



# Article The Role of Iron Minerals in the Preservation of Organic Carbon in Mangrove Sediments

Kang Li<sup>1,2</sup>, Huamei Huang<sup>1,\*</sup>, Di Dong<sup>1</sup>, Shengpeng Zhang<sup>1</sup> and Ran Yan<sup>1</sup>

- <sup>1</sup> South China Sea Institute of Planning and Environment Research, State Oceanic Administration, Guangzhou 510300, China; likang1116@163.com (K.L.); dongdide90@163.com (D.D.); mni\_roc@163.com (S.Z.); yanr7@mail2.sysu.edu.cn (R.Y.)
- <sup>2</sup> South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China
- \* Correspondence: scsmeei@163.com

Abstract: Although mangrove forests occupy only 0.5% of the global coastal area, they account for 10-15% of coastal organic carbon (OC) storage, and 49-98% of OC is stored in sediments. The biogeochemistry of iron minerals and OC in marine sediments is closely related. To better reveal the role of iron minerals in OC preservation in mangrove sediments, an established dithionite-citratebicarbonate (DCB) extraction method was used to extract iron-bound OC (Fe-OC), and then the parameters of OC, Fe-OC, iron content, carbon isotopes, infrared spectroscopy, and XRD diffractions of sediments at a 1 m depth in four typical mangrove communities in the Gaoqiao Mangrove Reserve, Guangdong, China, were systematically measured. XRD diffractograms showed that the iron minerals in mangrove sediments may mainly exist in the form of goethite, which is consistent with the predominant types of iron minerals in marine sediments. About 10% of OC is directly bound to iron, and it is further estimated that about 2.4  $\times$  10^{12}–3.8  $\times$  10^{12} g OC is preserved in global mangrove forests each year based on the high burial rate of OC in mangrove sediments. Lower Fe-OC/OC molar ratios indicated that iron mainly binds to OC via adsorption mechanisms. More depleted  $\delta^{13}C_{Fe-OC}$  relative to  $\delta^{13}C_{bulk}$  indicated that iron minerals are mainly associated with terrigenous OM, and the infrared spectra also revealed that iron minerals preferentially bind to terrigenous aromatic carbon. This work supports the "giant rusty sponge" view, elucidating that iron plays an important role in the preservation of OC in mangrove sediments.

**Keywords:** iron minerals; organic carbon; mangrove sediments; molecular composition; binding mechanism

# 1. Introduction

Protecting organic carbon stored in forests is considered important for mitigating climate change. Like terrestrial ecosystems, coastal ecosystems also store large amounts of carbon known as blue carbon. As typical coastal blue carbon ecosystems, mangrove forests play an important role in the global carbon cycle and are a place of material exchange between marine and terrestrial ecosystems [1,2]. Although mangrove forests occupy only 0.5% of the global coastal area, they account for 10–15% of coastal carbon storage [3], and 49–98% of organic carbon (OC) is stored in sediments [4]. However, despite the increasing recognition of the urgent need for climate change mitigation, stability assessments of sediment carbon pools for mangrove ecosystems have rarely been conducted.

The protective effect minerals have on OC is the product of a highly important stabilizing mechanism. More than 90% of organic matter (OM) in marine sediments cannot be separated from clay minerals and iron minerals, and this holds especially true for iron minerals that are closely associated with the long-term preservation of OC [5]. A previous study found that iron-bound OC (Fe-OC) in Arctic marine sediments persists below the uppermost oxygenated sediment layer over thousands of years [6]. In addition, the binding of iron and carbon in sediments can reduce the rate of OC decomposition through adsorption



Citation: Li, K.; Huang, H.; Dong, D.; Zhang, S.; Yan, R. The Role of Iron Minerals in the Preservation of Organic Carbon in Mangrove Sediments. *Water* **2024**, *16*, 1011. https://doi.org/10.3390/w16071011

Academic Editors: Luisa Bergamin and Hucai Zhang

Received: 18 February 2024 Revised: 22 March 2024 Accepted: 25 March 2024 Published: 31 March 2024



**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and co-precipitation due to the characteristics of iron minerals, such as their large specific surface area, strong adsorption capacity, and high reactivity [7].

As for the quantitative assessment of Fe-OC, the protective effect of iron minerals on OC in sediments of forests [8], grasslands [9], farmlands [10], plateau frozen soils [11], lakes [12], and other terrestrial ecosystems has been studied, with the results showing that about 40% of OC is preserved by iron. As for marine ecosystems, a recent study found that about 21.5% of the OC in global marine sediments is directly bound to iron minerals [13]. More recent research has investigated the percentage of iron-bound carbon ( $f_{Fe-OC}$ ) in continental margins (20.71–26.59%) [6,14,15], continental shelves (4.50–36.88%) [16–18], estuaries (7.40–22.96%) [19–23], deltas (8.1–22.2%) [24], and volcanic ash (79%) [16]. In one study, the  $f_{Fe-OC}$  was up to 79%, which strongly supports the view that iron serves as a "rust sink" for OC. Longman et al. (2022) further estimated that the marine Fe-OC sinks were between 31 and 70 Mt C/yr<sup>-1</sup> (average 52 Mt C/yr<sup>-1</sup>) [25].

The carbon sequestration rate of mangrove sediments is high, being twice that of coastal salt marsh, 10 times that of lake sediments, and 22 times that of dryland [26]. However, the importance of iron minerals' contribution to the mangrove sediment carbon pool and the characterization of Fe-OC in mangrove sediments have not been systematically studied and reported, respectively; therefore, sediment core samples from four typical mangrove communities in the Gaoqiao Mangrove Reserve in the Guangdong province were collected to assess the characteristics of Fe-OC and analyze the factors influencing these characteristics. The main aims of this study were as follows: (1) to carry out a quantitative evaluation of iron minerals' contribution to carbon sequestration and the burial rate of Fe-OC in mangrove sediments; (2) to analyze the factors influencing the binding of iron and OC; and (3) to analyze the binding mechanism and molecular composition of Fe-OC.

