Reactive iron as an important reservoir of marine organic carbon over geological timescales

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Reactive iron (FeR) has been suggested to serve as a semi-persistent sink of organic carbon (OC) in surface marine sediments, where approximately 10-20% of total OC (TOC) is associated with FeR (FeR-OC). However, the persistence of FeR-OC on geological timescales remains poorly constrained. Here, we retrieved FeR-OC records in two long sediment cores of the northern South China Sea spanning almost the past 100 kyr. Most prominently, the downcore marine-sourced FeR-OC contributes a relatively stable proportion of 13.3±3.2% to TOC. However, distinctly lower values of less than 5% of TOC, accompanied by notable $^{13}$C depletion of FeR-OC are observed in the sulfate-methane transition zone (SMTZ), where active sulfate reduction and potential iron reduction are indicated by microbial composition and geochemical modelling. FeR-OC is suggested to be remobilized by microbially mediated reductive dissolution of FeR (and might be substituted with freshly formed $^{13}$C-depleted OC).

The global budget of FeR-OC in microbially active Quaternary marine sediments could be as large as $219\pm133\times10^{17}$ g, which is 18-48 times the size of the atmospheric carbon pool. Thus, sedimentary FeR-OC as an exchangeable reservoir of labile OC may support deep life and play a role in regulating Earth’s carbon cycle over geological timescales.
Introduction

Reactive iron (Fe$_R$, defined as iron (oxyhydr)oxides that can be reductively dissolved by sodium dithionite) can promote the preservation of organic carbon (OC) in a wide range of terrestrial and marine environments$^{1-5}$, as OC associated with Fe$_R$ (Fe$_R$-OC) has long been believed to be more resistant to microbial degradation under aerobic conditions$^6, ^7$. A proportion of $\sim 21.5\pm 8.6\%$ of the OC in surface marine sediments was estimated to be directly associated with Fe$_R$, which corresponds to a global mass of 19-45×10$^{15}$ grams of OC$^1$ (roughly 2-5% of the amount of the atmospheric CO$_2$). This proportion was reassessed to 15.6±6.5% after incorporating more estuarine sediment samples$^8$, nevertheless demonstrating its great potential and significant role in preserving the sedimentary OC.

Besides protecting OC from degradation, Fe$_R$ also acts as active electron acceptor for anaerobic microbial respiration$^9, ^{10}$. Its reduction could potentially weaken or even break the association between Fe$_R$ and OC. Indeed, recent studies demonstrated that Fe$_R$-OC can be remobilized during microbial iron reduction and subsequently utilized as electron donor and/or carbon source for microbial communities$^{11-14}$. However, the evaluation on the fate of Fe$_R$-OC in marine sediments were mostly based on less than 0.5-m-long sediment cores, covering less than ten thousand years in age$^{15, ^{16}}$. A gradual decline in the Fe$_R$-OC percentage in total OC (TOC) on the centennial to millennial scale has been observed, suggesting the instability of Fe$_R$-OC$^{15}$. Sun et al. (2020) reconstruted the Fe$_R$-OC record of a sediment core in the Yangtze River.
Estuary, which showed potential persistent of FeR-OC for the past 55 kyrs\textsuperscript{17}. However, in this study age of the core bottom was calculated from the core length and estimated sedimentation rate, and there was no further data measured to explain the variation of FeR-OC in the core. Nevertheless, little is known about the behaviour of FeR-OC on longer timescales, especially with respect to the impact of diagenetic processes such as microbial degradation.

On geological timescales, the burial rate of sedimentary OC exerts major control on the concentrations of atmospheric O\textsubscript{2} and CO\textsubscript{2}\textsuperscript{18} and thus substantially influences Earth’s environmental conditions. As a significant proportion of sedimentary OC, the balance of preservation and remobilization of FeR-OC is thus of great importance for both the carbon cycle and its potential contribution for fueling subsurface microbial communities.

Here, two distinct gravity cores (QDN-G1 and QDN-14B, Fig. 1a) of the northern South China Sea were chosen in order to determine the fate of the sedimentary FeR-OC via its quantitative and isotopic analysis. The core QDN-G1 represents typical continental slope sediments (1478 m water depth), while core QDN-14B (1370 m water depth), around 35 km southwest away from the core QDN-G1, was influenced by nearby cold seeps expelling methane-rich fluids\textsuperscript{19}. Consequently, QDN-14B can be used to comparatively evaluate the influence of microbial activities on the potential remobilization of FeR-OC in the diagenetically active zones where sulfate reduction
coupled to either organic matter remineralization or methane oxidation occurs. Meanwhile, the core QDN-G1 with relatively low microbial activity is used for exploring the long-term preservation of FeR-OC on glacial/interglacial timescales.

To quantify the amount of FeR-OC, the citrate-bicarbonate-dithionite (CBD) method described in detail by Lalonde et al.¹ and Salvadó et al.² was applied in this study (see Methods). This method targets only reactive iron (oxyhydr)oxides, which are presumably accessible for microorganisms, and leaves unreactive phases such as iron-containing silicates untouched.²⁰ By incorporating analyses of pore water geochemistry, including the concentrations of sulfate, ferrous iron, dissolved inorganic carbon (DIC), and the carbon isotope ratio of DIC ($\delta^{13}$C$_{\text{DIC}}$), all of which are tied to microbially mediated processes, our study takes a critical step in assessing the stability of sedimentary FeR-OC in response to post-depositional microbial activities and sheds lights on its persistence and remobilization on geological timescales.

Fig. 1. Map of the cores studied in the northern South China Sea and age model of core
QDN-G1. (a) Map of cores QDN-G1 and QDN-14B. River systems entering the northern South China Sea are indicated by blue and red lines. (b) Age model of core QDN-G1. The age model of the upper 4.0 m (0-34.4 ka) was based on 7 accelerator mass spectrometry $^{14}$C ages of planktonic foraminifera (G. ruber) (red triangles). The age model of the lower 6.8 m (34.4-97.0 ka) was established by aligning the $\delta^{18}$O record of benthic foraminifera (C.wuellerstorfi) (blue line) to the global benthic $\delta^{18}$O stack LR04 (black line). The tie points used for the alignment are indicated by dashed grey lines (see Methods for detailed information).

Result and discussion

Content and biogeochemistry of Fe-OC in long-buried sediments

The core recovery of QDN-G1 and QDN-14B were 10.8 m and 8.4 m, respectively. These two cores penetrated vastly different benthic ecosystems. Microbially mediated early diagenetic redox reactions have resulted in a distinct geochemical zonation, i.e., the iron reduction zone (IRZ), the sulfate reduction zone (SRZ), the sulfate-methane transition zone (SMTZ), and the methanogenic zone (MZ) (Fig. S1 and S2). Despite similar TOC content in sediments from the two cores (Fig. 2b and g, black lines), the higher methane fluxes and the associated rapid depletion of sulfate via anaerobic oxidation of methane resulted in a shallower SMTZ in core QDN-14B (280-440 cmbsf) compared to core QDN-G1 (potentially around 720-960 cmbsf) (Fig. S1 and S2). This is backed up by geochemical modelling results (see Methods), which showed a more than two times higher net sulfate reduction rate in the SMTZ in core QDN-14B compared to core QDN-G1 (0.034 vs. 0.015 mol m$^{-3}$ yr$^{-1}$) (Fig. S3).
TOC content in the two cores ranges from 0.4 to 1.2%, except for low content in a coarsely grained layer (410-420 cmbsf in QDN-14B\(^{22}\)) (Fig. 2b and g, black lines).

