

## Organic carbon burial with reactive iron across global environments

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## Key Points

- Annual burial flux of OC with reactive iron estimated in marine and terrestrial environments by probabilistic modelling of compiled data.
- Reactive iron minerals bury c. 52 Mt C yr<sup>-1</sup> in marine sediments, and c. 472 Mt C yr<sup>-1</sup> in terrestrial soils.
- Terrestrial OC-Fe<sub>R</sub> rates vulnerable to changing climate, with changes in Fe<sub>R</sub> delivery to the ocean a control for long term OC burial.

## Abstract

Preservation of organic carbon (OC) in marine and terrestrial deposits is enhanced by bonding with reactive iron (Fe<sub>R</sub>) phases. The association of OC with Fe<sub>R</sub> (OC-Fe<sub>R</sub>) provides physical protection and hinders microbiological degradation. Roughly 20% of all OC stored in unconsolidated marine sediments and 40% of all OC present in Quaternary terrestrial deposits is preserved as OC-Fe<sub>R</sub>, but this value varies from 10 to 80% across depositional environments. In this work, we provide a new assessment of global OC-Fe<sub>R</sub> burial rates in both marine and terrestrial environments, using published estimates of the fraction of OC associated with Fe<sub>R</sub>, carbon burial, and probabilistic modelling. We estimate the marine OC-Fe<sub>R</sub> sink at between 31 – 70 Mt C yr<sup>-1</sup> (mean 52 Mt C yr<sup>-1</sup>), and the terrestrial OC-Fe<sub>R</sub> sink at between 171 - 946 Mt C yr<sup>-1</sup> (mean 472 Mt C yr<sup>-1</sup>). In marine environments, continental shelves (mean 17 Mt C yr<sup>-1</sup>) and deltaic/estuarine environments (mean 11 Mt C yr<sup>-1</sup>) are the primary locations of OC-Fe<sub>R</sub> burial. On land, croplands (279 Mt C yr<sup>-1</sup>) and grasslands (121 Mt C yr<sup>-1</sup>) dominate the OC-Fe<sub>R</sub> burial budget. Changes in the Earth system through geological time likely alter the OC-Fe<sub>R</sub> pools, particularly in marine locations. For example, periods of intense explosive volcanism may lead to increased net OC-Fe<sub>R</sub> burial in marine sediments. Our work highlights the importance of OC-Fe<sub>R</sub> in marine carbon burial and demonstrates how OC-Fe<sub>R</sub>

burial rates may be an order of magnitude greater in terrestrial environments, those potentially most sensitive to anthropogenic impacts.

## 1 Introduction

The burial of carbon in the marine realm exerts a controlling influence on the global carbon cycle (Falkowski et al., 2000). In particular, the burial of organic carbon (OC) in marine sediments is the largest long-term net sink for carbon on Earth (Burdige, 2007), with 200 megatonnes (Mt) of carbon buried in this manner per year (Canadell et al., 2021). Thus, OC burial in marine sediments plays a key role in controlling atmospheric CO<sub>2</sub> on geological timescales. As such, knowing the factors controlling the size, efficiency, and longevity of this sink is vital for understanding long-term carbon cycling (Burdige, 2007; Hedges and Keil, 1995).

The vast majority of organic carbon reaching the seafloor is remineralised before burial into the sediments (on average 87%; Burdige, 2007), meaning it returns to the ocean-atmosphere CO<sub>2</sub> system. However, with burial efficiency varying from >70% to <0.3% between depositional settings (Dunne et al., 2007), the OC fraction which does not get remineralized is highly dependent on burial location, and a range of environmental factors such as the duration of exposure to oxic water and sedimentation rate (Hartnett et al., 1998). Thus, it is important to understand these environmental factors and the physiochemical mechanisms which may impact, and in particular enhance, the efficiency of sedimentary organic carbon burial (Curti et al., 2021; Lalonde et al., 2012; Longman et al., 2019; Schrag et al., 2013).

In marine environments, large fractions of sedimentary OC are associated with the mineral matrix via sorption to clays or reactive metals (Keil and Mayer, 2014; Mayer, 1994). The association of OC to reactive metals, and particularly to reactive iron oxy(hydroxide) phases such as ferrihydrite (Fe<sub>R</sub>), provides physical protection (Fig. 1) and prevents microbiological degradation (Keil et al., 1994). As such, the binding of OC to Fe<sub>R</sub> (OC-Fe<sub>R</sub>) represents an efficient mechanism by which OC escapes early diagenetic degradation in marine sediments and is buried to depths that are not in diffusive or advective connection with the overlying water column. In marine environments, between 10 – 80% of the OC pool is bound to Fe<sub>R</sub> (e.g., Dicen et al., 2019; Faust et al., 2020; Lalonde et al., 2012; Longman et al., 2021b; Ma et al., 2018; Salvadó et al., 2015; Shields et al., 2016; Sun et al., 2020) and therefore this carbon-iron coupling constitutes an significant OC burial mechanism.

Since carbon-iron interactions are preserved in sediments which are hundreds of thousands of years old (Faust et al., 2021; Longman et al., 2021b), these interactions must be irreversible or at least kinetically inhibited under ambient conditions, as reversible reactions such as hydrogen bonding, hydrophobic interaction and cation bridging would result in OC solubilisation and breakdown

(Burdige, 2007). Fe(III) in marine sediments is either supplied from precipitation of Fe(II) at the Fe(II)/Fe(III) redox boundary, or from direct deposition of lithogenic Fe (Longman et al., 2021b). It has a strong affinity to various ions (in addition to OC) which results in an association between organic and inorganic phases (Chen et al., 2014; Faust et al., 2021; Homoky et al., 2021; Lalonde et al., 2012; Riedel et al., 2013). One of the primary mechanisms by which long lasting interactions are formed is between OC and nano-scale iron (oxyhydr)oxides such as ferrihydrite (Barber et al., 2017; Faust et al., 2021). A significant proportion of these interactions exists in the form of inner-sphere Fe-O-C, covalent interactions between  $\text{Fe}_\text{R}$  and functional (especially carboxyl) groups (Barber et al., 2017; Curti et al., 2021; Keil and Mayer, 2014). Such interactions are thought to explain 25 – 62% of OC- $\text{Fe}_\text{R}$  bonds in coastal sediments, but are assumed to be less important for deep-sea sediment OC- $\text{Fe}_\text{R}$  bonding (Barber et al., 2017). Another mechanism is mono- or multi-layer sorption between OC and less reactive  $\text{Fe}_\text{R}$  (e.g. goethite and haematite) phases, thought to be especially important in terrestrial soils (Wagai and Mayer, 2007). A final primary mechanism which has been proposed is the coprecipitation of OC with  $\text{Fe}_\text{R}$  at redox boundaries such as the oxic-anoxic boundary in marine sediments or peatlands (Chen et al., 2014; Lalonde et al., 2012; Riedel et al., 2013). To identify the bonding style between OC and  $\text{Fe}_\text{R}$  in marine sediments, the molar ratio of  $\text{Fe}_\text{R}$ -bound OC to  $\text{Fe}_\text{R}$  (OC: $\text{Fe}_\text{R}$ ) has been used as a simplistic indicator (Fig. 1). Low values ( $<1$ ) indicate the major OC- $\text{Fe}_\text{R}$  association to be mono-layer sorption, while higher ratios indicate co-precipitation (Wagai and Mayer, 2007). However, OC: $\text{Fe}_\text{R}$  values can be altered by other factors than the bonding mechanism. For example, organic matter composition can influence the OC:Fe ratio regardless of the bonding mechanism (Chen et al., 2014; Eusterhues et al., 2011; Mikutta and Kaiser, 2011) and especially low OC:Fe ratios might be biased as the chemical extraction of OC bound to  $\text{Fe}_\text{R}$  typically includes  $\text{Fe}_\text{R}$  that is not associated with OC. Moreover, besides the strong affinity of OC with  $\text{Fe}_\text{R}$ , phosphate, arsenic, and heavy metals also bind to iron (oxyhydr)oxide surfaces (e.g., Berner, 1973; Feely et al., 1991; Müller et al., 2002) and can therefore influence the OC:Fe ratio (Chen and Sparks, 2018). Marine sedimentary downcore data of As, Fe and  $\text{Fe}_\text{R}$  imply that arsenic sorption changes the mineral surface properties and reactivities of the Fe(III) phases and, therefore, their capacity to bind to OC (Chen and Sparks, 2018; Faust et al., 2021). Due to these complexities in natural biogeochemical systems, OC: $\text{Fe}_\text{R}$  values should only be interpreted with these caveats in mind.