## 2. Sample and Methods

#### 2.1. Sample Sites

The Gaoqiao Mangrove Reserve is located at the core of the Zhanjiang Mangrove National Nature Reserve in the Guangdong province, China, within the Yingluo Bay at the entrance of the Ximi River in the Beibu Bay. Their mangrove communities are mainly composed of *Aegiceras corniculatum*, *Bruguiera gymnorrhiza*, *Kandelia obvolata*, *Rhizophora stylosa*, and *Avicennia marina* communities, among others [27]. The natural zonation of the mangrove species is obviously influenced by various ecological and environmental factors, including geographical location, tidal conditions, soil composition, etc. [28]. The *Kandelia obvolata* plus *Bruguiera gymnorrhiza* communities, *Aegiceras corniculatum* community, *Rhizophora stylosa* community, and *Avicennia marina* community were selected for sediment collection in this study. The locations of the sampling sites are shown in Figure 1. The community structures and elevations of the different sampling sites are shown in Table 1. The *Avicennia marina* community had the lowest elevation (1.22 m) compared with the other three sites (*Kandelia obvolata* plus *Bruguiera gymnorrhiza* communities: 1.98 m; *Aegiceras corniculatum* community: 2.2 m; *Rhizophora stylosa* community: 1.84 m), indicating that this site is at low tide.

Table 1. Community compositions and mudflat elevations of the sampling sites.

Sampling Site	<b>Community Composition</b>	Elevation (m)	Longitude	Latitude
А	Kandelia obovate + Bruguiear gymnorrhiza	1.98	109.7559	21.5678
В	Aegiceras corniculatum	2.2	109.7678	21.5534
С	Rhizophora stylosa	1.84	109.7689	21.54727
D	Avicennia marina	1.29	109.7837	21.5329



Figure 1. Locations of the sampling sites in this study.

## 2.2. Sediment Collection

Sediment samples were collected from quadrats using a PVC pipe that was 7.5 cm in diameter and 1.2 m in length. Within each plant quadrat, three sediment columnar samples were collected before being divided into seven layers (0–5 cm, 5–10 cm, 10–20 cm, 20–30 cm, 30–40 cm, 40–60 cm, and 60–100 cm) and mixed evenly. All segmented samples were then sealed and stored in a plastic bag and transported to the laboratory for freezing at -4 °C. Dead roots, stems, stones, and large visible particles were removed from the sediment samples; then, each sample was ground using a mortar and sifted through a 60-mesh sieve.

# 2.3. Mineral Composition

The mineral compositions of the subsamples were analyzed using an X-ray diffractometer equipped with a Ni filter and Cu K $\alpha$  radiation (40 kV and 40 mA). The diffraction patterns were collected from 2° to 55° 2 $\theta$  at a scanning rate of 3° 2 $\theta$  min<sup>-1</sup>.

### 2.4. OC and Stable Carbon Isotope Analyses

The OC content and stable carbon isotope values of the bulk mangrove sediments were determined in the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The carbonate minerals were removed from the sediment samples with 10% hydrochloric acid, rinsed with deionized water, and dried at 40 °C. The OC concentrations were determined using a Sunset laboratory elemental analyzer, and the stable carbon isotope values were determined using an isotope mass spectrometer (IRMS). The error was no more than 1‰. The standard consisted of a homogenous batch of protein (casein) standard and was used to determine the carbon isotope values. The mean carbon isotope value was  $-26.98 \pm 0.13$ ‰.

# 2.5. Iron Extraction and Fe-OC Analyses

After analyzing the OC and carbon isotope values, iron minerals in the mangrove sediments were further extracted. A modified dithionite–citrate–bicarbonate method that involved the release of Fe-OC while being gentle with clay minerals was used for iron extraction [13,29]. The procedure involved the following: 0.5 g freeze-dried sediments were added into a 30 mL solution containing 0.27 mol/L trisodium citrate and 0.11 mol/L NaHCO<sub>3</sub>-neutral buffer in a 50 mL centrifuge tube and heated to 80 °C in a water bath. Then, 0.5 g sodium dithionite was added to the solution, which had been maintained at 80 °C for 15 min. Then, the solution was centrifuged at 3000 rpm for 10 min, the supernatant was separated, and the solid residue was cleaned thrice with pure deionized water. The rinse water was mixed with the supernatant, acidified, filtered, and diluted 10 times. Finally, iron concentration was measured using an atomic absorption spectrometer. The solid residue was dried and ground to analyze the OC and stable carbon isotope values.

Control experiments were carried out under the same conditions as the reduction treatment to prevent overestimates of the amount of iron-bound carbon ( $C_{\text{Fe-OC}}$ ), but we replaced trisodium citrate and sodium dithionite with sodium chloride with an equivalent ionic strength. Inorganic minerals in the mangrove sediments were removed by using a 10% hydrochloric acid solution, and the OC (OC<sub>control</sub>) and stable carbon isotope ( $\delta^{13}C_{\text{control}}$ ) values were subsequently determined. The content, proportion, and carbon isotope values of Fe-OC were determined using Equations (1)–(3), respectively.

$$C_{\text{Fe-OC}} = OC_{\text{control}} - OC_{\text{experiment}}$$
(1)

$$f_{Fe-OC} = C_{Fe-OC} / OC_{control} \times 100\%$$
<sup>(2)</sup>

$$\delta^{13}C_{\text{Fe-OC}} = \delta^{13}C_{\text{control}} - \delta^{13}C_{\text{experiment}} \times (1 - f_{\text{Fe-OC}})/f_{\text{Fe-OC}}$$
(3)

# 2.6. The Molecular Composition of Fe-OC

Fourier-transform infrared spectroscopy was carried out using a Bruker VERTEX 70V (origin: Germany) equipped with dual detectors based on DTGS (room temperature; origin: Germany) and InGaAs (room temperature; origin: Germany) to characterize the molecular composition of Fe-OC. The following simple steps were carried out: the freezedried sediment was mixed with potassium bromide (mass ratio 1:100), ground to a paste under an infrared lamp, and then pressed. Infrared spectrograms were obtained by using the aforementioned infrared spectrophotometer at room temperature.