The Fe\(_R\)-OC content ranges from 0.04 to 0.17% (Fig. 2b and g, red lines) and accounts for 10-20% of TOC (Fig. 2d and i). However, interestingly, both the lowest Fe\(_R\)-OC content and the lowest Fe\(_R\)-OC/TOC values occurred in the SMTZ of each core. In QDN-G1 and QDN-14B, the average content of Fe\(_R\)-OC in non-SMTZ sediments are 0.12% and 0.10%, respectively, but drop to 0.06% and 0.03% in the SMTZ sediments, respectively (Table 1). Similarly, the average Fe\(_R\)-OC/TOC values in the non-SMTZ layers are 14.0% and 13.0%, but drop to 12.3% and 5.2% in the SMTZ sediments, respectively (Table 1).

The carbon isotope ratios of TOC (\(\delta^{13}C_{\text{TOC}}\)) and Fe\(_R\)-OC (\(\delta^{13}C_{\text{FeR-OC}}\)) provide insights into the sources of the corresponding OC pool. In the two cores, \(\delta^{13}C_{\text{TOC}}\) varies mostly between −22.5‰ and −19.7‰ (Figure 2c and h, black lines), indicating the accumulation of mainly marine-algal OC, which in the sampled area has an average \(\delta^{13}C\) value of −20.8±0.4‰\(^{23}\). \(\delta^{13}C_{\text{FeR-OC}}\) is generally similar with \(\delta^{13}C_{\text{TOC}}\) (Figure 2c and h, red lines), suggesting that Fe\(_R\) are mainly associated with marine-sourced OC as well. However, somewhat lower \(\delta^{13}C_{\text{TOC}}\) and \(\delta^{13}C_{\text{FeR-OC}}\) values in SMTZ sediments are observed in both cores (Figure 2c and h). The average \(\delta^{13}C_{\text{TOC}}\) values of SMTZ sediments are 1.5‰ and 1.9‰ lower than those of non-SMTZ sediments in QDN-G1 and QDN-14B, respectively (Table 1). Similarly, the average \(\delta^{13}C_{\text{FeR-OC}}\) values of
SMTZ sediments are 3.1‰ and 2.8‰ lower than those of non-SMTZ sediments in QDN-G1 and QDN-14B, respectively (Table 1).

Taken together, lower Fe\textsubscript{R}-OC content, lower Fe\textsubscript{R}-OC/TOC values, along with more depleted $\delta^{13}$C\textsubscript{FeR-OC} are observed in SMTZ sediments, comparing to uniform records in non-SMTZ sediments. The conspicuous characteristics in the SMTZ could result from either processes before deposition such as coincidental changes in sediment provenance, OC input and burial efficiency, and/or post-depositional processes related to sedimentary microbial activity. The age model of core QDN-G1 shows that it covers a complete glacial-interglacial cycle since MIS5c (Fig. 1b), and no clear glacial-interglacial pattern of TOC and Fe\textsubscript{R}-OC records is evident (Fig. 2 and Fig. S4) (see Supplementary Text for details). Assuming similar sedimentation rates in core QDN-14B, the variations in TOC and Fe\textsubscript{R}-OC records do not follow the glacial-interglacial cycles either. Combining especially low Fe\textsubscript{R}-OC content and depleted $\delta^{13}$C\textsubscript{FeR-OC} in the SMTZ, which is usually a horizon of high microbial activity, we propose that the post-depositional microbial processes account for these distinctive characteristics of Fe\textsubscript{R}-OC records.
Fig. 2. Content and $\delta^{13}$C profiles of TOC and Fe$_R$-OC in cores QDN-G1(a-e) and QDN-14B (f-j). The marine isotope stages (MIS) assigned based on the age model are plotted against the depth axes for core QDN-G1. The pink and green bars indicate interglacial periods and the last glacial period, respectively. (a and f) Content of Fe$_R$. (b and g) Content of TOC (black lines) and Fe$_R$-OC (red lines). Separate x-axes are used for TOC and Fe$_R$-OC, respectively, labelled in the same color as the data profile. (c and h) Carbon isotope ratios of TOC (black lines) and Fe$_R$-OC (red lines). Separate x-axes are used for TOC and Fe$_R$-OC, respectively, labelled in the same color.
as the data profile. (d and i) Percentage of FεR-OC in TOC. (e and j) The molar ratio of FεR-OC and FeR. The locations of the SMTZ are highlighted by the purple bars.

Table 1 Comparisons of the content and carbon isotope ratios of TOC and FeR-OC between non-SMTZ and SMTZ sediments in two cores.

<table>
<thead>
<tr>
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<th>QDN-G1</th>
<th>QDN-14B</th>
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<tr>
<td></td>
<td>TOC (%)</td>
<td>FeR-OC (%)</td>
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<tr>
<td>Non-SMTZ (N = 21)</td>
<td>0.8±0.2</td>
<td>0.12±0.03</td>
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<tr>
<td>SMTZ (N = 7)</td>
<td>0.5±0.0</td>
<td>0.06±0.01</td>
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<td>Offset between non-SMTZ and SMTZ sedimentsb</td>
<td>0.3</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>δ¹³C TOC (‰, VPDB)</td>
<td>δ¹³C FeR-OC (‰, VPDB)</td>
</tr>
<tr>
<td>Non-SMTZ (N = 21)</td>
<td>-20.6±0.7</td>
<td>-21.8±1.8</td>
</tr>
<tr>
<td>SMTZ (N = 7)</td>
<td>-22.2±0.2</td>
<td>-24.8±3.0</td>
</tr>
<tr>
<td>Offset between non-SMTZ and SMTZ sedimentsb</td>
<td>1.9</td>
<td>2.8</td>
</tr>
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</table>

aGiven are means± standard deviation.
bOffsets of corresponding averaged values between non-SMTZ and SMTZ sediments.
cFeR-OC/TOC data at 410 and 420 cmbsf in QDN-14B are biased by extremely low TOC and are not included for calculations (N = 5).

FeR-OC remineralization coupled to microbial processes in the SMTZ

The SMTZ, as a discrete sedimentary horizon where anaerobic oxidation of methane is coupled to sulfate reduction (S-AOM)⁹⁴, ubiquitously occurs in organic-rich marine shelf and slope sediments. S-AOM is performed syntrophically by sulfate-reducing bacteria and methanotrophic archaea⁹⁵. In core QDN-14B, geochemical modelling reveals higher net sulfate reduction rates in the SMTZ (Fig. 3b), which is further supported by (1) the higher relative abundance and cell concentration of sulfate-
reducing bacteria (Fig. 3e and f), and (2) elevated copy number of methyl-coenzyme M reductase subunit A (mcrA) gene (Fig. 3g), the key marker gene for methane metabolism by archaea including S-AOM as the main process consuming sulfate in the SMTZ\(^{26}\). By contrast, in core QDN-G1, there is no evidence for elevated sulfate reduction activity in the SMTZ compared to the shallower sulfate reduction zone, based on modelled rates and both relative abundance and cell number of sulfate-reducing bacteria (Fig. S5b, e and f). This is consistent with the relatively moderate variation in Fe\(_R\)-OC/TOC record in core QDN-G1 compared to that in core QDN-14B. Collectively, these lines of evidence suggest that due to the particularly high methane flux at core QDN-14B, the microbial activity in the SMTZ has stimulated the remobilization of Fe\(_R\)-OC.

