}$) is commonly higher than bulk OC over a wide range of marine sediments, indicating that Fe$_R$ is in favor of marine OC preservation (Lalonde et al., 2012). But deltaic sediments have lower $\delta^{13}C_{OC\text{-}FeR}$ compared to $\delta^{13}C$ of bulk OC ($\delta^{13}C_{bulk}$), suggesting that Fe$_R$ in deltaic sediments is bound to more terrestrial OC (Lalonde et al., 2012; Shields et al., 2016; Sirois et al., 2018; Zhao et al., 2018a). Based on the radiocarbon age of OC-Fe$_R$ ($\Delta^{14}C_{OC\text{-}FeR}$) and $\delta^{13}C_{OC\text{-}FeR}$, Fe$_R$ appears to protect thawed ancient terrestrial permafrost OC in the East Siberian Arctic Shelf, which weakens climate feedback - via degradation of thawed permafrost OC (Salvadó et al., 2015). Despite such efforts, the mechanisms that control the age and composition of OC-Fe$_{\text{R}}$ from the river to the ocean remain poorly constrained.

The Changjiang (Yangtze River) is the largest river in China and delivers large amounts of terrestrial-derived suspended particulate matter (SPM), rich in OC and Fe$_{\text{R}}$ relative to coastal sediments, to the Changjiang Estuary and adjacent East China Sea (ECS) shelf (Milliman and Farnsworth, 2011; Wang et al., 2012; Zhu et al., 2012; Zhao et al., 2021a). A previous study revealed a positive correlation between burial efficiency (percentage of OC preserved) of terrestrial OC and net sediment accumulation rate over a range of marine environments (Canfield et al., 1994). However, the preservation efficiency of terrestrial OC in the Changjiang Estuary is lower (< 30%) than other sedimentary regimes with similar high sedimentation rates, due largely to processes associated with mobile/fluidized muds (Blair and Aller, 2012; Yao et al., 2014; Zhao et al., 2021a). Terrestrial OC is continually decomposed and aged in multiple re-suspension-deposition loops during sediment mobilization in mobile muds (Bao et al., 2016, 2019a; Zhao et al., 2021a). Large inputs of Fe$_{\text{R}}$, coupled with frequent physical reworking, result in rapid iron redox cycling, which is considered the primary diagenetic pathway in the Changjiang Estuary mobile muds (Zhao et al., 2017, 2018b). These mobile muds have higher OC and Fe$_{\text{R}}$ contents relative to the ECS shelf, but the fraction of OC-Fe$_{\text{R}}$ to bulk OC ($f_{\text{OC-FeR}}$) is low (Zhao et al., 2018a). One possible explanation is that rapid iron redox cycling in the estuary prevents Fe$_{\text{R}}$ from binding with marine OC (Zhao et al., 2018a). However, it is still unclear whether the low $f_{\text{OC-Fe}}$ in estuarine sediments is because OC-Fe$_{\text{R}}$ is continually reduced in this highly dynamic sedimentary environment, or because the $f_{\text{OC-FeR}}$ in estuarine SPM is inherently low. In addition, the variation of carbon isotopic composition of OC-Fe$_{\text{R}}$ from estuarine SPM to coastal sediments is also unknown. In this study, we analyzed $\delta^{13}C$ and $\Delta^{14}C$ of OC-Fe_R, as well as Fe phases, in estuarine SPM and coastal sediments of the Changjiang Estuary. Compared with previous work in this region (Ma et al., 2018; Sun et al., 2020; Wan et al., 2019; Zhao et al., 2018a), this is the first report of such data in estuarine particles. The overarching objective of this work is to build on previous studies and trace the variation of the age and composition of OC-Fe_R from estuarine SPM to coastal sediments, to better understand the role of Fe_R in the preservation of terrestrial OC exported from large rivers into marginal seas. This is also the first study to examine the linkages between carbon isotopic compositions of OC-Fe_R and iron phases from drainage basin soils to estuarine particles and coastal sediments, using state-of-the-art techniques for both Fe oxides and OC compositional analyses.

2. Materials and Methods

2.1 Study area

The ECS shelf is a shallow and broad epi-continental shelf (Blair and Aller, 2012). Annually, it can receive a large number of terrestrial particles from Changjiang, which is ranked as the fourth largest sediment flux in the world (~4.8 × 10^8 t/year) (Milliman and Farnsworth, 2011). During river SPM transportation, coarse-grained particles preferentially are deposited in riverbeds but fine-grained particles can be transported to mobile muds and even ECS shelf regions (Guo et al., 2018; Sun et al., 2021). The bed load results in the accumulation of coarse-grained sediments in the inner estuary (Chen et al., 1999; Wu et al., 2009). Once these terrestrial particles enter the coastal ocean, most of them are “trapped” and subjected to long-term hydrodynamic sorting and reworking processes in Changjiang estuary mobile muds (CEMM) and Zhe-Min coast mobile muds (ZMMM) along the coast (Liu et al., 2006; Xu et al., 2015; Zhao et al., 2021a) (Figure 1a). The CEMM are characterized by high sedimentation rates (1-3 cm yr^{-1}), shallow water depths, frequent physical reworking, and large terrestrial inputs (Xu et al., 2015; Yao et al., 2014; Zhao et al., 2018b). Although most of the Changjiang-derived sediment is transported to the south, a small fraction of the terrestrial SPM from the Changjiang is exported to the ECS shelf by cross-shelf transport (Iseki et al., 2003; Kao et al., 2003; Oguri et al., 2003). For the ECS shelf, sediments are dominated by relict sands, which are believed to be deposited during the Late Pleistocene when the sea level was low (Zhu et al., 2011). The ECS shelf is characterized by lower sedimentation rates (<0.5 cm/yr) and inputs of terrestrial OC compared to CEMM due to the barrier of the northward flowing Taiwan Warm Current (TWWC) (Liu et al., 2006). Nevertheless, most of the clay minerals, iron oxides, and terrestrial OC in ECS-shelf sediments are derived from Changjiang (Eisma et al., 1995; Li et al., 2014; Zhu et al., 2012).

2.2 Samples and data collection

Eleven SPM samples from the surface and bottom waters (< 2 m above the seabed) along the salinity gradient from *Xuliujing* (C1) (salinity ~0) in the inner estuary to the seaward side of the Changjiang Estuary (A6-5), were collected in July 2018 using a CTD-rosette water sampler (Seabird 911 Plus, USA) onboard the *R/V Chuangxin 2* (Figure 1b). In-situ salinity in the water column was also measured by this CTD-rosette system from C1 to A6-10 along this river-estuary shelf transect (Figure 1b). After collection, these water samples were filtered immediately through pre-combusted (550 °C for 5 h) and pre-weighed Whatman GF/F filters (0.7 μm nominal pore size), and the filters were wrapped in pre-combusted aluminum foil and stored at -20°C. Prior to chemical analyses, these filters were weighed again in the lab after freeze-drying to calculate the SPM concentrations. Eleven surface sediments (0-3 cm in depth) in the Changjiang Estuary were collected using a box core sampler during the same cruise. For avoiding disturbance, only the samples having an undisturbed sediment surface and clear overlying water were used for surface sediment sampling. All sediments were also stored frozen at -20°C prior to freeze-drying and further analyses.

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

2.3 Specific surface area and grain size composition

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

2.4 Organic carbon and its isotopic compositions ($\delta^{13}C_{bulk}$ and $\Delta^{14}C_{bulk}$)

The OC contents and $\delta^{13}C_{bulk}$ of SPM and surface sediments were measured using an elemental analyzer (Vario MICRO cube EA, Elementar, Germany), interfaced to a continuous flow isotope ratio mass spectrometer (Isoprime IRMS, Elementar, Germany) after removing the carbonates via acid fumigation (Wang et al., 2015). Briefly, ~30 mg of freeze-dried particles or sediments in silver capsules was acidified with a 12 M HCl vapor bath for 12 h to remove carbonates, and then dried in an oven at 60°C and crimp-sealed in tin capsules prior to analysis. The analytical precisions for OC and $\delta^{13}C$ are ± 0.02 wt% and ± 0.05‰ based on duplicate analyses ($n = 6$), respectively. Selected SPM and sediment samples were oxidized using the quartz tube oxidation method for ^{14}C analysis (Ge et al., 2020). Radiocarbon was determined using Accelerator Mass Spectrometry (AMS) after the graphitization of CO_2 at the Qingdao National Laboratory for Marine Science and Technology (QNLM) in China. Radiocarbon results are measured as fraction modern (F_m), and the $\Delta^{14}C$ values and conventional radiocarbon ages (years before present) are calculated based on Stuiver and Polach (1977). The analytical precision for $\Delta^{14}C$ measurements is generally <5‰.