### 2.7. Statistical Analyses

Statistical analyses were conducted using SPSS 27 software. A Pearson correlation analysis with a two-tailed test was carried out to identify correlations between all measured parameters. Based on the 95% confidence intervals, significant statistical differences were determined using a one-way analysis of variance and a *t* test. Regression analysis was performed to determine the relationship between the iron and OC concentrations.

#### 3. Experimental Results

#### 3.1. Mineral Composition

The mineral composition of the mangrove sediments in the four typical mangrove communities mainly consists of quartz and kaolinite minerals, accompanied by a small amount of calcite (Figure 2). It is worth noting that goethite was found in all subsamples, which is consistent with the conclusion that goethite is the main iron mineral in marine sediments (Figure 2) [13,21].



**Figure 2.** Mineral composition of sediments of four typical mangrove communities in Gaoqiao Mangrove Reserve. Kao: kaolinite; Q: quartz; Cal: calcite; Goe: Goethite.

## 3.2. Bulk OC Concentration and Carbon Isotope Signatures

The OC concentrations in the subsamples of the four mangrove communities gradually decreased with increasing depth, as shown by the vertical axis in Figure 3a. OC gradually decreased after reaching the maximum value of 1.23% at 20 cm depth in the *Avicennia marina* sediments, while a maximum value of 2.59% was achieved at 30 cm depth in the *in Rhizophora stylosa* sediments; a maximum value of 2.82% was achieved at 40 cm depth in the *Kandelia obvolata* plus *Bruguiera gymnorrhiza* sediments, and a maximum value of 3.14% was achieved at 60 cm depth in the *Avicennia marina* sediments. On average, the OC concentrations were lowest in the *Avicennia marina* sediments, with an average value of 0.78  $\pm$  0.39%, but the highest OC concentrations were found in the *Kandelia obvolata* plus *Bruguiera corniculatum* and *Rhizophora stylosa* sediments were 1.65  $\pm$  0.77% and 1.63  $\pm$  0.62%, respectively. In addition, the OC concentrations in the *Avicennia marina* sediments were significantly different compared with those of the other three sites (p < 0.001).

# 3.3. Characterization of Fe-OC and Carbon Isotope Values

The content and percentage of iron-bound carbon ( $C_{\text{Fe-OC}}$ ,  $f_{\text{Fe-OC}}$ ) were evaluated based on the differences in OC concentration in the extraction and control experiments (Figure 3b and Figure 4). The values of  $C_{\text{Fe-OC}}$  and  $f_{\text{Fe-OC}}$  were the highest ( $0.27 \pm 0.25\%$ ,  $11.48 \pm 8.4\%$ ) in the *Kandelia obvolata* plus *Bruguiera gymnorrhiza* sediments and the lowest ( $0.06 \pm 0.04\%$ ,  $5.54 \pm 3.45\%$ ) in the *Avicennia marina* sediments. The values of  $f_{\text{Fe-OC}}$  in the *Aegiceras corniculatum* and *Rhizophora stylosa* sediments were  $7.32 \pm 4.28\%$  and  $9.88 \pm 2.62\%$ , respectively. On average, it was estimated that about 10% of the OC in the subsamples from the four typical mangrove communities was directly bound to iron.



**Figure 3.** The characterization of iron-bound OC (Fe-OC) in mangrove sediments at four sampling sites in Gaoqiao Mangrove Reserve; (**a**) OC concentration (wt/%); (**b**) percentage of iron-bound OC (%); (**c**) carbon isotope values for bulk sediment (%); (**d**) carbon isotope value of Fe-OC (%); (**e**) iron concentration ( $\mu$ mol/g); (**f**) molar ratio of Fe-OC/OC.



**Figure 4.** Average content of Fe-OC and molar ratio of Fe-OC/OC. (a) Average percentage of Fe-OC ( $f_{Fe-OC}$ ) and iron concentration at four sampling sites (b) in the Gaoqiao Mangrove Reserve.

Although no significant differences between the  $\delta^{13}$ C values for the iron-bound carbon ( $\delta^{13}C_{Fe-OC}$ ) and bulk sediments ( $\delta^{13}C_{bulk}$ ) were found (p > 0.05), the average values of  $\delta^{13}C_{Fe-OC}$  were visibly more depleted <sup>13</sup>C than that of the bulk sediments (Figure 3c,d and Figure 5) (difference: up to 2‰).



**Figure 5.** Average carbon isotope values of bulk sediments ( $\delta^{13}C_{bulk}$ ) and Fe-OC ( $\delta^{13}C_{Fe-OC}$ ) at four sampling sites in the Gaoqiao Mangrove Reserve.

### 3.4. Iron Concentration

The iron concentrations gradually decreased with the increase in sampling depth, but the iron concentrations in the *Aegiceras corniculatum* sediments reached the lowest value at 30 cm (164.74 µmol/g) and then remained basically unchanged with increasing depth, ranging from 151.35 to 404.08 µmol/g (241.77  $\pm$  90.93 µmol/g). The iron concentrations ranged from 13.61 to 116.84 µmol/g (average: 81.82  $\pm$  34.59 µmol/g), 38.24 to 137.63 µmol/g (average: 101.33  $\pm$  30.84 µmol/g), and 151.35 to 404.08 µmol/g (average: 287.92  $\pm$  121.04 µmol/g) in the *Avicennia marina*, *Rhizophora stylosa*, and *Kandelia obvolata* plus *Bruguiera gymnorrhiza* sediments, respectively, while the *Avicennia marina* sediments had the lowest iron concentration (Figure 3e). Additionally, there were significant differences between the iron concentrations in the *Avicennia marina* sediments and those of the other three sites (*p* < 0.05).