In addition to its impact on OC storage in the marine realm, OC- $\text{Fe}_\text{R}$  bonding also plays an important role in terrestrial OC cycling. Research in this field has been ongoing for many years, since the development of the technique to extract Fe oxides from soil matrices in the 1950s (Mehra and Jackson, 1958), and pre-dates the more recent studies of marine sediments. Most recent estimates suggest that in soils, OC- $\text{Fe}_\text{R}$  may account for 40% of the total carbon inventory (Chen et al., 2020; Wagai and Mayer, 2007; Zhao et al., 2016), and may act to either enhance (Milne et al., 2015) or reduce nutrient bioavailability (Vitousek

et al., 2010; Walker and Syers, 1976). Similar processes to those that occur in marine sediments drive OC-Fe<sub>R</sub> interactions in terrestrial environments, but the dominant mechanisms depend more strongly on the climatic conditions and associated differences in, e.g., seasonality, rainfall or vegetation. For example, ligand exchange processes likely dominate sorption in tropical forest soils which are rich in minerals with protonated hydroxyl groups (Shen, 1999), and depleted in the 2:1 phyllosilicates that dominate OC sorption in the topsoil of temperate forests (Kaiser and Guggenberger, 2003). In systems with high OC:Fe ratios such as peatlands, co-precipitation likely dominates OC-Fe<sub>R</sub> interactions (Joss et al., 2022; Patzner et al., 2020; Riedel et al., 2013). Terrestrial environments also differ from most marine settings in the regularity and intensity of redox fluctuations, for example in association with wetting and drying cycles that can act to break down OC-Fe<sub>R</sub> (Bhattacharyya et al., 2018). However, preferential preservation of OC-Fe<sub>R</sub> relative to the bulk organic matter pool is still observed in these settings with mineral-bound carbon seen to have longer turnover times than bulk soil carbon in temperate soils (e.g. Torn et al., 1997) and to be significantly older than bulk soil carbon in permafrost soils (Mueller et al., 2015, 2017)

Whatever the exact bonding and transformation mechanisms are in marine and terrestrial environments, OC-Fe<sub>R</sub> interactions appear to provide a mechanism which reduces the breakdown of OC during early diagenesis, thereby enhancing its burial efficiency (Lalonde et al., 2012). This protection allows OC to be buried into anoxic sediments, below which oxidation and OC breakdown occurs at much slower rates (Hartnett et al., 1998; Henrichs, 1992). Hence, the carbon-iron coupling serves as a protective OC shuttle mechanism across the layers of most active remineralisation in sediments or soils. As mentioned above, the amount of OC associated with Fe<sub>R</sub> (fOC-Fe<sub>R</sub>) is between 10 – 80%, but the most frequently quoted figure is c. 20%, taken from the study of Lalonde et al. (2012). Since the publication of that work, a number of studies have estimated the fOC-Fe<sub>R</sub> in a range of new locations and depositional environments, highlighting the variability in this number in marine (e.g. Faust et al., 2020; Salvadó et al., 2015; Shields et al., 2016) and terrestrial systems (e.g. Huang et al., 2021; Joss et al., 2022; Mu et al., 2020). However, no comprehensive effort has been made to collate and evaluate these new data. In this work, we provide a new assessment of global OC-Fe<sub>R</sub> burial rates in a variety of marine and terrestrial environments, using published estimates of fOC-Fe<sub>R</sub>, OC burial, and probabilistic modelling to re-evaluate the size of the ‘rusty carbon sink’ the contributions of different Earth surface environments.

## 2 Methods and Materials

### 2.1 Qualifying OC-Fe<sub>R</sub> extraction methodologies

The standard method for assessing the amount of OC associated with Fe<sub>R</sub> in sediments is the citrate-bicarbonate-dithionite (CBD) method (Fisher et al., 2021).

This method was originally developed to extract Fe oxides from clays and soils (Mehra and Jackson, 1958), with widespread application to OC-Fe<sub>R</sub> in marine sediments since the study of Lalonde et al. (2012). For the Fe<sub>R</sub> extraction, dry and homogenised sediment samples are subjected to a short (15 minute) high temperature (80°C) leach in buffered 0.1M sodium dithionite (Fisher et al., 2021). Despite concerns regarding the ability of this approach to liberate not only the operational defined reactive Fe phases (Fisher et al., 2020, 2021), it is the most reliable method and therefore remains the ‘standard’. Its ubiquity as a method also means it is suitable for a synthesis of this nature, with all collated literature using nominally the same method. As such, the limitations should be the same for all studies, and comparison should be feasible. In our compilation, we include all studies that present an estimate of OC-Fe<sub>R</sub> via the CBD method in marine sediments, see Table S1. Historically, quantification of mineral associated organic carbon in terrestrial settings has more commonly deployed methods based on dispersion and density fractionation, which quantifies OC associated with heavy soil mineral phases (reviewed in Kögel-Knabner et al., 2008). However, the classical CBD method for direct quantification of fOC-Fe<sub>R</sub> has been recently deployed in numerous settings such as grasslands (Fang et al., 2019), forests (Zhao et al., 2016), wetlands (Wang et al., 2017) and peatlands (Huang et al., 2021). Several terrestrial studies have also modified the original method by extending extraction times (16 hours vs. 15 minutes), reducing temperature (room temperature vs 80°C) and omitting citrate from the extraction buffer (Wagai and Mayer 2007; Wagai 2013; Coward 2017). This latter methodological variation instead conducts a weak HCl rinse following dithionite extraction to redissolve Fe precipitated as acid-volatile sulfides and associated OC (Wagai and Mayer 2007; Wagai 2013; Coward 2017). An inorganic dithionite extraction has the benefit of enabling direct quantification of OC in the supernatant and does not appear to result in significantly different extractable Fe concentrations (Coward et al., 2017), whilst a lower temperature may be beneficial for subsequent analyses of organic carbon composition. However, the benefit of extending the extraction time under oxic conditions has been questioned (Fisher et al., 2021). Other work has therefore opted to use anoxic conditions when extending the extraction period (Joss et al., 2022; Patzner et al., 2020). Such comparative studies suggest the highlighted methodological variations have minimal influence on quantification of OC-Fe<sub>R</sub> itself, and we therefore include all existing studies utilising (variations of) the dithionite-based method in our compilation for terrestrial environments.