2.5 Analyses of Fe_R and OC-Fe_R

Fe_R and OC-Fe_R were determined using the bicarbonate-citrate buffered dithionite (BCD) reduction method according to Lalonde et al. (2012). Briefly, sediments (~ 1g dry weight) were freeze-dried, ground, and then extracted at 80°C for 15 min. in a solution of sodium dithionite, trisodium citrate, and sodium bicarbonate. The resulting suspension was centrifuged for 10 min. at 3000 rpm after extraction and rinsed three times with artificial seawater. The supernatant and rinsed water were acidified (pH < 2) and preserved at 4°C for Fe measurement. Before measurement, these water samples were centrifuged again to remove fine particles. Dissolved Fe in the supernatant and rinsed water was measured on 1:20 diluted aliquots in nitric acid (2%) using inductively-coupled plasma optical emission spectrometer (ICP-OES) (iCAP6300, Thermo Fisher Scientific., USA). The reported precision for dissolved Fe in duplicate samples was less than 2% (Zhao et al., 2017). The residual sediments were freeze-dried before analyzing OC, $\delta^{13}C$, and $\Delta^{14}C$. A control experiment was carried out before the extraction experiment to correct for the OC removed due to the conditions of the extraction (e.g., pH, ionic strength, physical mixing, and heat) (OC not associated with Fe_R) without the dithionite reducing agent. In the control experiment, all samples were extracted under the same protocol but using sodium chloride to replace the sodium dithionite.

Fe_R and OC-Fe_R were calculated by the following equations:

$$Fe_R\ (\mu mol/g) = (Fe_{extract} - Fe_{control}) \times V/M \quad (1)$$

$$OC\text{-}Fe_R\ (wt\%) = (OC_{control} - OC_{extract}) \quad (2)$$

$$f_{OC\text{-}FeR}\ (\%) = (OC_{control} - OC_{extract}) / OC_{bulk} \quad (3)$$

where, $f_{OC\text{-}FeR}$ (%) is the percentage of OC bound to Fe_R; $Fe_{control}$ and $OC_{control}$ are Fe content in the supernatant and rinsed water and OC content after the control experiment, respectively; V is the volume of the supernatant and rinsed water and M is the mass of sample; $Fe_{extract}$ is Fe content in the supernatant and rinsed water and $OC_{extract}$ is OC content after the extraction experiment; OC_{bulk} is the total OC in bulk sediment.

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

$$\delta^{13}C_{OC\text{-}FeR}\ (‰) = (\delta^{13}C_{control} \times OC_{control} - \delta^{13}C_{extract} \times OC_{extract})/(OC_{control} - OC_{extract}) \quad (4)$$

$$\Delta^{14}C_{OC\text{-}FeR}\ (‰) = (\Delta^{14}C_{control} \times OC_{control} - \Delta^{14}C_{extract} \times OC_{extract})/(OC_{control} - OC_{extract}) \quad (5)$$

where $\delta^{13}C_{control}$ and $\Delta^{14}C_{control}$ are isotopic signatures of the OC after the control experiment; $\delta^{13}C_{extract}$ and $\Delta^{14}C_{extract}$ are isotopic signatures of the OC after the extraction experiment.

2.6 Mössbauer spectroscopy

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

2.7 Lignin phenols

Lignin phenols are used as biomarkers for quantifying the contribution of terrigenous vascular plant tissues in bulk samples. Twelve lignin phenol oxidation products were quantified and analyzed using the alkaline CuO method, including three vanillyl phenols [V=vanillin (VAL) + acetovanillone (VON) + vanillic acid (VAD)], three syringyl phenols [S= syringaldehyde (SAL) + acetosyringone (SON) + syringic acid (SAD)], two cinnamyl phenols [C = p-coumaric acid (CAD) + ferulic acid (FAD)], three p-hydroxybenzenes [P = p-hydroxybenzaldehyde (PAL) + phydroxyacetophenone (PON) + p-hydroxybenzoic acid (PAD)], and 3,5-dihydroxybenzoic acid (3,5-Bd)] (Hedges and Ertel, 1982; Hedges and Mann, 1979). Briefly, powdered freeze-dried sediments containing ca. 3-5 mg OC were placed in a stainless-steel reaction vessel with 330 ± 4 mg CuO and 2.5 mL of 2 M NaOH in a nitrogen glove box. Each sealed vessel was digested for 3 h at 150 °C. Then, 50 μL of ethyl vanillin (EVAL) was added to each reaction vessel as an internal standard before the aqueous reaction products were separated from the sediments by centrifugation. The supernatant was acidified with HCl to $pH < 2$, extracted using ethyl acetate 3 times, and dried under a gentle N_2 stream. The oxidation products were derivatized with N, O-Bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) for 1 h, and then, the derivatives were measured using an Agilent 7890A gas chromatography-flame ionization detector (GC-FID). The identification and quantification of lignin phenols were based on the recovery of an internal standard (EVAL) and an absolute recovery (methyl 3,4-dimethoxybenzoate), and a mixture of lignin-phenol standards containing known amounts of compounds of interest. Σ_8 (mg/g dry sediment) and Λ_8 (mg/100 mg OC) are used as indicators of lignin concentrations, which is the total weight of the 8 lignin phenols (V+S+C) normalized to 1 g dry sediment and 100 mg OC, respectively. The acid-to-aldehyde ratios of V and S [$(Ad/Al)_V$ and $(Ad/Al)_S$] phenols are used as indicators for lignin oxidative degradation (Hedges et al., 1988). The P/(S + V) ratio is used as a specific indicator of the degradation state of lignin side chains by brown-rot fungi (Dittmar and Lara, 2001). The 3,5-Bd/V ratio is considered to be an indicator of OC oxidation in soils (Houel et al., 2006). Higher values of these indicators suggest stronger oxidative degradation of lignin phenols (Dittmar and Lara, 2001; Hedges et al., 1988; Houel et al., 2006).

2.8 Statistical analyses

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

3. Results

3.1 Hydrological characteristics and different sedimentary regimes

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

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

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

3.2 Bulk organic carbon and its carbon isotopic composition of SPM and surface sediments

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

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

3.3 OC-Fe$_R$ associations in SPM and surface sediments

Fe$_R$, OC-Fe$_R$ content, non-OC-Fe$_R$ content, $f_{OC\text{-}FeR}$, OC-Fe$_R$/Fe$_R$ ratios, $\delta^{13}C_{OC\text{-}FeR}$, and $\Delta^{14}C_{OC\text{-}FeR}$ values in SPM samples and surface sediments of the Changjiang Estuary are shown in Table S3. The Fe$_R$ contents in surface sediments are significantly lower than those in SPM samples ($p<0.01$), ranging from 28.0 to 162.7 μmol/g sed., with higher values in mobile muds and lower values in the inner estuary and ECS shelf (Figure 3a). The OC-Fe$_R$ content in SPM samples ranges from 0.03 to 0.08 wt%, which is very close to that in mobile-mud sediments (0.05 ± 0.01 wt%) but generally higher than those in inner-estuary (0.02 ± 0.01 wt%) and ECS-shelf sediments (0.04 ± 0.01 wt%) ($p<0.05$) (Table S3). The non-OC-Fe$_R$ content in SPM samples ranges from 0.64 to 1.19 wt%, which is significantly higher than those in mobile-mud (0.51 ± 0.04 wt%), inner-estuary (0.10 ± 0.06 wt%) and ECS-shelf sediments (0.24 ± 0.04 wt%) ($p<0.05$) (Table S3). Fractions of OC-Fe$_R$ in bulk OC ($f_{OC\text{-}FeR}$) in SPM samples (6.6 ± 1.9%) are similar to those in mobile-mud sediments (8.8 ± 1.8%) but significantly lower than inner-estuary (20.0 ± 5.0%) and ECS-shelf sediments (14.1 ± 3.3%) ($p<0.05$) (Figure 3c and Table S3). Molar ratios of OC-Fe$_R$ to total Fe$_R$ (OC-Fe$_R$/Fe$_R$) are generally low in SPM samples (0.20 ± 0.06), inner-estuary sediment (0.23 ± 0.08), and mobile-mud sediment (0.30 ± 0.10), but higher values in ECS-shelf sediment (0.79 ± 0.39) (Figure 3d).