# 3.5. Relationship between Iron Content and OC Concentration

A significant linear positive correlation between the iron content and OC concentration was observed in the four sample sites ( $R^2 = 0.367$ , p < 0.001) (Figure 6). In addition, the average molar ratio of Fe-OC/Fe in the four sample sites was  $0.8 \pm 0.02$ , which is lower than 1.0 (Figure 3f). At low tide, the *Avicennia marina* sediments had the lowest molar ratio ( $0.48 \pm 0.32$ ), but the highest ratio ( $1.32 \pm 0.42$ ) was found in the *Rhizophora stylosa* sediments. The molar ratios of Fe-OC/Fe in the *Aegiceras corniculatum* and *Kandelia obvolata* plus *Bruguiera gymnorrhiza* sediments were  $0.50 \pm 0.36$  and  $1.03 \pm 0.84$ , respectively.



**Figure 6.** Scatter graph of iron concentration  $(\mu mol/g)$  vs. OC content (wt %) in all collected subsamples.

# 3.6. The Molecular Composition of Fe-OC

An analysis of the mangrove sediments before and after iron extraction, carried out via attenuated total reflectance–Fourier-transform infrared spectroscopy (ATR–FTIR), was performed to qualitatively analyze the molecular composition of Fe-OC. The experimental results showed that obvious mineral peaks, including kaolinite and montmorillonite, appeared at 800–1200 cm<sup>-1</sup> whether iron minerals were extracted or not. Aliphatic carbon was enriched at 2800–3000 cm<sup>-1</sup> after extracting iron in the *Kandelia obvolata* plus *Bruguiera gymnorrhiza* sediments and *Aegiceras corniculatum* sediments. However, there was no obvious peaks at 2800–3000 cm<sup>-1</sup> in the *Avicennia marina* sediments before and after iron extraction, which may be due to the lower OC content.

# 4. Discussion

# 4.1. Percentage of Iron-Bound Carbon and Influencing Factors

In this study, the average OC concentration was lowest in the *Avicennia marina* sediments at low tide but highest in the *Kandelia obvolata* plus *Bruguiera gymnorrhiza* sediments at middle/high tide. The amount and dynamics of OC vary greatly among different mangrove forests, which are largely affected by tidal gradient, vegetation biomass, and primary productivity, as well as species composition and suspended matter deposition [30]. Higher tidal levels may increase the OC concentration for two possible reasons. Firstly, the increased productivity along tidal gradients leads to more plant litter and root exudates entering into the anaerobic soils [31,32]. Secondly, the extensive root system of mangrove forests at middle or high tide promotes the retention of organic matter (OM) and the deposition of fine sediment components with high OC concentrations [33].

More importantly, we observed that a significant amount of OC was bound to iron in the mangrove sediments (Figures 3b and 4). Our results show that the average value of  $f_{Fe-OC}$  in the four sampling sites is about 10%, which is slightly lower than that of classical marine sediments (21.5 ± 8.6%) [13] but higher than that of estuarine sediments (7.4 ± 3.5%) [19]. The binding of iron and OC is influenced by multiple factors, such as the deposition rate, the redox state, and hydrodynamic strength [21,25]. Previous studies have found that  $f_{Fe-OC}$  values are significantly different in continental margins, continental shelves, estuarine sediments, delta sediments, coastal sediments, tephra depositions, and other marine sedimentary environments [13], indicating that the sedimentary environment significantly affects the binding of iron and OC.

In mangrove sediments, the concentrations of OC and Fe-OC are affected by multiple factors, such as tree species, the tidal range, and mangrove productivity [31,32]. A previous study revealed that the OC concentration in *Avicennia marina* sediments is much lower than that of *Kandelia obvolata* plus *Bruguiera gymnorrhiza sediments* and *Rhizophora stylosa* sedi-

ments in the Gaoqiao Mangrove Reserve, which may indicate that community composition and tidal level significantly affect the OC concentration [33]. In addition, the accumulation of OC and the binding of iron to OC are also significantly influenced by tidal level [19,21]. Frequent leaching at low tide may prevent the binding of OC and iron minerals, but the less frequent leaching and relatively stable sedimentary environment at middle and high tide is beneficial for the binding of iron and OC [24,34]. In this study, the average value

tide is beneficial for the binding of iron and OC [24,34]. In this study, the average value of  $f_{Fe-OC}$  in the *Avicennia marina* sediments at low tide was also the lowest compared with the other three sites, which indicates that the tidal level may influence the binding of iron and OC.

# 4.2. Binding Mechanism of Iron and OC

The binding of iron and OC mainly occurs through adsorption and co-precipitation mechanisms, which can be determined based on the molar ratio of Fe-OC/Fe [35]. Adsorption refers to the ligand exchange between the carbonyl/hydroxyl functional groups on the surface of OM and the functional groups of iron [36], which have the characteristics of a high adsorption heat, low desorption, and high bond stability [37]. In addition, the amount of OC adsorbed by iron is relatively smaller, and adsorption occurs on the surface of minerals, so the molar ratio of Fe-OC/Fe is often lower than 1.0 [38,39]. Co-precipitation refers to the combination of Fe<sup>3+</sup> in solution with acidic functional groups of dissolved OM (DOM) to form insoluble an Fe<sup>3+</sup>–organic ligand complex and the subsequent transfer of OM to deeper anoxic sedimentary layers through deposition, physical modification, and bioturbation [40]. More OC is adsorbed by co-precipitation than by adsorption, and the molar ratio of Fe-OC/Fe is much higher than 1.0 [13,30].