## 2.2 Statistical analysis

We collate all individual results of the fraction of OC bound to iron of the total OC (fOC-Fe<sub>R</sub>) and group them by marine depositional environment (Fig. 2, Table S1). This grouping is intentionally broad, with all continental shelf and slope sediments represented in one group (Shelves and Slopes), a second group representing all estuarine/deltaic sediments (Deltaic), a third for anoxic and euxinic environments (Anoxic) and a final group representing deep sea envi-

ronments (Pelagic). To reflect developments highlighting their potential importance as OC burial locations (Duarte et al., 2005; Longman et al., 2019; Smith et al., 2015), we also include groups on fjord sediments, tephra, mangroves, salt marshes and seagrass. In the absence of directly observed fOC-Fe<sub>R</sub>, Fe<sub>R</sub> in fjord sediments is assumed to have the same fOC-Fe<sub>R</sub> values as continental shelves, whilst the fOC-Fe<sub>R</sub> in salt marshes and seagrass is assumed to be similar to mangrove sediments. For each of these groups we use the individual fOC-Fe<sub>R</sub> measurements to derive averages and standard deviation values that we use in further modelling (Table 1). All individual studies used, all raw data and an indication of groups are in Table S1, with locations in Figure S1.

To estimate the size of the ‘rusty carbon sink’ in marine environments, we use the values collated above in combination with estimates of total OC burial in each location (Fig. 3). To estimate the OC burial represented by each of our groups, we use the yearly OC burial estimates of Hedges & Keil (1995). For our group Shelves and Slopes we combine their shelf and slope estimates of carbon burial from their groups ‘Shelves and upper slopes’, ‘Biogenous sediments’, and ‘Shallow-water carbonates’. For our Deltaic group, we use their estimate of ‘Terrigenous deltaic-shelf sediments’. For our Anoxic group we use their ‘Anoxic basins’ designation, and for our Pelagic group we combine their estimates of pelagic ‘Biogenous sediments’ and ‘Pelagic sediments’ (Hedges and Keil, 1995). To estimate carbon burial in fjords, we use published estimates (Cui et al., 2016; Smith et al., 2015). For tephra, we use an OC value of 0.3 wt% (Longman et al., 2021b), an estimate of 1km<sup>3</sup> deposited per year (Pyle, 1995) and a density of 1400 kg/m<sup>3</sup> (Gudmundsson et al., 2012). For mangroves, salt marsh and seagrass sediment, we use previously published estimates (Duarte et al., 2005). All marine carbon burial estimates may be found in Table 1.

For terrestrial carbon, we use published estimates of OC burial and fOC-Fe<sub>R</sub> for a range of locations (Figs. 2, 4). As with marine environments, we use broad groupings and divide the terrestrial sink into four categories. First, we consider a single group ‘Permafrost and Peatlands’, due to the availability of data on fOC-Fe<sub>R</sub> in permafrost (Joss et al., 2022; Mu et al., 2020; Patzner et al., 2020), and good estimates of OC burial in peatlands (Gallego-Sala et al., 2018). Many peatlands are located in northern hemisphere locations and nearly half of all peatland OC stocks are influenced by permafrost (Hugelius et al., 2020), and so we feel this grouping is appropriate. Our second group is ‘Forest Soils’ which combines estimates of temperate, boreal and tropical forest soils to make a single estimate of the entire OC sink (Table 1). This approach uses the burial estimates of the period 2000 – 2007 from soils in forest environments (Pan et al., 2011). For grasslands, we use a published range of values (Zomer et al., 2017), and for croplands we take the best available estimate (Scurlock and Hall, 1998).

To make a ‘most likely’ estimate of the amount of OC burial in each environment, we use a Monte Carlo based approach (c.f. Longman et al., 2021a). For this, we take the mean and standard deviation of the fOC-Fe<sub>R</sub> values for each environment (Figs. 2, 3). For OC burial, where available we use mean and

standard deviations of published estimates. Where these do not exist, we apply an artificial 20% standard deviation for modelling purposes (Table 1). We use R studio and the package *rtruncnorm* to develop 10,000 iterations of each variable. For each iteration, we multiply the OC burial value by the fOC-Fe<sub>R</sub> estimate to attain a single estimate of OC burial and perform statistical analyses on the full set of iterations to derive most likely ranges of OC burial. We then combine all individual simulations for each group to attain 10,000 simulations of global OC burial via the ‘rusty carbon sink’ in both marine and terrestrial locations (Fig. 4).

## 3 Results and Discussion

### 3.1 New estimates of fOC-Fe<sub>R</sub>

Our compilation of marine locations yields an overall average fraction of OC bound to Fe<sub>R</sub> (fOC-Fe<sub>R</sub>) of  $20.22 \pm 15.52\%$  (1SD, n=406). This is remarkably similar to the estimate of Lalonde et al. (2012) and numerous subsequent studies (e.g. Faust et al., 2021; Salvadó et al., 2015; Shields et al., 2016), despite the addition of 364 new measurements, indicating the suitability of their approach and the robustness of their earlier conclusions. Our compilation of many new analyses, however, affords a new perspective on how distinct global OC burial is influenced by Fe<sub>R</sub> to greater and lesser extents across many depositional environments (Table 1).

For oxic continental shelves and slopes, we find the fOC-Fe<sub>R</sub> ( $18.59 \pm 9.44\%$ , 1SD, n=225) to be very similar to that of Lalonde et al. (2012), who derived an estimate of  $18.41 \pm 9.37\%$  (1SD, n=12). However, for other environments, we estimate mean fOC-Fe<sub>R</sub> values that are distinct from previous work (Table 1). For example, deep sea sediments were previously thought to contain fOC-Fe<sub>R</sub> of  $20.89 \pm 9.38\%$  (1SD, n=5), but our expanded data compilation suggests a lower value of  $13.72 \pm 8.73\%$  (1SD, n=13). We make a similar revision towards lower mean values of fOC-Fe<sub>R</sub> in deltaic environments, from  $21.66 \pm 7.55\%$  (1SD, n=16) to  $15.34 \pm 13.88\%$  (1SD, n=102) (Fig. 2). This diminished fraction of OC-Fe<sub>R</sub> in deltaic sediments is particularly important as these environments are thought to be the single largest sink for total OC in the marine environment (Hedges and Keil, 1995). We also estimate fOC-Fe<sub>R</sub> for a range of new environments, such as the amount of OC associated with Fe<sub>R</sub> in marine tephra deposits, which are thought to be potentially important settings for OC burial (Longman et al., 2019). Indeed, the estimates of fOC-Fe<sub>R</sub> from these locations are the highest recorded (mean  $79.02 \pm 12.92\%$ , 1SD, n=14), suggesting that OC-Fe<sub>R</sub> bonding is potentially most prevalent in marine locations of regular deposition of chemically unweathered, fine-grained volcanogenic material (Longman et al., 2021b). We also considered other OC-rich peripheral marine environments in this study, such as mangroves, seagrass meadows and salt marshes (Fig. 1). These locations are known to be extremely efficient locations of total OC burial (Duarte et al., 2005; Fourqurean et al., 2012; Pendleton et al., 2012), and so we include of an estimate

of their fOC-Fe<sub>R</sub> values to evaluate the potential contribution of Fe<sub>R</sub> to global marine OC sequestration in these settings.