A plausible mechanism for lower Fe\(_R\)-OC content in the SMTZ is the occurrence of reductive dissolution of Fe\(_R\) by the hydrogen sulfide produced during sulfate reduction\(^{27,28}\), and subsequent remobilization of Fe\(_R\)-OC. Apart from chemical reduction of Fe\(_R\), sulfate-reducing bacteria may also reduce Fe\(_R\) directly\(^{29}\), with the rate of reduction being enhanced by sulfate reduction and the presence of biogenic sulfide\(^{30}\). In addition, the process of AOM may be directly coupled with iron reduction (Fe-AOM)\(^{31}\) and facilitate Fe\(_R\) dissolution in this zone. In sum, the reduction of Fe\(_R\) could be enhanced by biological and chemical processes in the SMTZ, and result in the remobilization of Fe\(_R\)-OC.
The observed negative inflections of $\delta^{13}$C$_{\text{FeR-OC}}$ in the SMTZ of the two cores can be mainly caused by the re-adsorption of $^{13}$C-depleted dissolved organic carbon (DOC) in the pore waters produced in two ways. First, remobilized Fe$_R$-OC is released into the pore water as DOC and selectively remineralized by microorganisms, which preferentially degrade $^{13}$C-enriched labile DOC (e.g., carbohydrates and proteins) and leave behind $^{13}$C-depleted DOC. Second, $^{13}$C-depleted DOC can be produced during AOM in the SMTZ. The adsorption of DOC molecules depends on the availability of binding sites on Fe$_R$ mineral surface. The molar ratio of Fe$_R$-OC and Fe$_R$ has been interpreted as an indicator of the binding mechanism between Fe$_R$ and OC, with monolayer adsorption resulting in a molar ratio lower than 1 while coprecipitation leads to higher ratios of 6-10$^{34,35}$. The molar ratios of Fe$_R$-OC to Fe$_R$ in both SMTZs are below 1, indicating abundant binding sites available for DOC molecules (Fig. 2e and j). Isotopically depleted DOC in the pore waters of SMTZ sediments can therefore be re-adsorbed on the surface of Fe$_R$ and result in negative $\delta^{13}$C$_{\text{FeR-OC}}$ values.
Fig. 3. Geochemical modelling and microbial evidence show that a high sulfate reduction rate is associated with low FeR-OC/TOC ratios in the SMTZ of QDN-14B. (a) Measured (red dots) and fitted (black line) sulfate concentrations. A 5-point Gaussian filter was applied to the concentration with the weighting on the 5 points of: [0.06, 0.24, 0.4, 0.24, 0.06]. (b) Modelled net reaction rate profile of sulfate. Negative values indicate net consumption, and positive values indicate net production. The 1σ envelope is shown in dashed line (See Methods for details). (c) Downcore record of FeR-OC/TOC. (d) Down-core record of δ^{13}C_{FeR-OC}. (e) Relative abundance of Desulfobacterota in bacteria, to which most of the sulfate-reducing bacteria belong to. (f) The cell number of Desulfobacterota, translated from the cell number of bacteria by multiplying the relative abundance of Desulfobacterota in bacteria. (g) The copy number of mcrA gene (data from Niu et al., 2017). The grey bar shows the position of SMTZ.

Remineralization of FeR-OC supports microbial communities in the SMTZ

In the two cores studied, the depth interval of SMTZ in core QDN-14B is well defined.
with the depletion of sulfate, increasing DIC, and depleted $\delta^{13}$C$_{\text{DIC}}$ (Fig. S2).

Therefore, core QDN-14B is used to estimate the remineralization of TOC and Fe$_{R}$-OC in the SMTZ. The accumulation rate of TOC and Fe$_{R}$-OC are calculated by multiplying their content in sediments by the sediment mass accumulation rate (see Methods). Assuming that all the TOC and Fe$_{R}$-OC lost in the SMTZ is remineralized by heterotrophic microorganisms, the remineralization flux of TOC and Fe$_{R}$-OC in the SMTZ can be estimated as the difference of their mean accumulation rate between the sediment column above and within the SMTZ. This way, the TOC and Fe$_{R}$-OC remineralization fluxes are estimated to be 15.8 and 5.8 mol m$^{-2}$ kyr$^{-1}$ in the SMTZ of QDN-14B, respectively. Fe$_{R}$-OC remineralization contributes 36.7% of the TOC remineralization in QDN-14B. As the percentage of Fe$_{R}$-OC in TOC is 10-20% in core QDN-14B, Fe$_{R}$-OC is preferentially remineralized compared to non-Fe$_{R}$-OC in the SMTZ of QDN-14B. Therefore, stimulated by more active microbial processes, e.g., S-AOM, Fe-AOM, and iron reduction, Fe$_{R}$-OC is remobilized and potentially remineralized in the SMTZ. This may contribute a substantial part to OC remineralization in the SMTZ. Moreover, since Fe$_{R}$-OC is likely enriched in labile organic matter, it has the potential to enhance heterotrophic microbial communities in subsurface sediments and be rapidly recycled upon remobilization.

The magnitude of the Fe$_{R}$-OC remineralization flux estimated in the SMTZ in core QDN-14B is supported by a similar flux in core QDN-G1 (5.0 mol m$^{-2}$ kyr$^{-1}$); the latter flux was estimated in the same way with the limitation of the SMTZ interval.
being constrained with more uncertainty. Considering that the SMTZ is ubiquitous in continental slope sediments, and assuming an Fe<sub>R</sub>-OC remineralization flux of 5.8 mol m<sup>-2</sup> kyr<sup>-1</sup> in the SMTZ and a continental slope area of 3.01 × 10<sup>7</sup> km<sup>2</sup>, the global Fe<sub>R</sub>-OC remineralization flux in the SMTZ of the continental slope area is estimated to be 0.17 Tmol yr<sup>-1</sup>, which is about one third of the methane consumption flux in the SMTZ of continental slope sediments (0.56 Tmol yr<sup>-1</sup>) and 1% of the global sedimentary OC burial rate (13.3 Tmol yr<sup>-1</sup>). Using acetate as a proxy for OC, and the Gibbs energies of OC oxidation by sulfate of -81.5 KJ (per mol acetate) at 5°C and 100 bars of pressure (1000 m water depth), the remineralization of Fe<sub>R</sub>-OC in the SMTZ of the continental slope can provide a power supply of 6.9×10<sup>15</sup> J yr<sup>-1</sup>. Assuming the cellular power demand for organisms oxidizing OC with sulfate of 7.7×10<sup>-14</sup> W cell<sup>-1</sup>, the Fe<sub>R</sub>-OC remineralization in the SMTZ of continental slope area could sustain a biomass of 2.8×10<sup>21</sup> cells. Considering generally lower power demand of 10<sup>-20</sup> to 10<sup>-16</sup> W cell<sup>-1</sup> for microorganisms in marine subsurface sediments, this amount of energy could potentially support an even larger population of 10<sup>24</sup> to 10<sup>28</sup> cells. Given the estimated global microbial cell quota of 2.9×10<sup>29</sup> in marine sediments, the remineralization of Fe<sub>R</sub>-OC could support a substantial fraction of subseafloor microbial life.