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

3.4 Mössbauer Spectroscopy

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

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

3.5 Lignin phenols

The lignin phenols and related parameters in SPM samples and surface sediments are shown in Table S5. The Σ_8 of SPM samples range from 0.82 to 2.02 mg/g dry sediment and decrease with an increase in salinity (Figure S5). For surface sediments, higher Σ_8 is observed in mobile muds relative to the inner estuary and ECS shelf (Figure S5). The Λ_8 in SPM samples varies from 0.05 to 0.11 mg/100mg OC with no obvious variation trends (Figure S5). Similar to the distribution of Σ_8, high Λ_8 is found in estuarine sediments (e.g., A6-1 and A6-3) and low Λ_8 was found in the inner-estuary and ECS-shelf sediments (Figure S5). Lignin degradation indices, such as $(Ad/Al)_V$, $(Ad/Al)_S$, P/(S+V), and 3,5-Bd/V, all show similar distribution patterns, with higher values in the inner-estuary and ECS-shelf sediments, but lower values in SPM samples and mobile-mud sediments (Figure S5).

4. Discussion

4.1 OC, Fe_R, and OC-Fe_R associations from river-estuarine particles to coastal sediments

The overall compositional differences between SPM and surface sediments suggest that the majority of Changjiang-derived particles, containing mostly terrestrial OC, are deposited in the estuarine mobile muds, where significant losses of OC occurred. There are no significant differences in grain size composition and SSA values between SPM and mobile-mud sediments ($p>0.05$), indicating that most of the estuarine fine-grained SPM is deposited in the mobile mud region of the Changjiang Estuary (Figures 2a and 2b). High sedimentation rates partly result in higher OC content in mobile-mud sediments relative to inner-estuary and ECS-shelf sediments (Figure 2c) (Zhao et al., 2021a). Similarly, higher lignin concentrations (Σ_8 and Λ_8) in mobile-mud sediments also suggest greater deposition of terrestrial plant-derived OC relative to the inner-estuary and ECS-shelf sediments (Figure S5). This can be attributed to coastal currents and the limitation of cross-shelf sediment transport by TWWC (Liu et al., 2007).

However, this deposited terrestrial OC may not be well preserved because of frequent resuspension and redeposition of mobile muds (Bao et al., 2016; Yao et al., 2014, 2015; Zhao et al., 2018b). The OC/SSA ratio in SPM samples is significantly ($p < 0.05$) higher than that in mobile-mud sediments, with no significant differences ($p > 0.05$) between surface- and bottom-water SPM, indicating that loss of OC mainly occurs in sediments or at the sediment-water interface (Figure 2d). Similarly, the Fe_R in SPM is also significantly higher than that in mobile-mud sediments ($p < 0.05$) (Figure 3a). Surface fine-grained sediments can be resuspended into bottom-waters and involved in resuspension-redeposition loops in the Changjiang Estuary (Bao et al., 2019b; Guo et al., 2003), which is partly supported by higher SPM concentrations in bottom-waters compared to surface-waters in the estuarine mixing zone (Figure S1). At the same time, sediment in the mobile muds is well mixed because of frequent physical reworking (Xu et al., 2015), likely resulting in surface sediment with high OC and Fe_R contents mixed with deep sediment with low OC and Fe_R contents. Hence, higher OC and Fe_R content in bottom-water SPM compared to surface sediments indicates that most OC and Fe_R removal occurs in the sediments and/or at the sediment-water interface (Figures 2c and 3a). This is also supported by a higher fraction of (super)paramagnetic Fe^{3+} in SPM relative to surface sediments, reflective of the loss of highly reactive (super)paramagnetic Fe^{3+} (Figure S4). In the case of estuarine particles, OC and Fe_R are largely, although not exclusively, associated with particle surfaces (Blair and Aller, 2012; Mayer 1994; Poulton and Raiswell, 2005). Here SSA is considered to be primarily influenced by physical sorting processes (Blair and Aller et al., 2012; Mayer, 1994; Keil et al., 1997). Therefore, normalization of OC or Fe_R to SSA provides a way to examine net reaction or supply processes in particle populations independently of physical sorting (Blair and Aller et al., 2012; Poulton and Raiswell, 2005; Sun et al., 2021). Due to similar grain size composition and SSA values, the decrease of OC and Fe_R contents from estuarine SPM to mobile-mud sediment reflects net loss during sediment deposition rather than other physical processes (Figure 2c).

Simultaneous decreases of Fe_R and OC from estuarine SPM to mobile-mud sediments indicated that iron redox cycling may be partly responsible for the loss of OC in mobile-mud sediments (Figure S6). Previous work has indicated that iron reduction is an important early diagenetic pathway for OC remineralization in the CEMM (Zhao et al., 2017, 2018b). Results of whole-core incubation experiments showed that both dissolved inorganic carbon and Fe^{2+} concentrations increase in pore-water with incubation time in the CEMM, demonstrating that iron reduction is largely responsible for OC remineralization (Zhao et al., 2018b). Nevertheless, the role of Fe reduction is clearly underestimated in this incubation experiment due to the absence of physical mixing (Zhao et al., 2018b). Xu et al. (2015) found the depth of reworked mud is more than 20 cm in the CEMM, where high disturbance events usually occur over very short time intervals, e.g., days to weeks, based on multi-radiotracer techniques (Xu et al., 2015). However, despite frequent physical reworking in the CEMM, the oxygen penetration depth is ~1-3 mm at different seasons, reflective of anoxic or sub-oxic conditions (Song et al., 2020), which indicates that redox conditions in sediments may change quickly. In fact, anoxic or sub-oxic conditions coupled with physical reworking in mobile muds could enhance Fe reduction and OC remineralization because metal oxides help to shuttle electrons between O_2 and OC (Aller, 2004; Burdige, 1993; Canfield et al., 1993; Fu et al., 2019). Thus, iron reduction resulting in the loss of bulk OC and Fe_R in the CEMM is expected.