We provide the first estimates of fOC-Fe<sub>R</sub> across a diverse range of terrestrial environments. In terrestrial soils, our compilation indicates a mean fOC-Fe<sub>R</sub> of  $14.84 \pm 13.46\%$  (1SD, n=191). Previous estimates across all environments are not available for comparison, but this value for terrestrial soils is lower than often-cited values of up to 40% (Chen et al., 2020; Zhao et al., 2016), and most similar to that we estimate for deltaic environments. As we find for marine sediment, fOC-Fe<sub>R</sub> values also vary between the terrestrial environments studied here, with cropland apparently containing the highest mean fOC-Fe<sub>R</sub> ( $22.45 \pm 14.44\%$ ; 1SD, n=18) and grasslands the lowest at  $5.26 \pm 3.86\%$  (1SD, n=15). Peatlands and permafrost are found to contain a mean fOC-Fe<sub>R</sub> of  $15.98 \pm 12.37\%$  (1SD, n=106). Such environments contain stocks of OC that are especially vulnerable to rising temperatures and altered hydrology attributed to anthropogenic climate change, emphasizing the importance of understanding the role of Fe<sub>R</sub> in mediating the size and strength of these OC sinks (Lovelock and Duarte, 2019; Pendleton et al., 2012).

### 3.2 Re-assessment of the global ‘rusty carbon sink’

We use a Monte Carlo based approach to estimate the burial fluxes of OC associated with Fe<sub>R</sub>, based on our new estimates of fOC-Fe<sub>R</sub> across the full range of marine and terrestrial carbon-accumulating environments and previous estimates of their total OC accumulation rates (Fig. 2)

In the oceans, we find a most likely range for the total Fe<sub>R</sub>-associated OC sink of 31 – 70 Mt C yr<sup>-1</sup> (5th – 95th percentile), with a mean of 52 Mt C yr<sup>-1</sup> (Fig. 4). This estimate is roughly 25% of the total global marine sedimentary OC sink (200 Mt C yr<sup>-1</sup>; Canadell et al., 2021), and emphasizes the importance of OC coupling to metal (oxyhydr)oxides in controlling the burial of OC in the marine environments. On land, we find the Fe<sub>R</sub>-associated sink of OC is between 171 – 946 Mt C yr<sup>-1</sup> (5th – 95th percentile) with a mean of 472 Mt C yr<sup>-1</sup> (Fig. 4). This is equivalent to roughly 40% of all carbon sequestered in forest environments worldwide per year (Pan et al., 2011), or around 15% of the entire OC sink on land (3610 Mt yr<sup>-1</sup>; Keenan and Williams, 2018). By combining the estimates for marine and terrestrial settings, we yield a total global Fe<sub>R</sub>-associated OC sink between 222 – 995 Mt C yr<sup>-1</sup> (5th – 95th percentile), with a mean of 524 Mt C yr<sup>-1</sup> (Fig. 4) – a flux of carbon that was equivalent to roughly 5% of anthropogenic carbon emissions in the year 2020 (Friedlingstein et al., 2020).

Our approach also allows us to estimate and compare the size of the OC-Fe<sub>R</sub> sinks between depositional environments. The most important locations for marine OC-Fe<sub>R</sub> accumulation are continental shelves and slopes (mean 17 Mg C yr<sup>-1</sup>) and deltaic/estuarine environments (mean 11 Mg C yr<sup>-1</sup>), representing 33 and 21% of the total marine OC-Fe<sub>R</sub> sink, respectively (Figs. 4,5). These are the first estimates of OC-Fe<sub>R</sub> burial attributed to specific depositional environments



of the ocean, and appear to match our understanding that continental shelves and slopes are key locations for marine OC burial in general (Bianchi et al., 2018; Blair and Aller, 2012). We also provide the first estimates for OC-Fe<sub>R</sub> burial in fjords (3.4 Mt C yr<sup>-1</sup>), volcanic tephra (2.8 Mt C yr<sup>-1</sup>), mangroves (3.6 Mt C yr<sup>-1</sup>), salt marshes (8.8 Mt C yr<sup>-1</sup>) and seagrass sediment (4 Mt C yr<sup>-1</sup>); see Figure 5. Our findings illustrate the comparative roles each of these environments play in contributing to the burial of OC via Fe<sub>R</sub> (Duarte et al., 2005; Longman et al., 2019; Smith et al., 2015). For example, despite contributing one of the smallest fluxes of OC, the extremely high fOC-Fe<sub>R</sub> in tephra deposits (Longman et al., 2021b) indicates that, gram for gram, volcanic tephra deposition could in fact provide the most efficient means to enhance OC burial via Fe<sub>R</sub> in marine sediments.

OC-Fe<sub>R</sub> bonding is also an important feature of the terrestrial carbon cycle, accentuated by OC accumulation rates that are far higher than those estimated for the ocean. Our work shows grass- and croplands accumulate more carbon each year through OC-Fe<sub>R</sub> bonding than any other terrestrial environment. Croplands appear to be the most important single terrestrial environment (mean 279 Mt C yr<sup>-1</sup>), followed by grasslands (mean 121 Mt C yr<sup>-1</sup>), with these locations representing 59 and 26% of the terrestrial sink for OC-Fe<sub>R</sub>, respectively. These findings are consistent with the view that soil stocks of OC associated with grasslands also appear to be more stable and resilient to degradation than those in forest soils (Wei et al., 2018). Our estimates for OC-Fe<sub>R</sub> accumulation in peatlands and permafrost (mean 26 Mt C yr<sup>-1</sup>) indicate the substantial size of this OC sink. These areas may be disproportionately significant as a long-term terrestrial sink of OC (i.e., multi-millennial), but they are most susceptible to the impacts of climate change (Gallego-Sala et al., 2018; Hugelius et al., 2020).

Implicit in our findings is that the OC-Fe<sub>R</sub> sink on land is a more significant than it is in the ocean; mean OC-Fe<sub>R</sub> burial rates in ocean sediments are estimated to be 52 Mt/yr compared to 472 Mt/yr on land. However, it is vital to recognise OC stores on land are smaller with comparatively shorter residence times than those found in the ocean (Carvalhais et al., 2014), and it is ultimately the size of these OC reservoirs, and not the annual fluxes, that will impact the global carbon cycle on geological timescales. Nonetheless, there is an important gap in our understanding of OC-Fe<sub>R</sub> burial rates between land and sea, pertinent to OC burial more generally; that is the nature of land-to-sediment transfer OC-Fe<sub>R</sub>. Salvadó et al., (2015) found <sup>13</sup>C-Fe and  $\Delta^{14}\text{C}$ -Fe values were indicative of both substantial marine and terrestrial Fe-OC inputs to Arctic shelf surface sediments. However, the extent to which Fe<sub>R</sub>-associations could be responsible for facilitating this transfer of terrigenous OC into marine reservoirs is still unknown.

We believe our findings incorporate all previously published OC-Fe<sub>R</sub> data to date, as outlined above, but encourage future scientific endeavours to refine our assessment of OC-Fe<sub>R</sub> burial rates, by continuing to characterise the mechanisms that regulate the OC-Fe<sub>R</sub> sink. That is, to understand under exactly

which conditions OC transformations and protective bonds are formed with Fe (oxyhydr)oxides, and how these persist within and between depositional environments over time.