**Reactive iron as an important reservoir of labile OC over geological timescales in marine sediments**

The binding mechanism between Fe<sub>R</sub> and OC in marine sediments has been inferred.
from the molar ratio of FeR-OC to FeR, with adsorption and coprecipitation characterized by ratios of <1 and 6-10, respectively. In the two cores studied here, the molar ratio of FeR-OC to FeR is always larger than 1, except in the SMTZ, suggestive of a mixed binding mechanism of adsorption and coprecipitation (Fig. 2e and j). In marine sediments, FeR can be reductively dissolved under anaerobic conditions developed during early diagenesis. The upward diffusing Fe^{2+} can coprecipitate with marine OC into authigenic FeR after oxidation at the redox interface. Previous work in Arctic shelf sediments suggested that authigenic coprecipitation is not the dominant binding mechanism of OC and FeR. In our study, \( ^{\delta 13}C_{FeR-OC} \) in both sediment cores are typical for marine-sourced OC and the high molar ratio of FeR-OC to FeR indicates coprecipitation as an important binding mechanism. We propose that a large proportion of FeR-OC is formed at the redox interface in marine environments, which could be formed either autochthonously after deposition, or allochthonously in neighbouring surface sediments and transported to the core location as resuspended particulates.

The global budget of FeR-OC has been estimated to be \( 19-45 \times 10^{15} \) g C in surficial marine sediments, roughly 2-5% of the amount of the atmospheric CO\(_2\) (\( 875 \times 10^{15} \) g C). However, the estimation of the FeR-OC budget in long-buried sediments is hindered by the uncertain fate of FeR-OC after deposition during early diagenesis. Our results can fill this gap and advance the estimation of global FeR-OC budget in subsurface sediments. The average FeR-OC/TOC ratio in the two cores studied, except
within the SMTZ in QDN-14B, is 13.3±3.2%. As revealed by the records of QDN-14B, the percentage of Fe$_R$-OC in TOC is much lower in SMTZ sediments, where iron reduction is enhanced significantly by processes likely induced by sulfate reducing bacteria, methanotrophic archaea and/or biogenic sulfide. This leads to especially low Fe$_R$-OC/TOC in certain geochemical horizons with high microbial activities, e.g., SMTZ. A cryptic sulfur cycle driven by Fe$_R$ has been recently proposed to take place in methanic sediments$^{45,46}$, where sulfate is generated from the re-oxidation of sulfide by Fe$_R$ and sustain sulfate reduction. This may also cause the reductive dissolution of Fe$_R$ and remobilize Fe$_R$-OC. However, low Fe$_R$-OC/TOC values were not observed in the methanogenic zone of both QDN-14B and QDN-G1, which may be due to the low sulfate reduction rates in this zone$^{45}$. Furthermore, the records of QDN-G1 demonstrate that the percentage of Fe$_R$-OC in TOC remains relatively stable for almost 100 ka. The Fe$_R$-OC records in these two cores suggest that a stable proportion of TOC survives early diagenesis as Fe$_R$-OC and is sequestered in marine sediments over glacial/interglacial cycles, which facilitate the estimation of global Fe$_R$-OC budget in long-buried sediments by multiplying the corresponding TOC budget and Fe$_R$-OC/TOC ratios in surface marine sediments. LaRowe et al. (2020)$^{39}$ estimated the TOC budget in marine sediments throughout the Quaternary Period (0-2.59 Ma), which includes the most microbially active sediments. Therefore, the budget of Fe$_R$-OC in Quaternary marine sediments, regarded as exchangeable under the influence of microbial processes, can be estimated.
As the study on the fate of Fe\textsubscript{R}-OC in long buried sediments is still in its infancy and the supporting data are lacking, our estimation makes the following assumptions:

First, the Fe\textsubscript{R}-OC/TOC ratio remains relatively stable in Quaternary sediments. Although our records spanning the past around 100 kyrs strongly support this assumption, it is suggested that the degradation rate of Fe\textsubscript{R}-OC is slower than non-Fe\textsubscript{R}-OC\textsuperscript{6, 7, 16}. Therefore, an increasing percentage of Fe\textsubscript{R}-OC in TOC is expected in long-buried sediments, which could lead to a higher global Fe\textsubscript{R}-OC budget than our estimation. Second, our study gives the first record of Fe\textsubscript{R}-OC behavior during early diagenesis in continental shelf sediments. The fate of Fe\textsubscript{R}-OC in other depositional setting remains unknown. We assume that the Fe\textsubscript{R}-OC/TOC ratio in long buried sediments also stays relatively stable in other depositional settings. Third, there is only limited data available from abyssal sediments (water depth >3500 m), the Fe\textsubscript{R}-OC/TOC ratio in the surface sediments of marginal sediments (200m < water depth<3500m) is used to represent both marginal and abyssal environments. In spite of these caveats, our estimation provides a premilinary but straightforward view of how much OC has been sequestered by reactive iron phases and serve as a semi-stable carbon pool over geological timescales.

To estimate the global budget of Fe\textsubscript{R}-OC in Quaternary sediments, all the published Fe\textsubscript{R}-OC/TOC data in marine sediments using the CBD method are compiled with our measured data and grouped into four categories based on their study area information:
deep-sea sediments, and sediments in anoxic/sulfidic regions (Table S3). The mean values of FeR-OC/TOC are 15.7±7.8%, 11.2±3.7%, 20.1±9.3% and 22.9±4.8%, respectively (Figure 4). A one-way ANOVA was used to determine whether the FeR-OC/TOC values are significantly different among these marine environments. The results show that FeR-OC/TOC values significantly differ between anoxic/sulfidic sediments and continental shelf sediments (P<0.001) and between continental slope and deep-sea sediments and continental shelf sediments (P<0.05) (Figure 4). Considering the limited distribution and limited published data of the anoxic/sulfidic regions, this category is not further considered in the global estimation. Delta/estuary and continental shelf are combined, representing the marine environment with water depth shallower than 200 m. The FeR-OC/TOC ratios of all the study areas belonging to this environment are averaged to be 13.2±6.1% (Table S4). The continental slope and deep sea represent the marine environment with water depth deeper than 200 m, where the FeR-OC/TOC ratios of all the study areas belonging to this environment average at 20.1±9.3% (Table S4). Combining the published TOC storage of these two environments in Quaternary sediments 39, the global budget of FeR-OC in Quaternary marine sediments was estimated to be 291±133×10¹⁷ g C (Table S4), which is approximately 18-48 times the size of the atmospheric carbon pool.

Our results suggest FeR-OC as a persistent but exchangeable pool of labile OC that potentially plays a critical role in modulating Earth’s climate over geological timescales. This large preserved carbon pool can be especially remobilized in
microbial active zones like SMTZ. Given the context that the location of SMTZ can migrate upward and downward in response to sedimentation deposition with varied OC flux over glacial/interglacial timescales, FeR-OC in different sedimentary layers might be consequently remobilized and fuel up the surrounding microbial community. This would also bring uncertainties to the balance of OC preservation and degradation in long-buried sediments. Therefore, further researches are required to fully understand the role of reactive iron phases in long-term carbon sequestration in marine environments.

**Fig. 4.** FeR-OC/TOC values in different marine environments. All the published FeR-OC/TOC data obtained from marine sediments using the CBD method are compiled (detailed information of study areas and references are listed in Table S3). The FeR-OC/TOC value of each study area is represented by the mean value of all data collected from this study area in the same study case to...
avoid overrepresentation of study cases with large numbers of data points (Table S3). The FeR-
OC/TOC data of different study areas are then grouped into four categories according to the
depositional environments and used for one-way ANOVA and box-whisker plots.
Methods

Sediment core collection and age model establishment

The Qiongdongnan (QDN) basin lies in the rift belt of the northern continental margin of the South China Sea and receives terrestrial material mainly from the Indo-China Peninsula and Southeast China (especially Hainan Island) by river runoff and aeolian dust\textsuperscript{48, 49}. In addition, the material contribution of marine authigenic sources to the basin cannot be neglected\textsuperscript{49}.