From estuarine particles to mobile-mud sediments, there are no significant differences in OC-Fe_R content ($p>0.05$), but OC not bound to Fe_R (non-OC-Fe_R = bulk OC - OC-Fe_R) largely decreases from estuarine particles to mobile-mud sediments, indicating that OC-Fe_R is preserved better than non-OC-Fe_R (Figure 3b and Table S3). This also demonstrates that Fe_R can protect OC even in estuarine mobile muds with intense iron reduction. The $f_{OC\text{-}FeR}$ values in estuarine SPM ($f_{OC\text{-}FeR} = 6.6 \pm 1.9\%$) and mobile-mud sediments ($f_{OC\text{-}FeR} = 8.8 \pm 1.8\%$) are lower than those in inner-estuary ($f_{OC\text{-}FeR} = 20.0 \pm 5.0\%$) and ECS-shelf ($f_{OC\text{-}FeR} = 14.1 \pm 3.3\%$) sediments, showing Fe_R may play a more important role in OC preservation in sandy sediments (Figure 3c). Higher Fe_R and OC contents but lower $f_{OC\text{-}FeR}$ in estuarine SPM and mobile-mud sediments relative to inner-estuary and ECS-shelf sediment suggest that OC-Fe_R associations are not generally controlled by Fe_R and OC availability (Faust et al., 2021; Longman et al., 2021). These low $f_{OC\text{-}FeR}$ values in estuarine SPM samples and mobile-mud sediments are close to those in other deltaic sediments (e.g., ~7.6% in Mackenzie River Delta, and ~8.1% in the youngest subaerial region of Wax Lake Delta) (Lalonde et al., 2012; Shields et al., 2016). The $f_{OC\text{-}FeR}$ in the inner-estuary and ECS-shelf sediments is in the range of previous results of typical oxic or sub-oxic marine sediments, and close to the global average ($f_{OC\text{-}FeR} = 21.5 \pm 8.6\%$) (Lalonde et al., 2012). The fraction of fine-grained sediment (Clay+Silt%) has a negative relationship with $f_{OC\text{-}FeR}$, suggesting that sediment type is likely responsible for the interaction between OC and Fe_R, with high $f_{OC\text{-}FeR}$ in coarse-grained sediments (inner-estuary and ECS-shelf sediments) but low $f_{OC\text{-}FeR}$ in fine-grained sediments (SPM and mobile-mud sediments) (Figure 4a). This is possible because sandy sediments provide less surface area to adsorb OC, and thus binding with Fe_R becomes more important for OC preservation (Figure 4b). In addition, earlier work indicated that low Fe_R concentrations and less resuspension in the ECS shelf and inner estuary likely diminish the role of iron redox cycling, thus contributing to the greater proportion of OC bound to Fe_R (Figure 4c) (Zhao et al., 2018a). This is also supported by the negative correlation between $f_{OC\text{-}FeR}$ and the fraction of (super)paramagnetic Fe^{3+}, which suggests that Fe_R binds with more OC in the case of low fractions of reactive ferric oxide phases in ECS-shelf and inner-estuary sediments (Figure S4). As a result, binding with Fe_R not only protects OC in mobile-muds but is also likely a complementary mechanism for OC preservation when sediments lack fine-grained components. Clearly, a direct comparison of OC bound to clay mineral and OC-Fe_R is needed in future studies.

There is no significant change of OC-Fe_R from SPM to mobile-mud sediments, suggesting that OC-Fe_R associations are not broken up during sediment deposition (p>0.05) (Figure 3b). However, a large amount of Fe_R is removed as discussed before, which indicates that the greatest loss of Fe_R occurs with OC-free Fe_R (Figure 3a). Barber et al. (2017) pointed out that a quantitatively important fraction of Fe_R extracted by the BCD method is not directly associated with OC. In fact, OC-Fe_R associations not only protect OC from microbial degradation but also are considered to stabilize Fe_R (van der Zee et al., 2003; Schröder et al., 2016; Zhao et al., 2022). The OC-free Fe_R may be subjected to more intense reduction than OC-associated Fe_R, also leading to a higher OC-Fe_R/Fe_R ratio in mobile-mud sediments relative to SPM (Figure 3d). Therefore, a mutual protection mechanism of Fe_R and its associated OC likely contributes to the stability of OC-Fe_R associations in CEMM.

4.2 Association with Fe_R as a potential mechanism for long-term preservation of terrestrial OC in estuarine sediments

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

50‰, respectively (Galy et al., 2008; Wu et al., 2018). Increases in $\delta^{13}C_{bulk}$ and $\Delta^{14}C_{bulk}$ values of POC from the inner estuary with low salinity (e.g., C1 and C7) to mobile muds with high salinity (e.g., A6-5) indicate the addition of modern marine OC to the estuarine SPM (Figures 2e and 2f). This supports previous work that showed the replacement of terrestrial OC by marine OC on fine soil-derived particulates from rivers with increasing salinities in coastal margins (Keil et al., 1994, 1997; Prahl et al., 1994). $\delta^{13}C$ values of SOC also increase from the inner estuary to the ECS shelf, revealing the addition of marine OC to the sediments (Figure 2e). Increased $\delta^{13}C$ values may also occur with the addition of C_4 plant-derived OC with high $\delta^{13}C$ values (-9‰ to -16‰) (Pancost and Boot, 2004). However, as the POC of Changjiang is dominated by C_3 plants, the C_4 plant-derived OC contribution to OC in the Changjiang Estuary should be minimal (Wu et al., 2007). Even with the addition of marine OC, the OC/SSA ratios largely decrease from SPM to mobile-mud sediments, indicating that terrestrial OC must be decomposed and/or desorbed before final burial. No significant change of $\Delta^{14}C$ values of bulk OC between SPM and mobile-mud sediments ($p>0.05$) also indicates that the simultaneous addition of modern marine OC and loss of young terrestrial OC balance the $\Delta^{14}C_{bulk}$ value during sediment deposition (Figure 3f). This result supports previous work which showed that frequent physical reworking activities in the Changjiang Estuary mobile muds enhance the remineralization of young terrestrial OC via increased oxygen-exposure time (OET) (Zhao et al., 2021a). Clearly, the effect of young terrestrial OC loss on $\Delta^{14}C_{bulk}$ is balanced by the addition of modern marine OC, and thus the $\Delta^{14}C$ value of the remaining terrestrial OC is relatively low. Results from ramped pyrolysis-oxidation (RPO) analysis also suggest that the younger part of terrestrial OC could be selectively removed, resulting in aging terrestrial OC from Changjiang SPM to mobile-mud sediments (Bao et al., 2019b). Both the $\delta^{13}C_{bulk}$ value and OC/SSA ratio increase from mobile-mud to ECS-shelf sediments, but the $\Delta^{14}C_{bulk}$ value stays constant, further demonstrating the balance between marine OC addition and young terrestrial OC decomposition, desorption, and/or aging during cross-shelf transport (Figures 3e and 3f). The lowest $\Delta^{14}C$ values are observed in inner-estuary sediments (Figure 3f), which are likely affected by hydrodynamic sorting in the Changjiang Estuary. Petrogenic and aged plant-derived OC associated with coarse-sized particles are preferentially deposited and accumulated in the inner estuary, but relatively young soil-derived OC and/or plant-derived OC associated with fine-grained particles are transported to the mobile muds and even to the ECS shelf (Sun et al., 2021; Zhao et al., 2021a).

Associations with Fe_R allow for the long-term preservation of terrestrial OC in marine environments (Faust et al., 2021). Here we used $\Delta\delta^{13}C$ ($\delta^{13}C_{bulk}$-$\delta^{13}C_{OC\text{-}FeR}$) and $\Delta\Delta^{14}C$ ($\Delta\delta^{14}C_{bulk}$-$\Delta^{14}C_{OC\text{-}FeR}$) to determine the difference in carbon isotopes between bulk OC and OC-Fe_R where positive values indicate lower isotopic values in OC-Fe_R relative to bulk OC (Figures 3g and 3h). Similar to bulk OC, $\delta^{13}C_{OC\text{-}FeR}$ and $\Delta^{14}C_{OC\text{-}FeR}$ gradually increase from estuarine SPM to the mobile-mud sediments and then to the ECS shelf, suggesting the addition of marine OC to Fe_R (Figures 3e and 3f). This distribution trend of $\delta^{13}C_{OC\text{-}FeR}$ from the estuary to the shelf agrees well with previous results that OC-Fe_R is largely related to bulk OC sources (Salvadó et al., 2015; Shields et al., 2016; Zhao et al., 2018a). For example, Salvadó et al. (2015) found that OC-Fe_R is substantially older and more terrestrial than the bulk sediment OC in the Laptev Sea but younger and more dominated by marine plankton sources in the East Siberian Sea, mainly depending on the different biogeochemical characteristics of these shelf regimes.