### 3.3 Implications for the geological past

With recent evidence indicating the long-term preservation of OC-Fe<sub>R</sub> interactions (Faust et al., 2021; Longman et al., 2021b), the scale of the OC-Fe<sub>R</sub> sink in marine sediments highlights OC-Fe<sub>R</sub> bonding as an important component of the long-term carbon cycle. The ability of these bonds to persist for hundreds of thousands of years means changes in the OC-Fe<sub>R</sub> sink may have implications for carbon storage and global biogeochemical cycles on a range of geological timescales. For example, it is plausible that during periods in which intense OC-Fe<sub>R</sub> coupling occurred, such as due to enhanced tephra deposition, it may have led to enhanced OC preservation and partially account for periods of lowered  $p\text{CO}_2$  and global cooling (Longman et al., 2019). It is also shown that Fe<sub>R</sub> protected fractions of OC equivalent to those reported here would even be sufficient to impact the longer-term redox evolution and step-wise oxygenation of Earth over deep time (Zhao et al., submitted).

Our findings reinforce the fact that continental shelves and slopes are key components of the OC-Fe<sub>R</sub> sink. Modern continental configuration provides an estimated shelf area of  $27 \times 10^6 \text{ km}^2$ , which is small compared to periods of the Early Cretaceous (around 100 Ma) and Late Ordovician (c. 440 Ma), when shelf areas were estimated to be  $80 \times 10^6 \text{ km}^2$  (Harrison et al., 1983; Walker et al., 2002). Assuming modern shelf and slope values for fOC-Fe<sub>R</sub> are representative, this past shelf area alone could have sequestered  $50 \text{ Mt C yr}^{-1}$  via OC-Fe<sub>R</sub> interactions, equivalent to the burial flux of OC-Fe<sub>R</sub> we report for the global ocean today (Fig. 5). This indicates the potential size of increase in the sink related to greater continental shelf areas (Bernier and Canfield, 1989; Bjerrum et al., 2006). The size of this sink may be even greater when the impact of high sea levels on the area of peripheral vegetation, and of fjords is considered, but reconstructing the size of these environments remains a challenge. Ultimately, the global burial of organic carbon results from the balance of interactions between all sites of OC regeneration and burial. As such, the effect that changes in one aspect of the OC-Fe<sub>R</sub> sink may have on others OC-Fe<sub>R</sub> sinks is not yet understood. For example, it may be that as continental shelves grow, and their OC-Fe<sub>R</sub> sink increases, another sink such as peripheral vegetation decreases in size to offset and negate any impacts on the net burial of OC. Thus, to accurately account for changes to carbon cycling in specific environments, paleoenvironmental reconstructions must consider system changes to the C-cycle holistically when possible.

An interesting and potentially significant driver of changes to OC burial through geological time is linked to the variable intensity of volcanism. During the emplacement of large igneous provinces and the emergence of arc volcanism, volcanogenic sedimentation rates in the ocean may have been far higher than we observe today (Lee et al., 2018; McKenzie et al., 2016; Mills et al., 2014).

If these volcanic systems produced large amounts of volcanic ash, as is known to have occurred at times such as the Cretaceous and Ordovician (Lee et al., 2018; Longman et al., 2021c), it is possible the size of the ash-related OC-Fe<sub>R</sub> sink was also far greater than we report here for modern sediments. Estimates place the current yearly production of ash at around 1 km<sup>3</sup> yr<sup>-1</sup> (Longman et al., 2022; Pyle, 1995), but during periods of intense arc volcanism this value could be orders of magnitude greater. For example, individual eruptions from the Late Ordovician are known to have released >1000km<sup>3</sup> ash, and with other studies indicating these are not isolated events (Bryan et al., 2010; Ernst et al., 2021). Considering tephra and tephra-hosting sediments contain the highest fOC-Fe<sub>R</sub> values, it is likely these periods of time had the potential for a far larger OC-Fe<sub>R</sub> sink, provided there was sufficient OC available to be paired with this increased Fe<sub>R</sub> supply. For example, if we assume each 1000km<sup>3</sup> tephra deposition event buried 0.1 wt% OC and 80% fOC-Fe<sub>R</sub> (Longman et al., 2021b) with an ash density of 1400kg/m<sup>3</sup> (Gudmundsson et al., 2012), it would lead to the sequestration of 1120 Mt C – equivalent to >20 times the annual C burial flux via OC-Fe<sub>R</sub> interactions in the modern Earth system. This is before the impact of dispersed ash is accounted for, which appears to lead to ~10% increase in fOC-Fe<sub>R</sub> in sediments surrounding ash (Longman et al., 2021b), and would have led to a second considerable carbon sink.

The speed of carbon turnover in soils (mean of 23 years; Carvalhais et al., 2014) means they are unlikely to act as significant carbon sinks on geological (>100 kyr) timescales. However, it is possible that sequestration in peatlands can lead to long-term (million-year) burial. The formation of coal beds from ancient peatlands attests to this (Dai et al., 2020), with peatlands proposed to have acted as important carbon sink in the Pliocene and Paleocene (Kurtz et al., 2003; Panitz et al., 2016). The Paleocene, for example, was a time of significant worldwide peat accumulation (Kurtz et al., 2003), as was the Carboniferous period (Greb et al., 2006), and so the OC-Fe<sub>R</sub> sink in these locations would have been sizable, far greater than it is today.

In marine systems, what remains to be understood is the relationship between two major OC preservation mechanisms, which predominately operate under different ocean redox states: the OC-Fe<sub>R</sub> sink and the anoxic carbon sink. It is widely understood that anoxic conditions favour the preservation of OC in marine sediments because they do not sustain OC remineralisation rates found in oxygen-replete environments (Demaison and Moore, 1980; but see Calvert and Pedersen, 1992, for alternative view). However, under such reducing conditions, with plentiful OC, the reduced availability of iron (oxyhydr)oxides could limit fOC-Fe<sub>R</sub> values, and result in low total OC burial via OC-Fe<sub>R</sub>. In oxygen-replete settings, the availability of OC could become the limiting resource for OC-Fe<sub>R</sub> burial. For example, in regions where high tephra or terrigenous Fe deposition support comparatively high fOC-Fe<sub>R</sub>, it could be the supply of OC that ultimately limits the capacity of Fe<sub>R</sub> to increase OC-Fe<sub>R</sub> burial rates. For these reasons, the significant potential for Fe<sub>R</sub> supply to regulate a fraction of OC burial is clear, but its quantitative impact on the global carbon cycle

requires further examination.

### 3.4 How will the OC-Fe<sub>R</sub> sink change due to anthropogenic climate change?

Our work has outlined the scale of the OC-Fe<sub>R</sub> sink in the modern Earth system, but under anthropogenic climate change, this picture is likely to change. Rising global temperatures may increase primary productivity in some locations, and reduce it in others (Barange et al., 2014), meaning the overall impact of shelf-sea productivity variations on OC preservation by Fe<sub>R</sub> is unclear. It is likely a series of impacts will be driven by the rise of sea level worldwide (Rahmstorf, 2007). The flooding of lowland areas will result in an increase in the size of continental shelf area with the potential to alter carbon burial rates in these regions. In other locations, the size of the OC-Fe<sub>R</sub> sink could be reduced under projected temperature rise. For example, increased aridification and decreased fluvial discharge across North America appears to be a trend set to continue (Overpeck and Udall, 2020), with the potential to change terrestrial and coastal marine carbon sinks, such as grasslands, forests and deltaic environments, including those already undergoing degradation (Giosan et al., 2014; Syvitski et al., 2009). Climate change poses threats to coastal environments such as sea-grass and mangroves, from the combined effects of acidification, warming and rising sea levels (Duarte et al., 2018; Gilman et al., 2008; Lovelock and Duarte, 2019).