Core QDN-14B was recovered from the QDN basin at a water depth of 1370 m in 2015, ~600 m east of ROV1, which is an active seep site of “Haima” cold seeps\textsuperscript{50}. Core QDN-G1 was recovered outside the area of “Haima” cold seeps around 35 km away from QDN-14B at a water depth of 1478 m in 2018 (Fig. 1a). Sediment samples were subsampled every 40 cm and preserved at -80 °C. Known volumes of sediments were taken using tip cut-off syringes and sealed in glass vials for further measurements of density and porosity. For core QDN-G1, the age model of the upper 4.0 m was based on 7 accelerator mass spectrometry \(^{14}\text{C}\) ages of planktonic foraminifera (\textit{G. ruber}) (Table S1). The age model of the lower part (4.0-10.8 m) was established by aligning the benthic foraminifera (\textit{C. wuellerstorfi}) \(\delta^{18}\text{O}\) record to the global benthic \(\delta^{18}\text{O}\) stack LR04\textsuperscript{21} (Fig. 1b).

Pore water sampling and analysis

Pore water samples were extracted immediately onboard using Rhizon samplers (0.22
µm filter) before the core was cut open for sediment subsampling. To prevent oxidation of Fe(II), an aliquot of pore water was added to the ferrozine solution. Pore water samples for dissolved inorganic carbon measurements were preserved in pre-vacuumed glass vials. Pore water samples for ion measurements were acidified with concentrated HNO$_3$. The rest of the pore water samples were preserved in pre-combusted amber glass vials at −20°C for dissolved organic carbon measurements.

The Fe(II) concentration was determined by ferrozine assay using a spectrophotometer. The concentrations of major cations and anions were determined by ion chromatography (Dionex ICS-5000+). Dissolved inorganic carbon (DIC) was measured using a total carbon analyzer (Multi 3100, Jena).

Physical properties of bulk sediments

Known volumes of sediments were subsampled by tip cut-off syringes and preserved in sealed glass vials for the measurements of physical properties, such as porosity and dry bulk density. All the physical properties were only measured for QDN-G1 samples. The averaged porosity and dry bulk density were used to represent the general porosities of the two cores.

Porosity was calculated by the volume ratio of water and wet sediment, where the volume of water was calculated from the difference between the wet and dry sample weight. The dry bulk density was calculated by dividing the dry sample weight by the
original wet sample volume.

**Fe\textsubscript{R} and Fe\textsubscript{R}-OC extraction**

Fe\textsubscript{R} and Fe\textsubscript{R}-OC were extracted using the citrate-bicarbonate-dithionite (CBD) method according to Mehra and Jackson (1960)\textsuperscript{20}, as modified by Lalonde et al.\textsuperscript{1} and Salvadó et al.\textsuperscript{2}. Both poorly crystalline and crystalline iron (oxyhydr)oxides can be reduced by this method, including mainly goethite and hematite, which are the major iron (oxyhydr)oxides in marine sediments\textsuperscript{52,53}. Briefly, samples were freeze-dried and homogenized using an agate mortar and pestle. Samples (0.5 g) were weighed carefully into 40 mL Teflon tubes and extracted in a 30 mL solution of sodium dithionite and trisodium citrate buffered with sodium bicarbonate at 80°C for 15 min in a water bath. After the extraction, the suspensions were centrifuged for 10 min at 4000×g and then rinsed 5 times with artificial seawater. To evaluate the amount of OC remobilized during the extraction that was not associated with Fe\textsubscript{R}, another sample aliquot was extracted as a control under the same experimental conditions, but replacing sodium dithionite and trisodium citrate with sodium chloride with equivalent ion strength. The residuals were dried overnight in a 50°C oven, carefully weighed and manually ground.

The supernatant and rinse water were combined, acidified to pH<2 and filtered through 0.22 μm filters. The dissolved iron was determined using a ferrozine assay\textsuperscript{51}. The iron extracted in the control group were negligible; therefore, the amount of Fe\textsubscript{R...
was calculated based on the iron extracted in the dithionite reduction group without further correction.

**FeR-OC quantification and carbon isotope analyses**

The OC content and carbon isotope ratio were determined for both untreated and treated samples using an elemental analyser (Vario EL III, Elementar) coupled to an isotope ratio mass spectrometer (Isoprime, Elementar) at the instrumental analysis centre, Shanghai Jiao Tong University. The inorganic carbon was removed by acid fumigation before the analysis. The samples were measured in triplicate, and the standard deviation was <0.05% for TOC and <0.2‰ for δ¹³C. The analytical precision was <0.06% for TOC (standard deviation for repeated measurements of the low organic content soil standard; n=3) and <0.09‰ for δ¹³C (standard deviation for repeated measurements of the USGS40 standard, n=3).

**Calculation of FeR-OC percentage in TOC and δ¹³C_{FeR-OC}**

The amount of FeR-OC was determined as the difference of TOC amount in the residuals between the CBD extraction and control extraction.

FeR-OC percentage in TOC = \( \frac{(\text{TOC}_{\text{control}} - \text{TOC}_{\text{CBD}})}{\text{TOC}_{\text{bulk}}} \)

in which,

\( \text{TOC}_{\text{control}} \) = total organic carbon (mg) left after the control extraction,

\( \text{TOC}_{\text{CBD}} \) = total organic carbon (mg) left after the CBD extraction,

\( \text{TOC}_{\text{bulk}} \) = total organic carbon (mg) in the untreated sample.
A binary mixing model was used to calculate the carbon isotope ratio of FeR-OC, where the OC pool in the residual of the control group (TOC_{control}) is comprised of FeR-OC and OC remaining untouched after CBD extraction (TOC_{CBD}). The carbon isotope ratios of FeR-OC was calculated according to the following mass-balanced equations:

\[ \text{TOC}_{CBD} + \text{FeR-OC} = \text{TOC}_{control} \]

\[ f_{\text{TOC}_{CBD}} \times \delta^{13}C_{CBD} + f_{\text{FeR-OC}} \times \delta^{13}C_{\text{FeR-OC}} = \delta^{13}C_{\text{control}} \]

in which,

- FeR-OC= the amount of organic carbon (mg) associated with FeR,
- TOC_{CBD}= total organic carbon (mg) left after the CBD extraction,
- TOC_{control}= total organic carbon (mg) left after the control extraction,
- \( f_{\text{TOC}_{CBD}} = \frac{\text{TOC}_{CBD}}{\text{TOC}_{control}} \),
- \( f_{\text{FeR-OC}} = \frac{\text{FeR-OC}}{\text{TOC}_{control}} \),
- \( \delta^{13}C_{CBD} = \) the measured carbon isotope signature of TOC_{CBD},
- \( \delta^{13}C_{\text{control}} = \) the measured carbon isotope signature of TOC_{control},
- \( \delta^{13}C_{\text{FeR-OC}} = \) the carbon isotope signature of FeR-OC.

**Geochemical modelling**

Net reaction rates of sulfate were estimated using the MATLAB script published in Wang et al., 2008\textsuperscript{36}, considering molecular diffusion, sediment burial, fluid advection,
and reaction under the assumption that the sulfate concentration profiles represent steady-state conditions.