However, positive $\Delta\Delta^{14}C_{OC\text{-}FeR}$ and $\Delta\delta^{13}C_{OC\text{-}FeR}$ values in SPM and sediments at most sampling sites indicate that Fe_R helps to retain pre-aged soil OC of plant origin in the Changjiang Estuary (Figures 3g, 3h, and 5). Previous work also showed a more depleted $^{13}C_{OC\text{-}FeR}$ for deltaic sediments, which have higher terrestrially derived inputs (e.g., Mackenzie River Delta and Wax Lake Delta) than other coastal sediments with high marine inputs (Lalonde et al., 2012; Shields et al., 2016). In particular, higher $\Delta\Delta^{14}C_{OC\text{-}FeR}$ values and $\Delta\delta^{13}C_{OC\text{-}FeR}$ are observed in SPM and sediments in the estuarine mixing zone (from C7 to A6-2), which is partly due to estuarine flocculation (Figures 3g and 3h). Recent work showed that a substantial fraction of particulate Fe and colloidal Fe can be removed in the estuarine mixing zone through flocculation and sedimentation (Conrad et al., 2019). During flocculation processes, terrestrial OC-Fe_R also prefers sedimentation in the estuarine mixing zone rather than being transported to mid/outer shelf regions (Conrad et al., 2019; Jilbert et al., 2018). Estuarine flocculation can be demonstrated by higher SPM concentrations in the estuarine mixing zone relative to other regions (Figure S1). However, lower $\Delta\Delta^{14}C_{OC\text{-}FeR}$ and $\Delta\delta^{13}C_{OC\text{-}FeR}$ values in SPM relative to sediments at most sampling sites suggest that marine OC-Fe_R may be decomposed and/or desorbed during sediment deposition, but pre-aged soil OC of plant origin could be retained by Fe_R (Figures 3g and 3h). Pre-aged soil-derived OC develops from long-term residence times in the watersheds (Blair et al., 2010; Drenzek et al., 2009). A series of studies show that Fe_R preferentially binds with terrestrial plant-derived compounds, like lipids, cellulose, and lignins (Christl and Kretzschmar, 2007; Shields et al., 2016; Riedel et al., 2013; Zhao et al., 2018a). This is also supported by a positive relationship between Fe_R and Σ_8 ($p<0.01$) (Figure S7). Some terrestrial lipids in coastal regions like C_{22} *n*-alkane and C_{25} *n*-alkane may have very low $\delta^{13}C$ and $\Delta^{14}C$ values ($\delta^{13}C<-30‰$ and $\Delta^{14}C<-600‰$) (Feng et al., 2013), which is consistent with $\delta^{13}C_{OC\text{-}FeR}$ and $\Delta^{14}C_{OC\text{-}FeR}$ values in estuarine SPM and mobile-mud sediments (Figure 5). Fe_R decreases with increases in lignin-related degradation indices, suggesting that the remaining OC-associated Fe_R is mainly bound with degraded plant-derived OC (Figure S7). Common lignin-related degradation parameters are the ratios of acidic lignin phenols (e.g., SAD, VAD, CAD, and 3, 5-Bd) with carboxylic functional groups to others (e.g., $(Ad/Al)_V$ and P/(S + V)) (Figure S7). Previous work showed that lignin-related degradation parameters decreased after Fe_R extraction in deltaic sediments, indicating selective adsorption of acidic lignin phenols by Fe_R (Shields et al., 2016 Zhao et al., 2018a). Lignin-derived carboxylic compounds are preferentially adsorbed to Fe_R due to ligand exchange between carboxyl functional groups and Fe_R (Chen et al., 2014; Linkhorst et al., 2017; Lv et al., 2016), which likely increases OC sequestration and stabilization (Curti et al., 2021). The $\Delta\delta^{13}C_{OC\text{-}FeR}$ value is equal to ~0 in the ECS shelf (e.g., A6-8, A6-9, and A6-10) suggesting that both bulk OC and OC-Fe_R are from the same marine source (Figure 3g). This is partly because of high primary production and relatively stable sedimentary environments in the ECS shelf, which can contribute Fe_R to binding with more marine OC (Zhao et al., 2018a). Interestingly, although Fe_R can bind with modern marine OC, the radiocarbon age of OC-Fe_R is ~1000 years older than bulk OC in ECS-shelf sediments (~4360 yr for OC-Fe_R vs. ~3350 yr for bulk OC), further indicating that Fe_R still protects a part of pre-aged terrestrial OC in these sediments (Figure 3h).

Aging of terrestrial OC is common in passive continental margins where adequate accommodation space allows for extensive hydrodynamically-driven deposition/resuspension events (Bao et al., 2018; Blair and Aller, 2012; Chu et al., 2022). Recent studies have demonstrated that protection by fine-grained minerals (silt fraction) is an important mechanism for OC aging (Ausín et al., 2021; Bao et al., 2016; Hemingway et al., 2019; Keil and Mayer, 2014). Our results showed that binding with Fe_R may be an important way of preserving old terrestrial OC on particles and slowing or even precluding the replacement of terrestrial OC by marine OC (e.g., Keil et al., 1997; Blair and Aller, 2012), allowing for persistence of terrestrial OC-Fe$_R$ in the marine environment. Because most river-derived OC deposits in deltaic and mobile muds, these carbon isotopic results further support the hypothesis that OC-Fe$_R$ associations play an important role in the stabilization of terrestrial OC in estuarine regions (Shields et al., 2016; Sirois et al., 2018; Zhao et al., 2018a).

Iron oxides could transform with time to more stable forms by increased crystallinity, aggregation, and growth (Raiswell et al., 2011). In general, hematite is mainly formed in soils and is a more stable, mature, and higher density mineral, compared to those more commonly precipitated in the redox interface by co-precipitation, such as ferrihydrite (Jaynes and Bigham, 1986; Raiswell, 2011). Here we define the ratios of hematite to (super)paramagnetic Fe^{3+} (H/P ratio) to show the crystallinity of iron oxides, with a higher H/P ratio representing higher crystallinity of iron oxides. Higher H/P ratios are observed in inner-estuary sediments relative to mobile-mud and ECS-shelf sediments, suggesting higher crystallinity of iron oxides there (Figure S4). Hydrodynamic sorting of riverine-derived sediments may lead to the preferential deposition of high-density, crystalline phases such as hematite in the inner estuary, while the low-density, poorly crystalline (super)paramagnetic Fe^{3+} such as ferrihydrite is transported to mobile muds and the ECS shelf (Figure S4) (Zhao et al., 2018a). Both $\Delta^{14}C_{bulk}$ and $\Delta^{14}C_{OC\text{-}FeR}$ decrease with the increase in H/P ratio (Figure 6a and 6b), demonstrating that high-crystallinity iron oxide is mainly associated with old terrestrial OC and accumulated in the inner estuary, and low-crystallinity iron oxide is associated with relatively young terrestrial OC and transported to mobile muds and ECS shelf. ^{14}C-derived carbon residence time is positively correlated to Fe phase crystallinity in soils (Hall et al., 2018), suggesting that OC-associated Fe$_R$ may mature along with the aging of OC-Fe$_R$. The higher ratio of H/P ratio in the mobile muds relative to the ECS shelf could be due to the increase in the maturation of Fe oxides after experiencing long-term resuspension and re-deposition cycles before eventual burial (Figure S4) (Zhao et al., 2018a). Soil incubation experiments showed that while a substantial portion of the co-precipitated OC is lost during repeated redox fluctuations due to low crystallinity, a core OC-Fe$_R$ structure could still remain (Chen et al., 2020). Thus low-crystallinity iron oxides and their associated marine OC would not be well preserved in estuarine mobile-mud sediments (Figures 3e and S4). For ECS shelf sediments, a relatively quiescent sedimentary regime weakens iron redox cycling and contributes to the preservation of low-crystallinity iron oxides and their associated marine OC (e.g., A6-9) (Figures 3e and S4). It is worth noting that the $\delta^{13}C_{bulk}$ and $\delta^{13}C_{OC\text{-}FeR}$ did not show any significant relationships with H/P ratios (Figure S8). This is partly because H/P ratios are largely influenced by hydrodynamic sorting and maturation processes, but both $\delta^{13}C_{bulk}$ and $\delta^{13}C_{OC\text{-}FeR}$ are largely related to bulk OC sources. For example, inner-estuary sediments have higher H/P ratios because of hydrodynamic sorting (Figure S4), but ECS-shelf sediments have higher $\delta^{13}C_{bulk}$ and $\delta^{13}C_{OC\text{-}FeR}$ values relative to other regions due to marine OC input (Figures 2e and 3e). A key question that remains is how important the role of OC-Fe$_R$ associations is in determining the fate of terrestrially-derived OC in regions with low riverine inputs of Fe$_R$.