In our experimental results, the average molar ratios of Fe-OC/Fe at the four sampling sites (A, B, C and D) were all close to 1.0 ( $1.03 \pm 0.84$ ,  $0.50 \pm 0.36$ ,  $1.32 \pm 0.42$ , and  $0.48 \pm 0.32$ , respectively), indicating that adsorption was the main iron and OC binding mechanism. The adsorption mechanisms mainly included hydrogen bonding, hydrophobic interactions, ligand exchange, and cation bridging [41]. It has been found that the average molar ratios of Fe-OC/Fe in most mangrove sediments from coastal estuaries in China are lower than 1.0, which is consistent with our results [42]. However, other studies have also found that the average molar ratios of Fe-OC/Fe for mangrove sediments in six coastal areas of the Philippines and marine sediments are much greater than 1.0, suggesting that iron and OC are mainly bound by co-precipitation [30]. Differences in molar ratios in different regions may be influenced by sediment type, mineral compositions, and iron concentration [25]. The sediments featured in this study are mainly composed of clay minerals, goethite, and quartz, and they only contain a small amount of calcite; however, the sediments in the Philippines mangrove forests are mainly composed of silicate minerals, and their iron contents are relatively low [30]. Therefore, differences in mineral composition may affect the binding of iron to OC [13,21].

## 4.3. Carbon Isotope and Molecular Characteristics of Fe-OC

The OC in the mangrove sediments mainly included two sources, namely allochthonnus (tidally induced marine input and fluvially transported upstream sediments) and autochthonous (mangrove biomass) sources [43]. Additionally, the material circulation of mangrove ecosystems was promoted through the exchange of terrestrial and marine OM in mangrove ecosystems [44]. Stable carbon isotopes can be used to distinguish whether OC was sourced from terrestrial or marine sources, and it is generally believed that the carbon isotope of marine OC is more rich in <sup>13</sup>C than that in terrestrial OC ( $\delta^{13}C_{marine}$ : -20.9%;  $\delta^{13}C_{terrigenous}$ : -26.5%) [45,46], so the source of OC in mangrove sediments can be roughly determined. In our study, the carbon isotope values of the mangrove sediments ( $\delta^{13}C_{bulk}$ ) ranged from -28.53% to -23.81% (average:  $-26.55 \pm 0.85\%$ ), showing typical terrigenous input characteristics. However, the average value of  $\delta^{13}C$  in the *Avicennia marina* sediments ( $-25.64 \pm 1.02\%$ ) was significantly lower than that of the other three sites (p < 0.05) (*Kandelia obvolata plus Bruguiera gymnorrhiza*:  $-26.36 \pm 0.36\%$ ; *Aegiceras*  *corniculatum*:  $-27.25 \pm 0.6\%$ ; *Rhizophora stylosa*:  $-26.76 \pm 0.31\%$ ), indicating that the *Avicennia marina* sediments were more affected by marine OM input, which may be because the *Avicennia marina* community was located at lower tides, leading to greater marine OM deposition [33]. Furthermore, the carbon isotope value of Fe-OC ( $\delta^{13}C_{Fe-OC}$ ) in all subsamples was more depleted in  $^{13}C$  than in the bulk sediments (Figure 5), which indicated that more terrigenous OM preferentially combined with iron minerals.

To further analyze the molecular composition of Fe-OC, the molecular differences between the subsamples were compared via FTIR analysis. It has been found that infrared spectrum peaks at 1600–1750 cm<sup>-1</sup> and 2800–3000 cm<sup>-1</sup> can be used to study the molecular composition of OM, and spectra peaks in the range of 1600–1750 cm<sup>-1</sup> usually contain fingerprint peaks of amide, carboxylic acid, and aromatic functional groups [47]. Peaks at 2895 cm<sup>-1</sup>–2930 cm<sup>-1</sup> indicate aliphatic carbon [48], while peaks at 500–1200 cm<sup>-1</sup> indicate the presence of clay minerals and other iron/aluminum minerals, such as kaolinite and montmorillonite, which peak at 850–1200 cm<sup>-1</sup> [49,50]. In this study, obvious mineral peaks occurred at 400–1200 cm<sup>-1</sup> before and after the removal of Fe-OC (Figure 7), which was consistent with the diffraction peak of clay minerals found in our XRD analysis. More importantly, the spectra at 2895–2930 cm<sup>-1</sup> were more prominent after the removal of Fe-OC, indicating that the aliphatic carbon was enriched after extraction. Zhao et al. (2016) demonstrated that the Fe-OC in forest soils was less aliphatic, more carboxylic, and enriched in <sup>13</sup>C by considering an FTIR analysis, NEXAFS analysis (near-edge X-ray absorption fine structure analysis), and <sup>13</sup>C [48]; this finding is consistent with our experimental results.



**Figure 7.** Comparison of infrared spectra before and after Fe-OC extraction in sediments of four typical mangrove communities.

#### 4.4. Estimation of the Burial Rate of Fe-OC

Mangroves are highly productive wetlands that photosynthetically sequester atmospheric CO<sub>2</sub> as OC. A varying proportion of OC was buried in tidally inundated, hypoxic acid and anoxic sediments, and thus largely prevented from returning to the atmosphere. Based on the  $f_{Fe-oc}$  in this study and sediment OC burial rate in mangrove ecosystems on a global scale (24–38.3 Tg C a<sup>-1</sup>) [51], we believe that an average of 10% OC (2.4 × 10<sup>12</sup>–3.8 × 10<sup>12</sup> g C a<sup>-1</sup>) was buried by binding with iron at the global mangrove ecosystem (4). A previous study has shown that about 21% of OC in marine sediments is preserved by binding with iron minerals [13], which may overestimate the role of iron minerals in marine sediments. In fact, the deposition of nutrients and plant litter carried by seawater tides into the sediment could lead to higher OC burial rates in mangrove ecosystems [51–54]. In this study, although the  $f_{Fe-OC}$  was relatively low, the higher OC burial rate in mangrove ecosystems still lead to higher Fe-OC burial rates. Thus, our study suggests that iron plays an important role in the preservation of OC in mangrove sediments.

$$Fe-OC_{burial rate} = OC_{burial rate} \times f_{Fe-oc}$$
(4)