The mass balance of sulfate is expressed as:

$$\frac{\partial}{\partial x} \left( -\frac{D(x)}{\theta^2(x)} \frac{\partial [\phi(x)C(x)]}{\partial x} + [\phi(x)b(x) + \phi(x)\nu(x)]C(x) \right) + R(x) = 0$$

Where $C(x)$ is sulfate concentration in the pore water, $x$ is depth below the seafloor, $\phi(x)$ is porosity, $D(x)$ is the molecular diffusion coefficient of sulfate, $\theta^2(x)$ is tortuosity, $b(x)$ is pore water burial velocity, $\nu(x)$ is externally driven flow velocity, $R(x)$ is the rate of diagenetic reaction per unit volume of sediment\textsuperscript{36}.

The model applied a 5-point Gaussian filter to the sulfate concentration profile, with the weighting on the 5 points of: [0.06, 0.24, 0.4, 0.24, 0.06]. All parameters used for modelling are listed in Table S2. Porosity profile was measured using QDN-G1 samples. The averaged porosity was applied as the constant porosity value for both cores assuming similar sediment properties in the study area. Diffusion coefficients of sulfate in the two cores were obtained using R package marelac\textsuperscript{54} with the input of respective salinity, temperature and pressure values (Table S2). The tortuosity $\theta^2$ was calculated by the relation, $\theta^2 = \phi f$, where $f$ is the formation factor, which can be calculated based on the empirical relationship $f = 1.3 \times \phi^{-1.45}$ \textsuperscript{55,56}. We used the sedimentation rate near the seafloor $1.2 \times 10^{-4}$ m yr$^{-1}$ as the pore water burial velocity for both cores, assuming a similar sedimentation rate in the study area, which is calculated by the radiocarbon dating ages of the first two sampling layers below the seafloor in QDN-G1. A constant external flow advection velocity near the sediment-
water interface of $10^{-5}$ m yr$^{-1}$ was used$^{36}$. A minimum of three measured concentration data points were used to determine each reaction zone$^{36}$. The model quantifies uncertainties in the rate estimates by using a Monte Carlo technique$^{36}$. The depth-integrated net reaction rate yielded the total flux at steady state for the sediment column.

The accumulation rate of TOC and Fe$_R$-OC in QDN-14B

The accumulation rate of TOC and Fe$_R$-OC were calculated as$^{57}$:

$\text{TOC accumulation rate} = LSR \times DBD \times \text{TOC}\%$

$\text{Fe}_R$-OC accumulation rate = $LSR \times DBD \times Fe_R$-OC\%$

where DBD is the dry sediment bulk density in $g$ cm$^{-3}$, LSR is the linear sedimentation rate in cm kyr$^{-1}$, TOC\% and Fe$_R$-OC\% are the weight percentage of TOC and Fe$_R$-OC in sediments, respectively. The TOC and Fe$_R$-OC accumulation rate is expressed in mol m$^{-2}$ kyr$^{-1}$. The average sedimentation rate (11.1 cm kyr$^{-1}$) and the average dry bulk density (0.9 g cm$^{-3}$) of QDN-G1 was used for the calculation for core QDN-14B, assuming similar sedimentation rate and bulk sediment properties in the study area.

DNA extraction, qPCR and amplicon sequencing

The 16S rRNA gene data was obtained for core QDN-G1 according to the following procedures.
The DNA for qPCR and V4 region of 16S rRNA gene sequencing was extracted from ~0.25 g of sediments using DNeasy® PowerSoil® Pro Kit (Qiagen), according to the manufacturer’s instructions.

The extracted DNA was used as template for qPCR to determine the abundance of bacterial 16S rRNA gene with the primer set 331F/797R. Standard curves were constructed using a 10-fold series dilution of the plasmids for six gradients carrying the bacteria 16S rRNA gene. qPCR was carried out in a volume of 20 μL, including 10 μL 2 × PowerUp™ SYBR™ Green Master Mix (Thermo Fisher), 1.6 μL each primer (10 μM), 2 μL template DNA and 4.8 μL sterilized deionized water. The qPCR program consisted of an initial cycle of 95 °C for 5 min; 40 cycles of 95 °C for 30 s, 60 °C for 30 s, 72 °C for 30 s, 80 °C for 10 s, and the data was collected at the final step of each cycle. The melting curve was generated using default program. All samples were subject to qPCR measurement with three technical replicates. The bacterial cell number was evaluated based on the abundance of 16S rRNA gene, applying the average copy number of the 16S rRNA gene on genomes of Bacteria (5.3 copies genome, rrnDB version 5.8).

The V4 region of 16S rRNA gene was amplified using the primer set 515F/806R. DNA was amplified using the following cycling conditions: 95°C, 5 min; 30 cycles (95°C, 30 s; 50°C, 30 s; 72°C, 30 s); 72°C, 7 min. The PCR products of samples were
sent to Shanghai Personal Biotechnology Co., Ltd. (Shanghai, China) for high-throughput sequencing of the 16S rRNA gene using the Illumina Novaseq PE250 platform.

**Sequence analysis**

The raw reads of 16S rRNA gene of both cores QDN-G1 and QDN-14B were processed and analyzed using the QIIME 2 platform (version 2020.11)\(^{61}\). The primers and adaptors were first trimmed out using Cutadapt (version 3.1)\(^{62}\). Raw sequences were then processed using DADA2\(^{63}\), including quality filtering, denoising, paired-end sequence merging, chimera filtering and producing amplicon sequence variants (ASVs) and ASV Table. Taxonomy was assigned using q2-feature-classifier (a scikit-learn naive Bayes machine-learning classifier)\(^{64}\) with Silva database release 138\(^{65}\).

Multiple sequence alignment and phylogenetic tree construction were performed using the QIIME 2 plugin q2-phylogeny (align-to-tree-mafft-iqtree). Unassigned sequences, singletions and sequences affiliated with eukaryotes were discarded.

Eventually, to eliminate uneven sequencing depths, the ASV table was rarefied to 14935 and 71773 sequences per sample for QDN-14B and QDN-G1, respectively, determined by the sample with the fewest sequences.

**Data availability**

Raw Illumina sequence data of the 16S rRNA gene generated for cores QDN-14B and QDN-G1 in this study has been deposited in the NODE (the National Omics Data Encyclopedia,
https://www.biosino.org/node/ database under the project number OEP004264 and OEP004265, respectively. All other data discussed in the paper are available in the Source Data.

References

15. Faust, J. C. et al. Millennial scale persistence of organic carbon bound to iron in...


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Author contributions

F.W designed the research and secured funding. Y.C. collected geochemical data, performed data analysis, and wrote the first draft of the manuscript. L.D constructed the age model. W.S and M.N. collected and analyzed microbial data. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

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Supplementary Information for

Reactive iron as an important reservoir of marine organic carbon over geological timescales

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Supplementary Text

Variations of TOC and Fe<sub>R</sub>-OC records over glacial/interglacial cycles

Because of relatively weak microbial activities and well-established age model, core QDN-G1, representing typical continental slope sediments, is used to constrain the variation of TOC and Fe<sub>R</sub>-OC records controlled by environmental changes across glacial/interglacial cycles.

In global marine sediments, except polar regions, the burial of OC has natural variations over glacial/interglacial cycles, with much higher accumulation rate in glacial periods than during interglacial periods for higher marine primary productivity and more efficient preservation<sup>1</sup>. If the environmental factors being the main controlling factor of OC content, higher content should be expected in glacial periods. However, in core QDN-G1, we found consistently low TOC and Fe<sub>R</sub>-OC content across MIS5 (interglacial) and MIS4 (glacial) (Figure S4b).