A possible future impact on the stabilization of OC by iron minerals across terrestrial and marine environments stems from the fact that these associations may become less stable under anoxic conditions. The onset of anoxia promotes activity of anaerobic FeIII-reducing bacteria, which act to dissolve reactive iron phases. However, the potential for such states of anoxia to alter efficacy of mineral-organic preservation are not yet well understood. This is because redox gradients can also enhance the proportion of Fe minerals present as Fe (oxyhydr)oxides suited to the adsorption of OC (Riedel et al., 2013). Climate models predict that higher global temperatures will result in increased precipitation in the tropics (Feng et al., 2019; Su et al., 2017), with the potential to promote more anoxic soil conditions and a reduction in reactive iron minerals which could release associated OC as dissolved organic carbon in these areas (Barcellos et al., 2018). Meanwhile, zones of persistent ocean anoxia are expanding as a result of rising global temperatures (Altieri and Gedan, 2015).

Temperature-driven thawing of permafrost will also increase waterlogging and anoxia in some northern permafrost regions (Kreplin et al., 2021). In extreme cases, permafrost thaw has been shown to result in almost complete loss of OC-Fe<sub>R</sub> (Patzner et al., 2020), although the extent of this loss varies between vegetation types (Mu et al., 2020). On the other hand, permafrost thaw also opens new percolation pathways for groundwater drainage that can lead to surface drying (Kreplin et al., 2021). Such an increase in drainage and ingress of oxygen could alter redox cycling of Fe and the presence of OC-Fe<sub>R</sub>. Projected

increases in soil acidification associated with nitrogen fertilization (Tian and Niu, 2015) and acid deposition (Guo et al., 2010), may also impact the redox cycling of Fe and preservation of OC. Ye et al. (2022) found that pH is likely the key predictor of OC-Fe<sub>R</sub> abundance in terrestrial soils, suggesting future decreases in soil pH may increase OC-Fe<sub>R</sub>.

Our work shows that in the marine environment, as much as 52 Mt C yr<sup>-1</sup> is buried as OC-Fe<sub>R</sub>, with the primary locations of burial continental shelves and deltaic environments. In terrestrial environments, the flux of OC-Fe<sub>R</sub> is estimated to be 472 Mt C yr<sup>-1</sup> – an order of magnitude more than the OC-Fe<sub>R</sub> flux in marine sediments – with as much as half of this terrestrial flux attributed to cultivated cropland soils. The significant size of these terrestrial fluxes, the susceptibility of terrestrial carbon stores to pressures resulting from land use and climate changes, and the potential transfer of these terrestrial stores to marine coastal environments means that OC-Fe<sub>R</sub> needs to be better understood and monitored. Our work shows OC-Fe<sub>R</sub> must be considered as an integral component of carbon accounting and sequestration strategies within and from critical zones on land and into the marine realm.

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## Open Research

All data used in this publication is compiled from previous publications (see Table S1). No new sedimentary data were produced during this study. The model outputs may be found at [10.6084/m9.figshare.19691905](https://doi.org/10.6084/m9.figshare.19691905).

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## Tables

Table : Mean fractions of organic carbon associated with reactive iron (fOC-Fe<sub>R</sub>) for all environments considered here. These mean values, and the standard deviations presented alongside were used for Monte Carlo simulation of the total OC-Fe<sub>R</sub> sink (see Methods). This was completed using the estimates of carbon burial presented here, along with the publications from which they were taken.

Marine sedi- ments	Mean fOC- FeR (%)	fOC- FeR Stan- dard Devia- tion	Mean annual OC burial (Mt/yr)	SD annual OC burial (Mt/yr)	Mean annual OC- FeR burial (Mt/yr)	References for OC burial
Anoxic						(Hedges and Keil, 1995)
Shelves & Slopes						(Hedges and Keil, 1995)
Pelagic						(Hedges and Keil, 1995)
Deltaic						(Hedges and Keil, 1995)
Fjords						(Cui et al., 2016)

Marine sedi- ments	Mean fOC- FeR (%)	fOC- FeR Stan- dard Devia- tion	Mean annual OC burial (Mt/yr)	SD annual OC burial (Mt/yr)	Mean annual OC- FeR burial (Mt/yr)	References for OC burial
Tephra						(Longman et al., 2021b)
Mangroves						(Duarte et al., 2005)
Seagrass						(Duarte et al., 2005)
Salt Marshes						(Duarte et al., 2005)
<b>Total Marine</b>	<b>20.22</b>	<b>15.52</b>	<b>304.9</b>		<b>51.85</b>	
Terrestria Sedi- ments	Mean fOC- FeR (%)	fOC- FeR Stan- dard Devia- tion	Mean annual OC burial (Mt/yr)	SD annual OC burial (Mt/yr)	Mean annual OC- FeR burial (Mt/yr)	References for carbon sink
Permafrost & Peat- land						(Gallego- Sala et al., 2018)
Forests						(Pan et al., 2011)
Grasslands						(Scurlock and Hall, 1998)
Croplands						(Zomer et al., 2017)
<b>Total Terres- trial</b>	<b>22.45</b>	<b>14.44</b>	<b>2805</b>		<b>472.16</b>	

## Figures

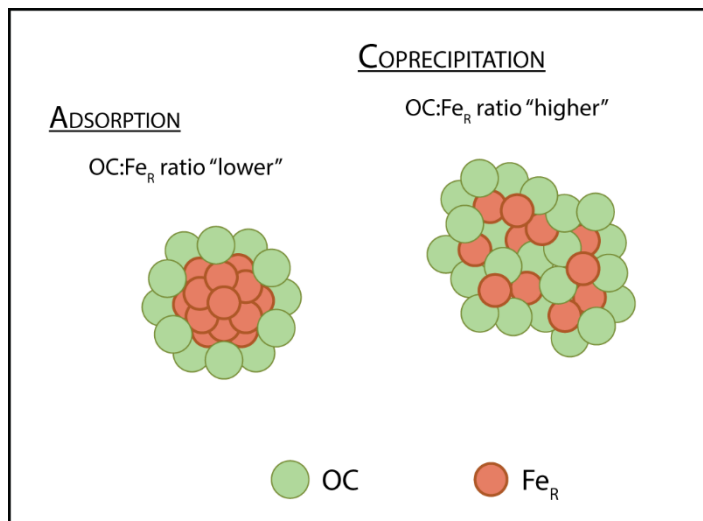


Figure : Illustration of the two styles of binding mechanism discussed in this work. First is adsorption, whereby organic carbon (OC) compounds adhere to the reactive Fe surfaces, a process that results in lower OC:Fe<sub>R</sub> ratios. Second is co-precipitation, whereby OM and Fe<sub>R</sub> precipitate at the same time, and result in higher OC:Fe<sub>R</sub> ratios.