## 5. Conclusions

More than 90% of OM in marine sediments cannot be separated from clay minerals and iron minerals (with this holding especially true for the latter), but the role of iron minerals in mangrove sediments has been rarely revealed. In this study, four one-meter soil cores were collected from Aegiceras corniculatum plus Kandelia obovate, Aegiceras corniculatum, Rhizophora stylosa, and Avicennia marina sediments in the Gaoqiao Mangrove Reserve, Guangdong province, China, respectively. A dithionite-citrate-bicarbonate reduction procedure was employed to extract iron from these sediments. The OC concentrations, carbon isotope values, mineral compositions, and iron contents were measured before and after sediment extraction. About 10% of OC in mangrove sediments is bound by iron through an adsorption mechanism, and the binding between iron and OC was mainly influenced by community composition and tidal level. Carbon isotope signatures of Fe-OC  $(\delta^{13}C_{\text{Fe-OC}})$  indicate that iron preferentially preserved terrigenous organic matter, implying that iron aids the incorporation of terrigenous OC. The differences in the infrared spectra before and after iron extraction also indicated that the iron-bound OC was less than aliphatic carbon. Based on the global OC burial rate in mangrove sediments, it is estimated that a global mass of  $2.1 \times 10^{12}$ – $3.8 \times 10^{12}$  g OC a<sup>-1</sup> is preserved by iron. Thus, we conclude that iron plays an important role in stabilizing terrestrial OC in mangrove sediments. Furthermore, iron serves as an effective rust sink for the preservation of OC in sediments and contributes to the global carbon cycle.

**Author Contributions:** K.L.: data collection, formal analysis, visualization, and writing—original draft. H.H.: conceptualization, validation, formal analysis, writing—review and editing, supervision, and funding acquisition. D.D.: data collection and analysis. S.Z.: formal analysis. R.Y.: formal analysis. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the Marine Economy Special Project of the Guangdong Province in 2024 for the "Identification and Model Prediction of Key Restoration Areas of Typical Blue Carbon Ecosystem". Science and Technology Project of Guangdong Forestry Administration (2024): Monitoring and Ecological Value Assessment of Coastal Wetland Resources in the Guangdong Province. The Science and Technology Project of Guangdong Forestry Administration (2023): Verification of Human Activities in Marine Protected Areas and Monitoring and Assessment of Typical Ecosystems. The Science and Technology Project of Guangdong Forestry Administration (2023): Research on Carbon Storage Verification, Potential Assessment and Car-bon Sink Trading Mechanism of Typical Coastal Wetlands. Marine Economy Special Project of Guangdong Province in 2023 for "Marine Carbon Source, Carbon Sink, Carbon Flux Investigation and Assessment of Carbon Sequestration Technology and Application Research". The APC was funded by the Science and Technology Project of Typical Eco-systems.

Data Availability Statement: Data are contained within the article.

Acknowledgments: Thanks to the two reviewers and editors for their valuable suggestions on this paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

# References

- Atwood, T.B.; Connolly, R.M.; Almahasheer, H. Global patterns in mangrove soil carbon stocks and losses. *Nat. Clim. Chang.* 2017, 7, 523–528. [CrossRef]
- 2. Alongi, D.M. Carbon Sequestration in Mangrove Forests. *Carbon Manag.* 2012, *3*, 313–322. [CrossRef]
- Duarte, C.M.; Middelburg, J.J.; Caraco, N. Major role of marine vegetation on the oceanic carbon cycle. *Biogeosciences* 2005, 2, 1–8. [CrossRef]
- Donato, D.C.; Kauffman, J.B.; Murdiyarso, D.; Kurnianto, S.; Stidham, M.; Kanninen, M. Mangroves among the most carbon-rich forests in the tropics. *Nat. Geosci.* 2011, 4, 293–297. [CrossRef]