4.3 Variation of OC-Fe$_R$ associations from land to ocean

The land-to-ocean aquatic continuum (LOAC) is a ‘river pipeline’ of OC transport from upland soils to the ocean, playing an important role in controlling atmospheric CO_2 on annual to centennial timescales (Regnier et al., 2022). Here, for a better understanding of the preservation mechanism of OC by Fe_R in a typical LOAC, the variation of OC-Fe_R associations from land to ocean in the Changjiang sedimentary system is investigated by incorporating our data with results from previous work on soils in the Changjiang basin and sediments in ZMMM (Wan et al., 2019; Zhao et al., 2018a). This is because most of Changjiang estuarine SPM is derived from the Changjiang basin soils, firstly deposited in CEMM and then transported to the south (ZMMM) along the coast by currents (Liu et al., 2006; Wu et al., 2007). These soil sampling sites cover the main soil types in the Changjiang basin soils (Wan et al., 2019; Yu et al., 2007). Furthermore, data on OC-Fe_R associations in global soils and different marine environments are also collected for providing additional information on the role of Fe_R in protecting OC from land to ocean.

OC-Fe_R associations vary significantly from soils to estuarine SPM in the Changjiang sedimentary system. Terrestrial OC in estuarine particles is derived from the Changjiang drainage basin soils (Wu et al., 2018). Although OC and Fe_R contents vary across different soils, there are no significant differences in OC and Fe_R contents in soils and estuarine SPM ($p>0.05$) (Figures 7a and 7b). However, $f_{OC\text{-}FeR}$ and OC-Fe_R/Fe_R ratios largely decrease from soils ($f_{OC\text{-}FeR}$ = 17.8 ± 9.2%, OC-Fe_R/Fe_R ratio=1.21 ± 1.15) to estuarine SPM ($f_{OC\text{-}FeR}$ = 6.6 ± 1.9%, OC-Fe_R/Fe_R ratio = 0.20 ± 0.06) (Figures 7c and 7d). Similarly, high $f_{OC\text{-}FeR}$ values are found in permafrost soils ($f_{OC\text{-}FeR}$ = 19.5 ± 12.3%) and alpine grasslands soils of the Qinghai-Tibetan Plateau ($f_{OC\text{-}FeR}$ = 15.8 ± 12%), where the Changjiang originates (Fang et al., 2019; Mu et al., 2016). One possible reason for the decrease in $f_{OC\text{-}FeR}$ and OC-Fe_R/Fe_R ratios is that a fraction of OC is decomposed during sediment transport in Changjiang. Although soils and estuarine SPM have similar $\delta^{13}C_{bulk}$, the $\delta^{13}C_{OC\text{-}FeR}$ values in estuarine SPM are lower than those in soils, indicating selective protection of specific plant-derived compounds by Fe_R during river sediment transport (Figures 7e and 7f). For example, plant-derived lignin usually has a lower $\delta^{13}C$ value compared to plant-derived polysaccharides, such as cellulose (Loader et al., 2003). Synchrotron Radiation-based Fourier Transform Infrared (SR-FTIR) microspectroscopy analysis shows that more plant-derived polysaccharides and aliphatic compounds than carboxylic acids and lignin derivatives are bound with iron oxides in soils of the Changjiang drainage basin (Wan et al., 2019). However, the sorption of the more labile polysaccharide-derived OC on iron oxides is weaker than recalcitrant lignin-derived OC (Kaiser et al., 2000). Thus, the greater loss of Fe_R-associated polysaccharides, relative to Fe_R-associated lignin during transport along the Changjiang, may explain the lower $\delta^{13}C_{OC\text{-}FeR}$ values in estuarine SPM compared to soils. Another possible reason is the selective transport of fine-grained soils with low $f_{OC\text{-}FeR}$ to estuarine regions. In fact, soils in the lower reaches of the Changjiang have a lower clay fraction relative to estuarine SPM (mean of 17.4% vs. 27.3%, respectively) (Wu et al., 2020) (Table S1), indicating that more fine-grained soils are transported to the estuarine region by the river, and fine-grained estuarine particles and sediments have low $f_{OC\text{-}FeR}$ values (Figure 4a). There still remains limited knowledge on the controls and variability of OC-Fe_R associations in riverine particles during transport along the main channel of the Changjiang, and most other large rivers.

As discussed before, although OC and Fe_R largely decrease from estuarine SPM to CEMM, $f_{OC\text{-}FeR}$ and $\delta^{13}C_{OC\text{-}FeR}$ keep constant, indicating that Fe_R plays an important role in protecting terrestrial OC in estuarine mobile muds (Figure 7). Similarly, there are no significant differences in OC, Fe_R, $f_{OC\text{-}FeR}$, OC-Fe_R/Fe_R, and $\delta^{13}C_{OC\text{-}FeR}$ between CEMM and ZMMM sediments, but the $\delta^{13}C_{bulk}$ value significantly increases from CEMM to ZMMM ($p<0.05$) (Figure 7). This indicated that frequent physical reworking in mobile muds may inhibit Fe_R from binding with more marine OC, but the Fe_R still protects terrestrial OC. The $f_{\text{OC-FeR}}$, OC-Fe$_R$/Fe$_R$, and $\delta^{13}C_{\text{OC-FeR}}$ all increase from estuarine SPM and mobile-mud sediments to ECS-shelf sediments, indicating that Fe$_R$ binds more marine OC during cross-shelf sediment transport (Figure 7). This is partly due to less re-suspension in the ECS shelf relative to mobile muds in the ECS inner shelf during this prolonged lateral transport (Bao et al., 2019b). At the same time, estuarine flocculation likely leads to a large fraction of terrestrial OC-Fe$_R$ that is deposited in mobile muds rather than being transported to ECS shelf regions. It is worth noting that Fe$_R$ content in surface sediments in the Okinawa Trough is very low (0.40 ± 0.05 mg/g), partly due to less terrestrial input, but OC-Fe$_R$/Fe$_R$ ratio is high (>10), demonstrating that Fe$_R$ binds with more OC in this deep-sea region (Sun et al., 2020).

The distribution of $f_{\text{OC-FeR}}$ is investigated in soils and marine sediments on a global scale for a better understanding of the role of Fe$_R$ in OC protection in both land and ocean settings (Figure 8a). Overall, the $f_{\text{OC-FeR}}$ values in estuarine SPM and deltaic regions are lower than those in soils and marine sediments in continental margins, anoxic and sulphidic, and deep-sea regions (Figure 8b). The $f_{\text{OC-FeR}}$ has no significant relationship with OC and Fe$_R$ contents, further supporting that availability of OC and Fe$_R$ is not the exclusive controlling factor for OC-Fe$_R$ associations both in soils and marine sediments (Figures 8c and 8d). Many factors like iron oxide type, OC composition, and environmental conditions (e.g., sedimentation rate, mixing dynamics, and redox conditions) likely greatly influence OC-Fe$_R$ associations (Chen et al., 2020; Faust et al., 2021; Zhao et al., 2018a; Zhao et al., 2022). For example, in sediments with abundant Fe$_R$ content, the dominant Fe oxides are more crystalline iron like hematite and goethite, which have relatively low reactivity and cannot provide enough surface area to stabilize OC (Faust et al., 2021). In addition, sedimentary conditions like estuarine physical reworking likely prevent Fe$_R$ from binding with more OC (Zhao et al., 2018a). Our integrated dataset shows an average of 16.7 ± 13.7% of bulk OC is bound to Fe_R in different soil types (e.g., forest, crop, and grassland) (Figure 8b) (Ye et al., 2022 and references therein). Meanwhile, there are no significant differences between $\delta^{13}C_{bulk}$ and $\delta^{13}C_{OC\text{-}FeR}$ in soils, demonstrating relative consistency of OC source for bulk OC and OC-Fe_R (Figure 8e). However, from soils to estuarine SPM and deltaic sediments, $f_{OC\text{-}FeR}$, bulk OC, and Fe_R contents all largely decrease ($p<0.05$), reflective of decomposition or selective transport of OC-Fe_R associations as discussed above (Figures 8c and 8d). At the same time, lower $\delta^{13}C_{OC\text{-}FeR}$ relative to $\delta^{13}C_{bulk}$ in estuarine SPM and deltaic sediments further supports the importance of Fe_R in the protection of plant-derived OC during sediment transport in the river (Figure 8e). However, continental margins, coastal and freshwater wetlands, anoxic/sulphidic, and deep-sea sediments have higher $f_{OC\text{-}FeR}$ and $\delta^{13}C_{OC\text{-}FeR}$, demonstrating that more marine/algal OC is bound to Fe_R in marine settings (Figures 8c and 8e). The variations of these global data on OC-Fe_R associations from land to ocean further demonstrate that OC-Fe_R associations are largely related to different sedimentary regimes, such as OC sources, Fe_R compositions, and sedimentary dynamics.