The variations in the carbon isotope ratio of OC in marine sediments are generally ascribed to three reasons: variable contribution of terrestrial- and marine-sourced OC (sediment provenance), variable isotope composition of marine-sourced OC and selective microbial degradation after deposition<sup>2</sup>. If the carbon isotope ratio reflects the relative contribution of terrestrial and marine OC, it should be in lower in MIS 2 and MIS 4, when the sea-level stand was at least 40 meters lower than that in MIS 5 (Fig. S4e) and terrestrial supply was higher for the closer river mouth to the study sites<sup>3</sup>.
However, the carbon isotope ratio of TOC and Fe\textsubscript{R}-OC were consistently depleted during MIS 5 to MIS 4 and became more enriched during MIS 3 to 1 (Figure. S4c). Therefore, the variations can be hardly explained by the changes in sediment provenance. If it reflects variation in the isotope composition of marine OC, we should also expect lower values in interglacials (MIS 1 and MIS 5) and lower values in glacial (MIS 2 and MIS 4). Similarly, this possibility is also ruled out. Collectively, the distinctive low content and depleted carbon isotope ratio of TOC and Fe\textsubscript{R}-OC can be hardly explained by the controlling of environmental changes before deposition on glacial/interglacial timescales.
Table S1. AMS ^14C age control points used to reconstruct the age model of core QDN-G1

<table>
<thead>
<tr>
<th>Depth (cmbsf)</th>
<th>AMS ^14C age (BP)</th>
<th>Error</th>
<th>Calendar Age (cal BP)</th>
<th>Dating foraminifera species</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2030 ±30</td>
<td>1603</td>
<td></td>
<td><em>G. ruber</em></td>
</tr>
<tr>
<td>80</td>
<td>8090 ±30</td>
<td>8538</td>
<td></td>
<td><em>G. ruber</em></td>
</tr>
<tr>
<td>120</td>
<td>10500 ±30</td>
<td>11657</td>
<td></td>
<td><em>G. ruber</em></td>
</tr>
<tr>
<td>200</td>
<td>14050 ±40</td>
<td>16457</td>
<td></td>
<td><em>G. ruber</em></td>
</tr>
<tr>
<td>280</td>
<td>21070 ±70</td>
<td>24878</td>
<td></td>
<td><em>G. ruber</em></td>
</tr>
<tr>
<td>360</td>
<td>27450 ±120</td>
<td>31069</td>
<td></td>
<td><em>G. ruber</em></td>
</tr>
<tr>
<td>400</td>
<td>30810 ±170</td>
<td>34387</td>
<td></td>
<td><em>G. ruber</em></td>
</tr>
</tbody>
</table>
Table S2. The input parameters for geochemical modelling of net sulfate reaction rate after the MATLAB script of Wang et al. 2008\textsuperscript{5}.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value for core QDN-G1</th>
<th>Value for core QDN-14B</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>0.7</td>
<td>0.7</td>
<td>\</td>
</tr>
<tr>
<td>Formation factor</td>
<td>2.2</td>
<td>2.2</td>
<td>\</td>
</tr>
<tr>
<td>Sedimentary rate near the seafloor</td>
<td>0.000115</td>
<td>0.000115</td>
<td>m yr\textsuperscript{-1}</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>0.0175</td>
<td>0.0175</td>
<td>m\textsuperscript{2} yr\textsuperscript{-1}</td>
</tr>
<tr>
<td>External flow advection velocity</td>
<td>0.00001</td>
<td>0.00001</td>
<td>m yr\textsuperscript{-1}</td>
</tr>
<tr>
<td>Significance level (F-test)</td>
<td>0.05</td>
<td>0.05</td>
<td>\</td>
</tr>
<tr>
<td>Minimum number of measured data within each reaction zone</td>
<td>3</td>
<td>3</td>
<td>\</td>
</tr>
<tr>
<td>Relative precision of concentration measurements</td>
<td>0.01</td>
<td>0.01</td>
<td>\</td>
</tr>
<tr>
<td>Number of random concentration profiles to estimate the uncertainty of reaction rates</td>
<td>50</td>
<td>50</td>
<td>\</td>
</tr>
<tr>
<td>Temperature</td>
<td>4</td>
<td>4</td>
<td>°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>147.8</td>
<td>137.0</td>
<td>bar</td>
</tr>
<tr>
<td>Salinity</td>
<td>35</td>
<td>35</td>
<td>\</td>
</tr>
<tr>
<td>Water depth</td>
<td>1478</td>
<td>1370</td>
<td>m</td>
</tr>
<tr>
<td>Dry bulk density</td>
<td>0.9</td>
<td>0.9</td>
<td>g cm\textsuperscript{-3}</td>
</tr>
</tbody>
</table>
Table S3. Compilation of Fe<sub>2</sub>-OC/TOC data in different marine environments. The data are presented as means ± standard deviation for each study area.