- 5. Hedges, J.I.; Keil, R.G. Sedimentary organic matter preservation: An assessment and speculative synthesis. *Mar. Chem.* **1995**, *49*, 81–115. [CrossRef]
- Faust, J.C.; Tessin, A.; Fisher, B.J.; Zindorf, M.; Papadaki, S.; Hendry, K.R.; Doyle, K.A.; März, C. Millennial scale persistence of organic carbon bound to iron in Arctic marine sediments. *Nat. Commun.* 2021, 12, 275. [CrossRef] [PubMed]
- 7. Boudot, J.P.; Hadj, A.B.; Steiman, R.; Seigle-Murandi, F. Biodegradation of synthetic organo-metallic complexes of iron and aluminium with selected metal to carbon ratios. *Soil Biol. Biochem.* **1989**, *21*, 961–966. [CrossRef]
- 8. Chen, J.; Hu, Y.; Hall, S.J.; Hui, D.; Li, J.; Chen, G.; Sun, L.; Zhang, D.; Deng, Q. Increased interactions between iron oxides and organic carbon under acid deposition drive large increases in soil organic carbon in a tropical forest in southern China. *Biogeochemistry* **2022**, *158*, 287–301. [CrossRef]
- Che, M.; Gong, Y.; Xu, M.; Kang, C.; Lv, C.; He, S.; Zheng, J. Effects of elevation and slope aspect on the distribution of the soil organic carbon associated with Al and Fe mineral phases in alpine shrub-meadow soil. *Sci. Total Environ.* 2021, 753, 141933. [CrossRef]
- 10. Hu, J.; Zeng, Q.; Chen, H.; Dong, H. Effect of bacterial cell addition on Fe (III) reduction and soil organic matter transformation in a farmland soil. *Geochim. Cosmochim. Acta.* 2022, 325, 25–38. [CrossRef]
- 11. Mu, C.C.; Zhang, T.J.; Zhao, Q.; Gao, H.; Zhong, W.; Su, H.; Wu, Q.B. Soil organic carbon stabilization by iron in permafrost regions of the Qinghai-Tibet Plateau. *Geophys. Res. Lett.* **2016**, *43*, 286–294. [CrossRef]
- Peter, S.; Sobek, S. High variability in iron-bound organic carbon among five boreal lake sediments. *Biogeochemistry* 2018, 139, 19–29. [CrossRef]
- 13. Lalonde, K.; Mucci, A.; Ouellet, A.; Gelinas, Y. Preservation of organic matter in sediments promoted by iron. *Nature* **2012**, *483*, 198–200. [CrossRef] [PubMed]
- 14. Ma, W.W.; Zhu, M.X.; Yang, G.P.; Li, T. 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.* **2018**, *178*, 62–74. [CrossRef]
- 15. Wang, D.; Zhu, M.X.; Yang, G.P.; Ma, W.W. Reactive iron and iron-bound organic carbon in surface sediments of the riverdominated Bohai Sea (China) Versus the Southern Yellow Sea. *J. Geophys. Res. Biogeosci.* **2019**, *124*, 79–98. [CrossRef]
- 16. Longman, J.; Gernon, T.M.; Palmer, M.R.; Manners, H.R. Tephra deposition and bonding with reactive oxides enhances burial of organic carbon in the Bering Sea. Global Biogeochem. *Cycles* **2021**, *35*, e2021GB007140. [CrossRef]
- Salvadó, J.A.; Tesi, T.; Andersson, A.; Ingri, J.; Dudarev, O.V.; Semiletov, I.P.; Gustafsson, O. Organic carbon remobilized from thawing permafrost is resequestered by reactive iron on the Eurasian Arctic Shelf. *Geophys. Res. Lett.* 2015, 42, 8122–8130. [CrossRef]
- Ghaisas, N.A.; Maiti, K.; Roy, A. Iron-Mediated Organic Matter Preservation in the Mississippi River-Influenced Shelf Sediments. J. Geophys. Res-Biogeo. 2021, 126, e2020JG006089. [CrossRef]
- 19. Zhao, B.; Yao, P.; Bianchi, T.S.; Cui, X.Q.; Zhang, X.W.; Huang, X.Y.; Schroeder, C.; Zhao, J.; Yu, Z.G. The role of reactive iron in the preservation of terrestrial organic carbon in estuarine sediments. *J. Geophys. Res-Biogeo.* **2018**, *123*, 3556–3569. [CrossRef]
- 20. Sirois, M.; Couturier, M.; Barber, A.; Gelinas, Y.; Chaillou, G. Interactions between iron and organic carbon in a sandy beach subterranean estuary. *Mar. Chem.* 2018, 202, 86–96. [CrossRef]
- Zhao, B.; Yao, P.; Bianchi, T.S.; Shields, M.R.; Cui, X.Q.; Zhang, X.W.; Huang, X.Y.; Schroeder, C.; Zhao, J.; Yu, Z.G. Preferential preservation of pre-aged terrestrial organic carbon by reactive iron in estuarine particles and coastal sediments of a large river-dominated estuary. *Geochim. Cosmochim. Acta.* 2023, 345, 34–49. [CrossRef]
- Sun, C.H.; Zhu, M.X.; Ma, W.W.; Sun, Z.L.; Zhang, X.R.; Ding, K.Y.; Liu, S.H. 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. 2020, 207, 103344. [CrossRef]
- 23. Bai, J.; Luo, M.; Yang, Y.; Xiao, S.; Zhai, Z.; Huang, J. Iron-bound carbon increases along a freshwater—oligohaline gradient in a subtropical tidal wetland. *Soil Biol. Biochem.* 2021, 154, 108128. [CrossRef]
- 24. Shields, M.R.; Bianchi, T.S.; Gélinas, Y.; Allison, M.A.; Twilley, R. Enhanced terrestrial carbon preservation promoted by reactive iron in deltaic sediments. *Geophys. Res. Lett.* **2016**, *43*, 1149–1157. [CrossRef]
- 25. Longman, J.; Faust, J.C.; Bryce, C.; Homoky, W.B.; Marz, C. Organic carbon burial with reactive iron across global environments. *Glob. Biogeochem. Cycles* **2022**, *36*, e2022GB007447. [CrossRef]
- Bouillon, S.; Borges, A.V.; Castañeda-Moya, E.; Diele, K.; Dittmar, T.; Duke, N.C.; Kristensen, E.; Lee, S.Y.; Marchand, C.; Middelburg, J.; et al. Mangrove production and carbon sinks: A revision of global budget estimates. Global Biogeochem. *Cycles* 2008, 22, 2. [CrossRef]
- Lin, P. Ecological notes on mangroves in southeast coast of China including Taiwan Province and Hainan Island. *Acta Ecol Sin.* 1981, 1, 283–290.
- 28. Hong, P.N.; San, H.T. Mangroves of Vietnam; IUCN. The World Conservation Union: Bangkok, Thailand, 1993; p. 193.
- 29. Mehra, O.P.; Jackson, M.L. Iron oxide removal from soils and clays by a dithionite–citrate system buffered with sodium bicarbonate. In *Clays and Clay Minerals*; Pergamon: Oxford, UK, 2013; pp. 317–327.
- 30. Dicen, G.P.; Navarrete, I.A.; Rallos, R.V.; Salmo, S.G.; Garcia, M.C.A. The role of reactive iron in long-term carbon sequestration in mangrove sediments. *J. Soils Sediments*. **2019**, *19*, 501–510. [CrossRef]
- Gleason, S.M.; Ewel, K.C. Organic matter dynamics on the forest floor of a micronesian mangrove forest: An investigation of species composition Shifts1. *Biotropica* 2002, 34, 190–198. [CrossRef]