The Changjiang sedimentary system is a typical LOAC, with a large river and a highly dynamic estuary, like the Mississippi and Amazon river sedimentary systems (Blair and Aller, 2012; Nittrouer et al., 2021). It is worth noting that each of these river systems is characterized by high Fe_R and plant-derived OC concentrations in river particles, rapid Fe redox cycling in estuarine mobile muds, and selective retention of older terrestrially-derived OC during lateral sediment transport (Aller et al., 2004; Blair and Aller, 2012; Poulton and Raiswell, 2002; Zhao et al., 2021a). Protection of OC during the lateral transfer from land to ocean is a key process controlling the release of carbon back into the atmosphere in these LOAC systems (Regnier et al., 2022). Here, we propose that in addition to other forms of mineral protection (i.e. clay sorption), OC-Fe_R association is a significant variable regarding the fate of pre-aged terrestrial OC in the coastal ocean. Clearly, this mechanism of OC stabilization and aging needs to be further verified in other large river sedimentary systems. In addition, for a global assessment of the role of Fe_R in OC preservation, the variation of OC-Fe_R associations from land to ocean in small mountain river sedimentary systems also needs to be further studied.

5. Conclusion

OC-Fe_R associations in the Changjiang sedimentary system vary dynamically from soils in drainage basins to estuarine SPM and to estuarine and ECS shelf sediments, which are controlled mainly by sedimentary regimes, OC sources, and Fe_R compositions. The formation of OC-Fe_R associations occur initially in soils, and then a large part of OC-Fe_R is decomposed and/or desorbed from iron oxides during long-distance sediment transport in the river basin. Some plant-derived OC is selectively protected by Fe_R during sediment transport in the river. When the river-derived particles and associated OC reach the estuary, frequent physical reworking coupled with rapid Fe redox cycling in mobile muds leads to the remineralization of non-OC-Fe_R and loss of OC-free Fe_R. The OC-Fe_R in mobile muds is composed of mostly pre-aged soil OC of terrestrial plant origin, and preserved better than non-OC-Fe_R from this process, indicating that association with Fe_R is an important mechanism for old terrestrial OC preservation in estuarine sediments. Complex and intense hydrodynamic and sedimentary dynamic processes in estuarine regions also greatly influence the distribution of iron oxides and their associated OC. The high-crystallinity iron oxides are largely associated with pre-aged terrestrial OC and preferentially deposited in inner-estuary sediments, but low-crystallinity iron oxides are associated with relatively young terrestrial OC and transported to mobile muds and ECS shelf. In the ECS shelf, low Fe_R concentrations coupled with less resuspension weaken iron reduction, which contributes to Fe_R binding with more marine OC. Our global dataset on OC-Fe_R associations in land and ocean coupled well with the results in the Changjiang sedimentary system, further showing that the OC-Fe_R associations are largely related to sedimentary regimes. Our work supports that Fe_R plays an important role in the stabilization and transport of pre-aged terrestrial OC from land to the ocean.

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Appendix A. Supplementary Material

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

References

Aller R. C. (1998) Mobile deltaic and continental shelf muds as suboxic, fluidized bed reactors. *Mar. Chem. 61*(3–4), 143–155.

Aller R. C. (2004) Conceptual models of early diagenetic processes: the muddy seafloor as an unsteady, batch reactor. *J. Mar. Res.* 62, 815–835.

Ausín B., Bruni E., Haghipour N., Welte C., Eglinton T. I. (2021) Controls on the abundance, provenance and age of organic carbon buried in continental margin sediments. *Earth Planet. Sci. Lett. 558*, 116759.

Bai J., Luo M., Yang Y., Xiao S., Zhai Z., and Huang J. (2021) Iron-bound carbon increases along a freshwater- oligohaline gradient in a subtropical tidal wetland. *Soil Biol. Biochem.* 154, 108128.

Bao R., Mcintyre C., Zhao M., Zhu C., Kao S. J., and Eglinton T. I. (2016) Widespread dispersal and aging of organic carbon in shallow marginal seas. *Geology* 44, 37941–37948.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Eisma D., Ji Z., Chen S., Chen M., and Van der Gaast S. J. (1995). Clay mineral composition of recent sediments along the China coast. *Nederlands Instituut voor Onderzoek der Zee (report)* 4, 1–13.

Eusterhues K., Hädrich A., Neidhardt J., Küsel K., Keller T. F., Jandt K. D., and Totsche, K. U. (2014) Reduction of ferrihydrite with adsorbed and coprecipitated organic matter: Microbial reduction by Geobacter bremensis vs. abiotic reduction by Na-dithionite. *Biogeosciences* 11(4), 6039–6067.

Fang K., Qin S., Chen L., Zhang Q., Yang Y. (2019) Al/Fe mineral controls on soil organic carbon stock across Tibetan alpine grasslands. *J. Geophys. Res. Biogeosci.* 124, 247–259.

Faust J. C., Stevenson M. A., Abbott G. D., Knies J., Tessin A., Mannion I., Ford A., Hilton R., Peakall J., März C. (2020) Does Arctic warming reduce preservation of organic matter in Barents Sea sediments? *Philos. Trans. A Math. Phys. Eng. Sci.* 378, 20190364.

Faust J. C., Tessin A., Fisher B. J., Zindorf M., Papadaki S., Hendry K. R., Doyle K. A., and März Z. (2021) Millennial scale persistence of organic carbon bound to iron in Arctic marine sediments. *Nat. Commun.* 12, 275.

Feng X., Benitez-Nelson B. C., Montluçon D. B., Prahl F. G., McNichol A. P., Xu L., Repeta D. J., and Eglinton T. I. (2013) ^{14}C and ^{13}C characteristics of higher plant biomarkers in Washington margin surface sediments. *Geochim. Cosmochim. Acta* 105, 14–30.

Fu L., Zhou T., Wang J., You L., Lu Y., Yu L., Zhou S. (2019) NanoFe$_3$O$_4$ as solid electron shuttles to accelerate acetotrophic methanogenesis by methanosarcina barkeri. *Front. Microbiol.* 10, 388.

Galy V., France-Lanord C., Beyssac O., Faure P., Kudrass H., Palhol F. (2007) Efficient organic carbon burial in the Bengal fan sustained by the Himalayan erosional system. *Nature.* 450, 407–10.

Galy V., Beyssac O., France-Lanord C., and Eglinton, T. (2008) Recycling of graphite during Himalayan erosion: A geological stabilization of carbon in the crust. *Science 322*, 943–945.

Ge T., Xue Y., Jiang X., Zou L., and Wang X. (2020) Sources and radiocarbon ages of organic carbon in different grain size fractions of Yellow River-transported particles and coastal sediments. *Chem. Geol.* 534, 119452.

Ghaisas N. A., Maiti K., and Roy A. (2021) Iron-mediated organic matter preservation in the Mississippi River-influenced shelf sediments. *J. Geophys. Res. Biogeosci.* 126(4), e2020JG006089.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Schröder C., Köhler I., Muller F. L. L., Chumakov A. I., Kupenko I., Rüffer R., and Kappler A. (2016) The biogeochemical iron cycle and astrobiology. *Hyperfine Interact.* 237, 85.

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

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

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

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

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

Stuiver M., Polach H. A., (1977) Discussion: Reporting of ^{14}C data. *Radiocarbon* 19, 355–363.