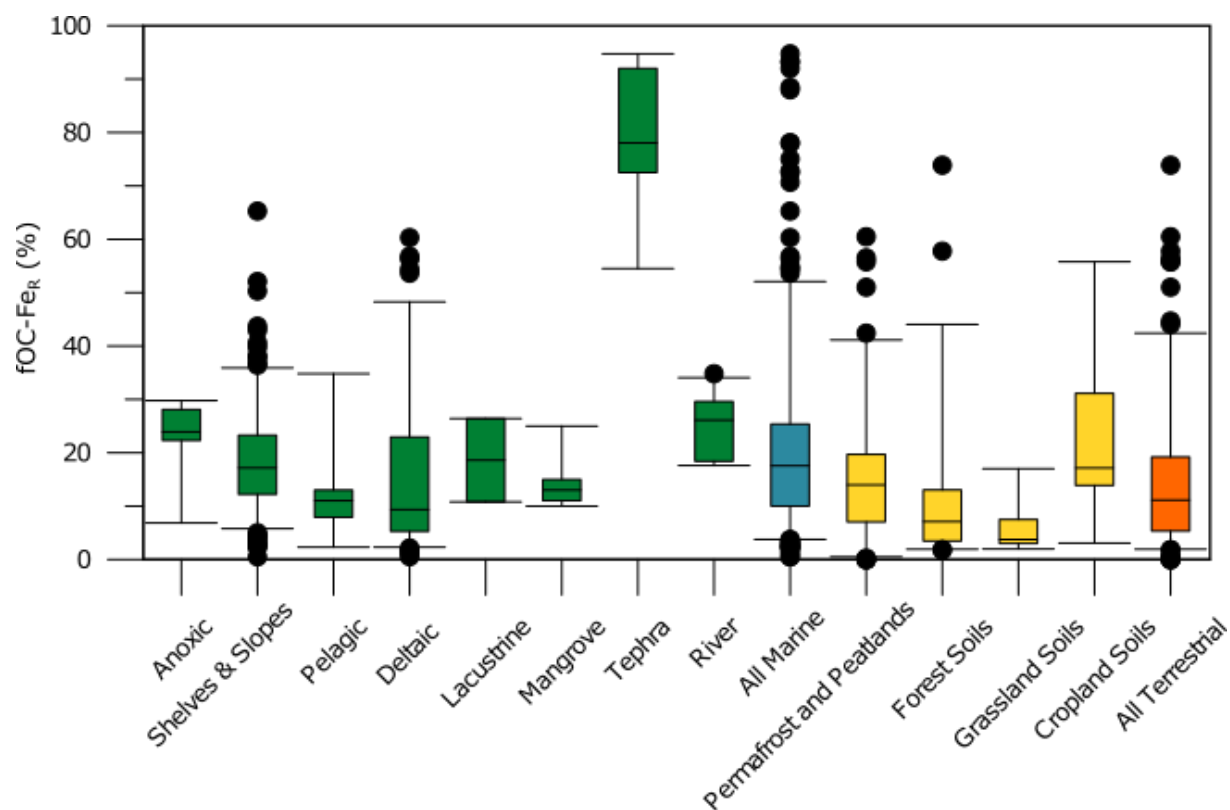


Figure 2: Box plots of collated fOC-Fe<sub>R</sub> data from marine environments. Panel a is grouped by depositional environment, with all individual study locations highlighted in panel b, using the same colour scheme.

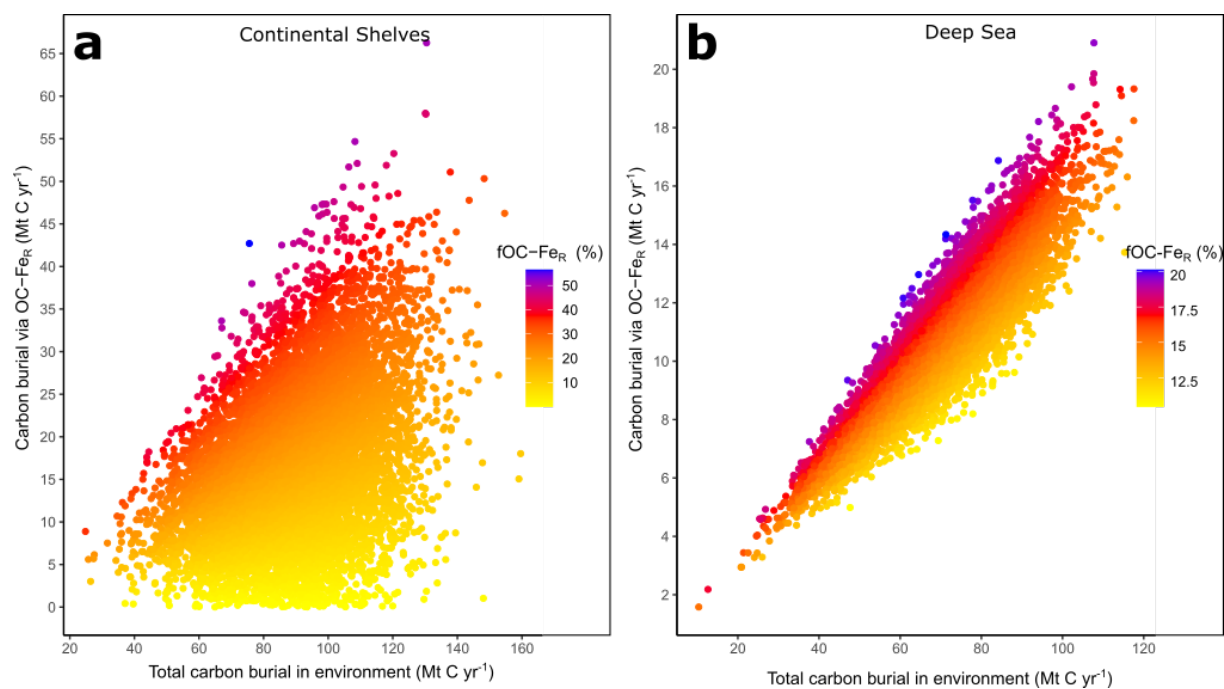


Figure : Example outputs of Monte Carlo modelling, displaying impact of fOC-Fe<sub>R</sub> (colour of points) on total carbon burial in the specific environment via OC-Fe<sub>R</sub> (y-axis) when compared to total carbon burial in that environment (x-axis). Panel a shows the modelling for continental shelves while panel b is the modelling for deep sea environments.