<table>
<thead>
<tr>
<th>Marine environments</th>
<th>Study area</th>
<th>Average Fe&lt;sub&gt;2&lt;/sub&gt;-OC/TOC (%)</th>
<th>Number of data points</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delta/Estuary</td>
<td>Changjiang Estuary</td>
<td>11.3±3.6</td>
<td>5</td>
<td>Zhao et al., 2018&lt;sup&gt;6&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Changjiang Estuary</td>
<td>5.7±2.3</td>
<td>9</td>
<td>Sun et al., 2020&lt;sup&gt;7&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Wax Lake Delta</td>
<td>15.1±8.7</td>
<td>37</td>
<td>Shields et al., 2016&lt;sup&gt;8&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Washington Coast</td>
<td>24.4±8.4</td>
<td>8</td>
<td>Lalonde et al., 2012&lt;sup&gt;9&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>St-Lawrence Estuary</td>
<td>23.1±2.4</td>
<td>3</td>
<td>Lalonde et al., 2012&lt;sup&gt;9&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>St-Lawrence Gulf</td>
<td>23.0±6.0</td>
<td>2</td>
<td>Lalonde et al., 2012&lt;sup&gt;9&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Mackenzie River delta</td>
<td>7.6</td>
<td>1</td>
<td>Lalonde et al., 2012&lt;sup&gt;9&lt;/sup&gt;</td>
</tr>
<tr>
<td>Continental shelf</td>
<td>East China Sea</td>
<td>13.2±8.9</td>
<td>12</td>
<td>Ma et al., 2018&lt;sup&gt;10&lt;/sup&gt;</td>
</tr>
<tr>
<td>(water depth&lt;200 m)</td>
<td>South Yellow Sea</td>
<td>8.8±7.7</td>
<td>10</td>
<td>Ma et al., 2018&lt;sup&gt;10&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>East China Sea</td>
<td>6.1±2.1</td>
<td>26</td>
<td>Zhao et al., 2018&lt;sup&gt;6&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Mobile-muds Zone</td>
<td>9.4±5.1</td>
<td>7</td>
<td>Zhao et al., 2018&lt;sup&gt;6&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Eurasian Arctic Shelf</td>
<td>11.0±5.5</td>
<td>29</td>
<td>Salvado et al., 2015&lt;sup&gt;11&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>Bohai Sea</td>
<td>11.5±8.3</td>
<td>20</td>
<td>Wang et al., 2019&lt;sup&gt;12&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>South Yellow Sea</td>
<td>13.0±7.4</td>
<td>27</td>
<td>Tao et al., 2017&lt;sup&gt;13&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>South Yellow Sea</td>
<td>8.7±4.7</td>
<td>10</td>
<td>Sun et al., 2020&lt;sup&gt;7&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>Barents Sea</td>
<td>18.9±7.6</td>
<td>127</td>
<td>Faust et al., 2020, 2021&lt;sup&gt;14,15&lt;/sup&gt;</td>
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<tr>
<td>Continental slope and deep</td>
<td>Southern Ocean</td>
<td>29.0</td>
<td>1</td>
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<tr>
<td>sea (water depth&gt;200 m)</td>
<td>Station M</td>
<td>14.3±4.1</td>
<td>2</td>
<td>Lalonde et al., 2012&lt;sup&gt;9&lt;/sup&gt;</td>
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<td></td>
<td>Equatorial Pacific 0°N</td>
<td>34.8</td>
<td>1</td>
<td>Lalonde et al., 2012&lt;sup&gt;9&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>Equatorial Pacific 9°N</td>
<td>12.2</td>
<td>1</td>
<td>Lalonde et al., 2012&lt;sup&gt;9&lt;/sup&gt;</td>
</tr>
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<td></td>
<td>Madeira turbidite</td>
<td>29.8</td>
<td>1</td>
<td>Lalonde et al., 2012&lt;sup&gt;9&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>Arabian Sea</td>
<td>22.8±5.7</td>
<td>2</td>
<td>Lalonde et al., 2012&lt;sup&gt;9&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Mexican Margin</td>
<td>16.2±7.1</td>
<td>9</td>
<td>Lalonde et al., 2012&lt;sup&gt;9&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Okinawa Trough</td>
<td>8.6±3.5</td>
<td>8</td>
<td>Sun et al., 2020&lt;sup&gt;7&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>South China Sea&lt;sup&gt;a&lt;/sup&gt;</td>
<td>13.3±3.2</td>
<td>57</td>
<td>This study</td>
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<td>Anoxic/sulfidic regions</td>
<td>Black Sea</td>
<td>15.9±12.8</td>
<td>2</td>
<td>Lalonde et al., 2012&lt;sup&gt;9&lt;/sup&gt;</td>
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<td>Indian Margin</td>
<td>26.6</td>
<td>1</td>
<td>Lalonde et al., 2012&lt;sup&gt;9&lt;/sup&gt;</td>
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<tr>
<td>Marine environments</td>
<td>Study area</td>
<td>Average FeR-OC/TOC (%)</td>
<td>Number of data points</td>
<td>Reference</td>
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<tr>
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<td>Saanich inlet</td>
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<td>1</td>
<td>Lalonde et al., 2012⁹</td>
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<td></td>
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<td>22.8±5.7</td>
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<td>Mexican margin</td>
<td>21.2±2.4</td>
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<td>Lalonde et al., 2012⁹</td>
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⁹Data derived from SMTZ sediments in QDN-14B in this study are excluded from the calculations, as they are affected by especially strong early diagenesis processes.
Table S4. Global budget of FeR-OC (10^{17} g C) in microbially reactive Quaternary sediments. The FeR-OC budget was calculated by multiplying the TOC budget in these two marine environments by the corresponding average FeR-OC/TOC ratio in surface sediments, with the assumption that the percentage of FeR-OC in TOC stays mostly stable during early diagenesis and can persist over geological timescales.

<table>
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<th>Estuary and continental shelf (water depth &lt; 200 m)</th>
<th>Continental slope and deep sea (water depth &gt; 200 m)</th>
<th>Total</th>
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<td>TOC budget(^a)</td>
<td>20.4</td>
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<td>FeR-OC/TOC (%)</td>
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<td>20.1±9.3</td>
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<td>FeR-OC budget</td>
<td>2.7±1.2</td>
<td>288±133</td>
<td>291±133</td>
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</table>

\(^a\)Data from LaRowe et al., 2020\(^{16}\), where global datasets, including bathymetry, sedimentation rates, POC content at the sediment-water interface and POC reactivity were used to model the distribution of organic carbon in Quaternary marine sediments.
Fig. S1. Pore water geochemistry in core QDN-G1. Sulfate, DIC and Fe(II) concentrations are presented to estimate the location of geochemical horizons, i.e., the iron reduction zone (IRZ), the sulfate reduction zone (SRZ), the sulfate-methane transition zone (SMTZ), and the methanogenic zone (MZ). The low concentrations of Fe(II) are consistent with precipitation of Fe(II) with sulfide produced during sulfate reduction, indicating overlapped IRZ and SRZ. Given the data available, the potential upper boundary of SMTZ was determined by abrupt increased DIC at 720 cmbsf. The lower boundary of SMTZ was determined by the depletion of sulfate at 960 cmbsf.
Fig. S2. Pore water geochemistry in core QDN-14B. Sulfate concentration, DIC concentration, and DIC carbon isotope ratio ($\delta^{13}$C$_{DIC}$) are presented to estimate the location of geochemical horizons, i.e., sulfate reduction zone (SRZ), sulfate-methane transition zone (SMTZ), and methanogenic zone (MZ). The estimated upper boundary of SMTZ was determined by increasing DIC concentration and depleted $\delta^{13}$C$_{DIC}$ at 280 cmbsf. The lower boundary of SMTZ was determined by the depletion of sulfate and depleted $\delta^{13}$C$_{DIC}$ at 440 cmbsf. All the data have been published in Hu et al. (2019)$^{17}$. The data between 300 and 400 cmbsf were suspected to be influenced by seawater during core recovery, and are therefore not presented.
Fig. S3. Geochemical modelling of net sulfate reaction rate in cores QDN-G1 (a) and QDN-14B (b). Negative values indicate net consumption, and positive values indicate net production. The net sulfate reduction rate in SMTZ in QDN-14B is more than two times higher than that in QDN-G1.
Fig. S4. Content and carbon isotope ratios of TOC and FeR-OC in core QDN-G1 over glacial/interglacial cycles. The pink and green bars indicate interglacial periods and the last glacial period, respectively. (a) Content of FeR. (b) Content of TOC (black line) and FeR-OC (red line). (c) Carbon isotope ratios of TOC (black line) and FeR-OC (red line). (d) Percentage of FeR-OC in TOC. (e) $\delta^{18}$O record of benthic foraminifera (black line) and global relative sea level record from Waelbroeck et al, 2002 (blue line). The location of the SMTZ is highlighted in purple.
Fig. S5. Geochemical modelling and microbial evidence show that low sulfate reduction rate results in moderate decrease in Fe₉-OC in the SMTZ of core QDN-G1. (a) Measured (red dots) and fitted (black line) sulfate concentrations. A 5-point Gaussian filter was applied to the concentration with the weighting on the 5 points of: [0.06, 0.24, 0.4, 0.24, 0.06]⁵. (b) Modelled net reaction rate profile of sulfate. Negative values indicate net consumption, and positive values indicate net production. The 1 σ uncertainty envelope is shown in dashed line. (c) Down-core record of Fe₉-OC/TOC. (d) Down-core record of δ¹³C₉-OC. (e) Relative abundance of Desulfobacterota in bacteria, which is the phylum most of the sulfate-reducing bacteria belong to¹⁹. (f) The cell number of Desulfobacterota, translated from the cell number of bacteria by multiplying the relative abundance of Desulfobacterota in bacteria. The gray bar shows the position of SMTZ.
References


14. Faust, J. C. et al. Millennial scale persistence of organic carbon bound to iron in