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

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

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

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

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

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

Wang D., Zhu M., Yang G., and Ma W. W., (2018) Reactive iron and iron-bound organic carbon in surface sediments of the river-dominated Bohai Sea (China) versus the Southern Yellow Sea. *J. Geophys. Res. Biogeosci.* 124, 79–98.

Wang J., Yao P., Bianchi T. S., Li D., Zhao B., and Cui X. Q., Pan H. H., Zhang T. T., and Yu Z. G. (2015) The effect of particle density on the sources, distribution, and degradation of sedimentary organic carbon in the Changjiang Estuary and adjacent shelf. *Chem. Geol.* 402, 52–67.

Wang X., Ma H., Li R., Song Z., and Wu J. (2012) Seasonal fluxes and source variation of organic carbon transported by two major Chinese Rivers: The Yellow River and Changjiang (Yangtze) River. *Global Biogeochem. Cycles* 26, GB2025.

Wu C, Qian P, Zheng X, Zhou L, Wang H, Xu H. (2020) Quartz grain characteristics of the late Pleistocene hard clay in the Yangtze River delta and implications for sedimentary environment and provenance. *Quaternary Res.* 1–17.

Wu J., Wang Y., and Cheng H. (2009) Bedforms and bed material transport pathways in the Changjiang (Yangtze) Estuary. *Geomorphology* 104(3–4), 175–184.

Wu Y., Eglinton T., Yang L., Deng B., Montluçon D., and Zhang J. (2013) Spatial variability in the abundance, composition, and age of organic matter in surficial sediments of the East China Sea. *J. Geophys. Res. Biogeosci.* 118, 1495–1507.

Wu Y., Eglinton T. I., Zhang J., and Montlucon D. B. (2018) Spatiotemporal variation of the quality, origin, and age of particulate organic matter transported by the Yangtze River (Changjiang). *J. Geophys. Res. Biogeosci.* 123, 2908–2921.

Wu Y., Zhang J., Liu S. M., Zhang Z. F., Yao Q. Z., Hong G. H., Cooper L. (2007). Sources and distribution of carbon within the Yangtze River system. *Estuar. Coast shelf S.* 71(1–2), 13–25.

Xu B. C., Bianchi T. S., Allison M. A., Dimova, N. T., Wang H. J., Zhang L. J., Diao S. B., Jiang X. Y., Zhen Y., Yao P., Chen H. T., Yao Q. Z., Dong W. H., Sui J. J., and Yu Z. G. (2015) Using multi-radiotracer techniques to better understand sedimentary dynamics of reworked muds in the Changjiang River Estuary and inner shelf of East China Sea. *Mar. Geol.* 370, 76–86.

Yao P., Zhao B., Bianchi T. S., Guo Z., Zhao M., Li D., Pan H. H., Wang J., Zhang T. T., and Yu Z. G. (2014) Remineralization of sedimentary organic carbon in mud deposits of the Changjiang Estuary and adjacent shelf: Implications for carbon preservation and authigenic mineral formation. *Cont. Shelf Res.* 91, 1–11.

Yao P., Yu Z. G., Bianchi T. S., Guo Z. G., Zhao M. X., Knappy C. S., Keely B. J., Zhao B., Zhang T. T., Pan H. H., Wang J. P., and Li D. (2015) A multiproxy analysis of sedimentary organic carbon in the Changjiang Estuary and adjacent shelf. *J. Geophys. Res. Biogeosci.* 120, 1407–1429.

Ye C., Huang W., Hall S. J., and Hu S., (2022) Association of organic carbon with reactive iron oxides driven by soil pH at the global scale. *Global Biogeochem. Cycles* 36, e2021GB007128.

Yu H., Wu Y., Zhang J., Yao Q. Z., and Zhu Z. Y. (2007) The characteristics of lignin of plants and soil samples in the Yangtze River (Changjiang) drainage basin. *Acta Sci. Circumst.* 27, 817–823 (in Chinese with English abstract).

Zhang J., Wu Y., Jennerjahn T. C., Ittekkot V., and He Q. (2007) Distribution of organic matter in the Changjiang (Yangtze River) Estuary and their stable carbon and nitrogen isotopic ratios: Implications for source discrimination and sedimentary dynamics. *Mar. Chem.* 106, 111–126.

Zhao B., Yao P., Bianchi T. S., Xu Y. H., Liu H., Zhang X. H., Liu J. W., Yu Z. G. (2017) Early diagenesis and authigenic mineral formation in mobile-muds of the Changjiang Estuary and adjacent shelf. *J. Mar. Syst.* 172, 64–74.

Zhao B., Yao P., Bianchi T. S., Shields M. R., Cui X. Q., Zhang X. W., Huang X. Y., Schröder C., Zhao J., and Yu Z. G. (2018a) The role of reactive iron in the preservation of terrestrial organic carbon in estuarine sediments. *J. Geophys. Res. Biogeosci.* 123, 3556–3569.

Zhao B., Yao P., Bianchi T. S., Arellano A. R., Wang X. C., Yang J. B., Su R., Wang J., Xu Y., Huang X., Chen L., Ye J., and Yu Z. (2018b) The remineralization of sedimentary organic carbon in different sedimentary regimes of the Yellow and East China Seas. *Chem. Geol.* 495, 104–117.

Zhao B., Yao P., Bianchi T. S., and Yu Z. G. (2021a) Controls on organic carbon burial in the Eastern China Marginal Seas: A regional synthesis. *Global Biogeochem. Cycles* 35, e2020GB006608.

Zhao B., Yao P., Li D., and Yu Z. (2021b) Effects of river damming and delta erosion on organic carbon burial in the Changjiang Estuary and adjacent East China Sea inner shelf. *Sci Total Environ.* 793, 148610.

Zhao Y., Moore O. W., Xiao K. Q., Curti L., Fariña A. O., Banwart S. A., Peacock C. L. (2022) The role and fate of organic carbon during aging of ferrihydrite. *Geochim.*

Cosmochim. Acta 335, 339-355.

Zhu, C., Weijers, J., Wagner, T., Pan, J. M., and Pancost, R. D. (2011) Sources and distributions of tetraether lipids in surface sediments across a large river-dominated continental margin. *Org. Geochem.* 42(4), 376-386.

Zhu M. X., Hao X. C., Shi X. N., Yang G. P., and Li T. (2012) Speciation and spatial distribution of solid-phase iron in surface sediments of the East China Sea continental shelf. *Appl. Geochem.* 27(4), 892–905.

Figure Captions

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

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

Figure 3. Distributions of reactive iron (μmol/g) (a), OC-Fe_R (wt%) (b), $f_{OC\text{-}FeR}$ (%) (c), OC-Fe_R/Fe_R (mol/mol) (d), $\delta^{13}C_{OC\text{-}FeR}$ (‰) (e), $\Delta^{14}C_{OC\text{-}FeR}$ (‰) (f), $\Delta\delta^{13}C_{OC\text{-}FeR}$ (g), and $\Delta\Delta^{14}C_{OC\text{-}FeR}$ of the suspended particulate matter (SPM) and surface sediments in the Changjiang Estuary and adjacent East China Sea (ECS) shelf. Yellow shadow denotes the estuarine mixing zone.

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

Figure 5. Relationships of $\Delta^{14}C$ versus $\delta^{13}C$ in the suspended particulate matter (SPM) and surface sediments in the Changjiang Estuary and adjacent East China Sea (ECS) shelf. The $\Delta^{14}C$ and $\delta^{13}C$ values of C_3 plants in the Changjiang basin were from Yu et al. (2007) and Wu et al. (2018). The $\Delta^{14}C$ and $\delta^{13}C$ values of the Changjiang river basin soils were from Wu et al. (2018). The $\Delta^{14}C$ and $\delta^{13}C$ values of Himalayan rock are from Galy et al. (2008). The $\Delta^{14}C$ and $\delta^{13}C$ values of kerogen are from Jia et al. (2005). The $\Delta^{14}C$ and $\delta^{13}C$ values of East China Sea marine phytoplankton were from Zhang et al. (2007). The $\Delta^{14}C$ and $\delta^{13}C$ values of Changjiang delta sediments were from Wu et al. (2013).

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

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

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

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