- 32. Sherman, R.E.; Fahey, T.J.; Martinez, P. Spatial patterns of biomass and aboveground net primary productivity in a mangrove ecosystem in the Dominican Republic. *Ecosystems* **2003**, *6*, 384–398. [CrossRef]
- 33. Wang, G.; Guan, D.; Peart, M.R.; Chen, Y.; Peng, Y. Ecosystem carbon stocks of mangrove forest in Yingluo Bay, Guangdong Province of South China. *For. Ecol. Manag.* **2013**, *310*, 539–546. [CrossRef]
- Fisher, B.J.; Moore, O.W.; Faust, J.C.; Peacock, C.L.; Marz, C. Experimental evaluation of the extractability of iron bound organic carbon in sediments as a function of carboxyl content. *Chem. Geol.* 2020, 556, 119853. [CrossRef]
- Johnson, D.W.; Todd, D.E. Relationships among iron, aluminum, carbon, and sulfate in a variety of forest soils. *Soil Sci. Soc. Am. J.* 1983, 47, 792–800. [CrossRef]
- Mikutta, R.; Mikutta, C.; Kalbitz, K.; Torn, M. Biodegradation of forest floor organic matter bound to minerals via different binding mechanisms. *Geochim. Cosmochim. Acta.* 2007, 71, 2569–2590. [CrossRef]
- 37. Gu, B.; Schmitt, J.; Chen, Z.; Liang, L. Adsorption and desorption of natural organic matter on iron oxide: Mechanisms and models. *Environ. Sci. Technol.* **1994**, *28*, 38–46. [CrossRef] [PubMed]
- Chen, C.; Dynes, J.J.; Wang, J.; Sparks, D.L. Properties of Fe-organic matter associations via coprecipitation versus adsorption. *Environ. Sci. Technol.* 2014, 48, 13751–13759. [CrossRef]
- 39. Han, L.; Sun, K.; Keiluweit, M.; Yang, Y.; Jin, J.; Sun, H.; Wu, F.; Xing, B. Mobilization of ferrihydrite-associated organic carbon during Fe reduction: Adsorption versus coprecipitation. *Chem. Geol.* **2019**, *503*, *61–68*. [CrossRef]
- Riedel, T.; Zak, D.; Biester, H.; Dittmar, T. Iron traps terrestrially derived dissolved organic matter at redox interfaces. *Proc. Natl. Acad. Sci. USA* 2013, 110, 10101–10105. [CrossRef] [PubMed]
- 41. Barber, A.; Brandes, J.; Leri, A.; Lalonde, K.; Balind, K.; Wirick, S.; Wang, J.; Gelinas, Y. Preservation of organic matter in marine sediments by inner-sphere interactions with reactive iron. *Sci. Rep.* **2017**, *7*, 366. [CrossRef]
- 42. He, T.R. Preservation of Organic Carbon Promoted by Iron in Estuarine Wetland Sediments; East China Normal University: Shanghai, China, 2021.
- 43. Alongi, D.M. Carbon cycling and storage in mangrove forests. Annu. Rev. Mar. Sci. 2014, 6, 195–219. [CrossRef]
- Middelburg, J.J.; Nieuwenhuize, J. Carbon and nitrogen stable isotopes in suspended matter and sediments from the Schelde Estuary. Mar. Chem. 1998, 60, 217–225. [CrossRef]
- 45. Fontugne, M.R.; Jouanneau, J.M. Modulation of the particulate organic carbon flux to the ocean by a macrotidal estuary: Evidence from measurements of carbon isotopes in organic matter from the Gironde system. *Estuar. Coast. Shelf Sci.* **1987**, *24*, 377–387. [CrossRef]
- 46. Kendall, C.; Silva, S.R.; Kelly, V.J. Carbon and nitrogen isotopic compositions of particulate organic matter in four large river systems across the United States. *Hydrol. Process* **2001**, *15*, 1301–1346. [CrossRef]
- 47. Parikh, S.J.; Goyne, K.W.; Margenot, A.J. Soil chemical insights provided through vibrational spectroscopy. *Adv. Agron.* **2014**, *126*, 1–148.
- 48. Zhao, Q.; Poulson, S.R.; Obrist, D.; Sumaila, S.; Dynes, J.J.; McBeth, J.M.; Yang, Y. Iron-bound organic carbon in forest soils: Quantification and characterization. *Biogeosciences* **2016**, *13*, 4777–4788. [CrossRef]
- 49. Madejová, J. FTIR techniques in clay mineral studies. *Vib. Spectrosc.* **2003**, *31*, 1–10. [CrossRef]
- 50. Senesi, N.; D'Orazio, V.; Ricca, G. Humic acids in the first generation of EUROSOILS. *Geoderma* 2003, *116*, 325–344. [CrossRef]
- 51. Wang, F.; Sanders, C.J.; Santos, I.R.; Tang, J.; Schuerch, M.; Kirwan, M.L.; Kopp, R.E.; Zhu, K.; Li, X.; Yuan, J.; et al. Global blue carbon accumulation in tidal wetlands increases with climate change. *Natl. Sci. Rev.* **2021**, *8*, nwaa296. [CrossRef]
- Mcleod, E.; Chmura, G.L.; Bouillon, S.; Salm, R.; Björk, M.; Duarte, C.M.; Lovelock, C.E.; Schlesinger, W.H.; Silliman, B.R. A blueprint for blue carbon: Toward an improved understanding of the role of vegetated coastal habitats in sequestering CO<sub>2</sub>. Front. *Ecol. Environ.* 2011, *9*, 552–560. [CrossRef]
- 53. Wang, G.; Guan, D.; Xiao, L.; Peart, M.R. Ecosystem carbon storage affected by intertidal locations and climatic factors in three estuarine mangrove forests of South China. *Reg. Environ. Chang.* **2019**, *19*, 1701–1712. [CrossRef]
- Yu, C.; Feng, J.; Liu, K.; Wang, G.; Zhu, Y.; Chen, H.; Guan, D. Changes of ecosystem carbon stock following the plantation of exotic mangrove Sonneratia apetala in Qi'ao Island, China. *Sci. Total Environ.* 2020, 717, 137142. [CrossRef] [PubMed]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.