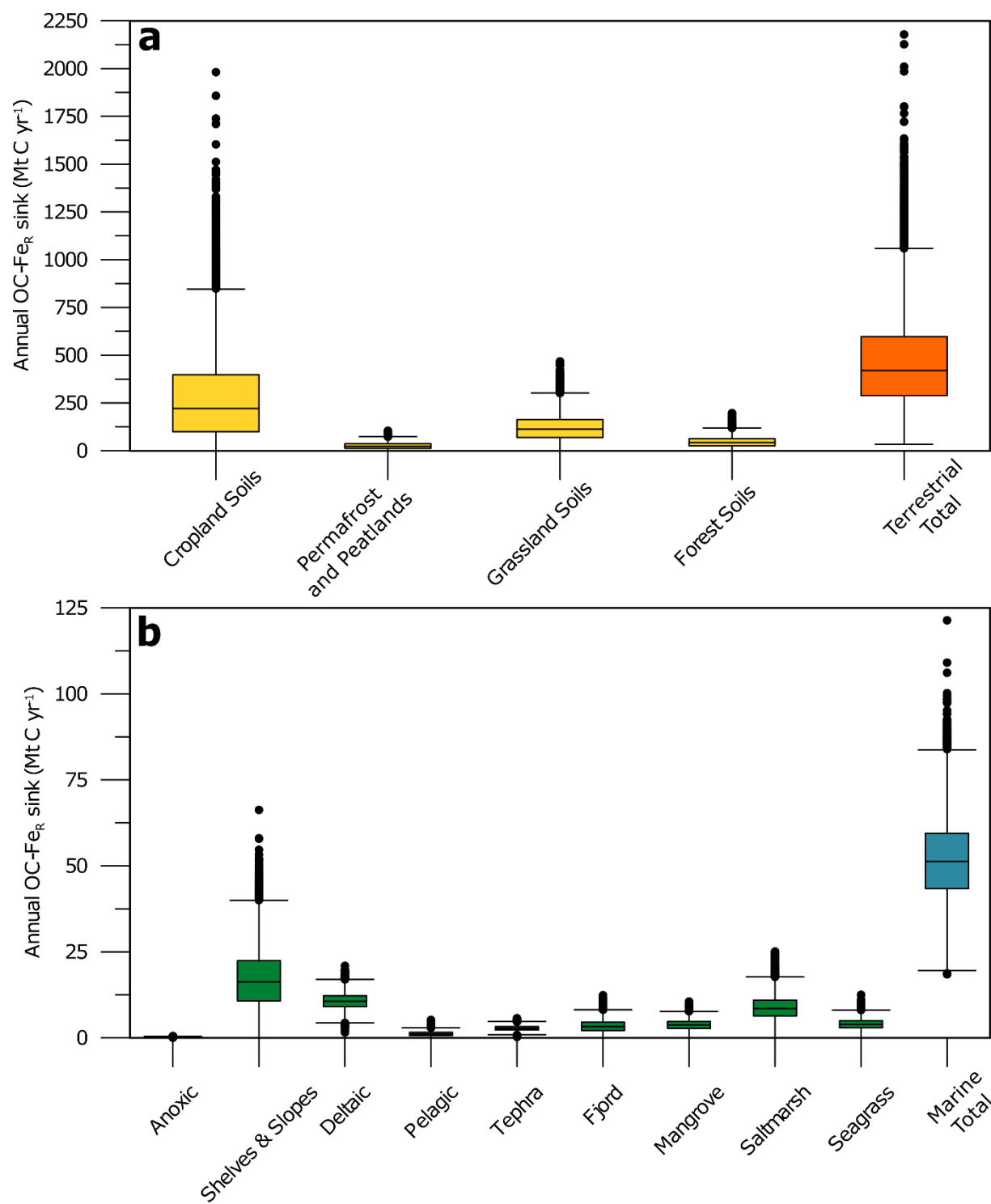
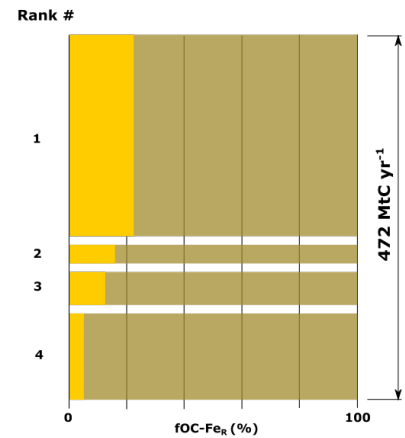
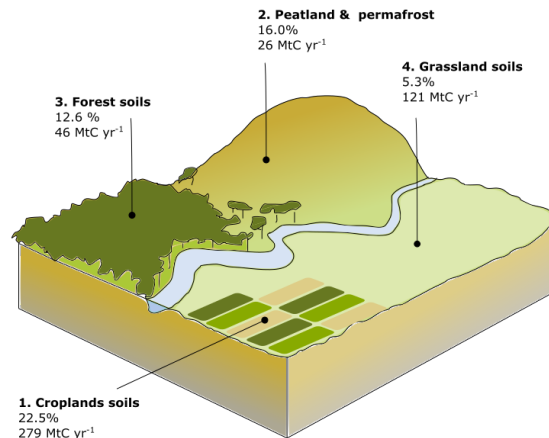


Figure : Outputs of Monte Carlo modelling exercise for marine sedimentary environments. Displayed here are the range of possible C burial values for each of the environments considered. Individual box plots for each of the environments are displayed in blue, with the synthesis of the ‘rusty carbon sink’ in marine sediments in green.

(a) Terrestrial soil sinks of OC-Fe<sub>R</sub>



(b) Marine sedimentary sinks of OC-Fe<sub>R</sub>

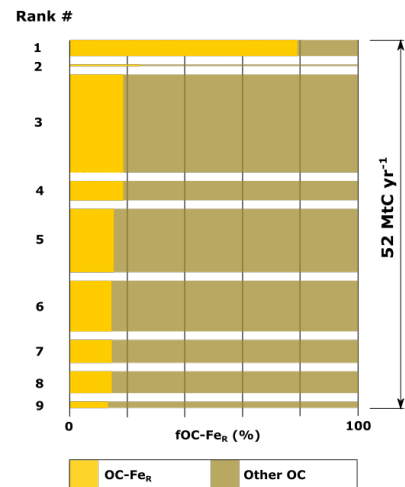
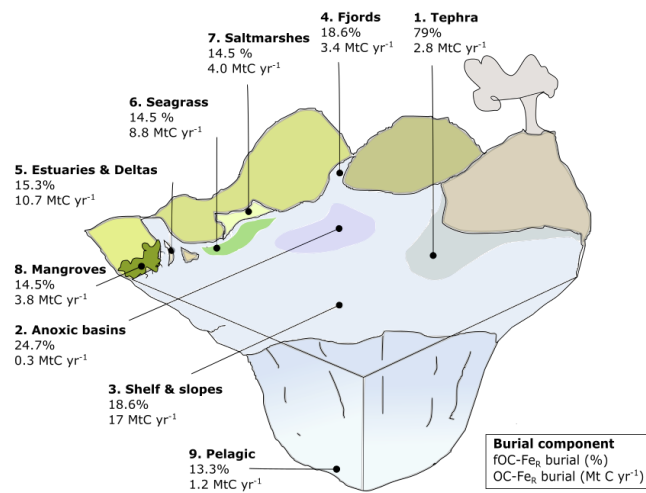


Figure : Ranked variable contributions of reactive iron ( $\text{Fe}_R$ ) to the burial of organic carbon (OC) in the soils and sediments of (a) terrestrial and (b) marine environments. To the left, idealised diagrams depict component sinks of terrestrial and marine environments evaluated for OC burial via interactions with  $\text{Fe}_R$ . Burial fluxes ( $\text{OC-Fe}_R$ ) and fractions ( $\text{fOC-Fe}_R$ ) are derived from the mean outputs of Monte Carlo model simulations. To the right, stacked area charts depict the ranked order of burial components within which the fraction of OC burial attributed to  $\text{Fe}_R$  ( $\text{fOC-Fe}_R$ ) is highest relative to other OC burial mechanisms. Numbers relate to the numbers of the environment denoted on the idealised diagrams. Component bar thickness is proportional to the OC-FER burial flux relative to the summed total in the mare or terrestrial environment.