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Organic Carbon Burial With Reactive Iron Across Global Environments

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Key Points:

- Annual burial rates of organic carbon (OC) with reactive iron (Fe_R) estimated by probabilistic modeling of compiled data
- Fe_R minerals bury c. 52 Mt C yr^{-1} in marine sediments, and c. 446 Mt C yr^{-1} in terrestrial soils
- Terrestrial stocks of OC bound to Fe_R (OC- Fe_R) vulnerable to changing climate, while oceanic Fe_R inputs influence long term OC burial

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Preservation of organic carbon (OC) in marine and terrestrial deposits is enhanced by bonding with reactive iron (Fe_R). Association of OC with Fe_R (OC- Fe_R) 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_R , but this value varies from 10% to 80% across global depositional environments. Here, we provide a new assessment of global OC- Fe_R burial rates in both marine and terrestrial environments, using published estimates of OC associated with Fe_R , carbon burial, and probabilistic modeling. We estimate the marine OC- Fe_R sink between 31 and 70 Mt C yr^{-1} (average 52 Mt C yr^{-1}), and the terrestrial OC- Fe_R sink at between 146 and 917 Mt C yr^{-1} (average 446 Mt C yr^{-1}). In marine environments, continental shelves (average 17 Mt C yr^{-1}) and deltaic/estuarine environments (average 11 Mt C yr^{-1}) are the primary settings of OC- Fe_R burial. On land, croplands (279 Mt C yr^{-1}) and grasslands (121 Mt C yr^{-1}) dominate the OC- Fe_R burial budget. Changes in the Earth system through geological time impact the OC- Fe_R pools, particularly in marine settings. For example, periods of intense explosive volcanism may lead to increased net OC- Fe_R burial in marine sediments. Our work highlights the importance of OC- Fe_R in marine carbon burial and demonstrates how OC- Fe_R burial rates may be an order of magnitude greater in terrestrial environments, but here OC- Fe_R stocks are most sensitive to the anthropogenic impacts of climatic change.

Plain Language Summary Most biomass, which is organic carbon (OC) accumulated in living organisms, decomposes to carbon dioxide and enters Earth's atmosphere, but some escapes complete decomposition, becoming stored in soils on land, and in sediments under the ocean. This storage of OC is part of a global carbon sink that helps to balance carbon dioxide levels in Earth's atmosphere over time, and any process that impacts OC storage may alter Earth's climate. Iron oxide minerals protect OC from decomposition, enhancing carbon storage in soils and sediments. Here, we collated measurements of OC associated with iron oxides from hundreds of observations world-wide. Combining these data with estimates of the global carbon sink and modeling, we evaluate the importance of iron minerals for OC burial. Half a billion tonnes of OC is buried every year bound to iron minerals or 14% of the global carbon sink. The largest sinks for iron-bound OC in the ocean are continental shelves and deltas, whilst the greatest proportions of iron-bound OC are found in volcanic ash deposits. Croplands and grasslands are the largest contributors to iron-bound OC burial on land, locations vulnerable to changes in land use and climate.

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 of carbon buried in this manner per year (Mt C yr^{-1} , Canadell et al., 2021). Thus, OC burial in marine sediments plays a key role in controlling atmospheric CO_2 on geological timescales. Therefore, knowing the factors controlling the size, efficacy, and longevity of this sink is vital for understanding long-term carbon cycling (Burdige, 2007; Hedges & Keil, 1995).

The vast majority of OC reaching the seafloor is remineralized before burial within the sediment (on average 87% of OC is remineralized at the sediment water interface; Burdige, 2007), meaning it returns to the equilibrating ocean-atmosphere CO_2 system. Burial of the OC fraction which does not get remineralized is highly dependent on

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a range of environmental factors such as the oxygen exposure time and sedimentation rate (Hartnett et al., 1998), so that burial efficiency varies from >70% to <0.3% between depositional settings (Dunne et al., 2007). However, it is also important to understand these environmental factors in the context of other physiochemical mechanisms which may impact and, in particular, enhance the preservation of OC during sedimentation (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 & Mayer, 2014; Mayer, 1994). The association of OC to reactive metals, particularly to reactive iron (Fe_R) oxy(hydroxide) phases such as ferrihydrite, provides physical protection (Figure 2) and prevents microbiological degradation (Keil et al., 1994). Complexation of organic molecules with metals such as iron is another stabilization mechanism, albeit one that has mostly been studied in terrestrial environments (e.g., Lützow et al., 2006; Monhonval et al., 2022). Therefore, the binding of OC to Fe_R (OC- Fe_R) 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. Some evidence suggests these bonds can be destabilized under certain conditions such as by Fe reducing microbes (Zhao et al., 2017), or via transformation reaction during early diagenesis (Kleber et al., 2021), but the majority of evidence suggests reactive Fe minerals promote long-term OC protection. In marine environments, between 10% and 80% of the OC pool is bound to Fe_R (e.g., Dicen et al., 2019; Faust et al., 2020; Lalonde et al., 2012; Longman, Gernon, Palmer, & Manners, 2021; Ma et al., 2018; Salvadó et al., 2015; Shields et al., 2016; Sun et al., 2020) and therefore this carbon-iron coupling constitutes a 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, Gernon, Palmer, & Manners, 2021), 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 solubilization 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, Gernon, Palmer, & Manners, 2021). 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). Long lasting interactions are formed 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 Fe_R and functional (especially carboxyl) groups (Barber et al., 2017; Curti et al., 2021; Keil & Mayer, 2014). Such interactions are thought to explain 25%–62% of OC- Fe_R bonds in coastal sediments, but are assumed to be less important for deep-sea sediments (Barber et al., 2017). Another mechanism is mono- and multi-layer sorption between OC and less reactive Fe_R (e.g., goethite and hematite) phases, thought to be especially important in terrestrial soils (Wagai & Mayer, 2007). Finally, the direct coprecipitation of OC with Fe_R is also thought to be an important process promoting the protection of OC 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 predominant type of bonding present between OC and Fe_R in marine sediments, the molar ratio of Fe_R -bound OC to Fe_R (OC: Fe_R) has been used as a simplistic indicator (Figure 2). Low values (<1) indicate OC- Fe_R association to be mono-layer sorption, while higher ratios indicate co-precipitation (Wagai & Mayer, 2007). However, OC: Fe_R values can be altered by factors other 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 & Kaiser, 2011), and especially low OC:Fe ratios might be biased as the chemical extraction of OC bound to Fe_R typically includes Fe_R that is not associated with OC (Fisher et al., 2020). Moreover, besides the strong affinity of OC with Fe_R , phosphate, arsenic, and transition 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 & Sparks, 2018). Marine sedimentary downcore data of As, Fe and Fe_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 & Sparks, 2018; Faust et al., 2021). Due to these complexities in natural biogeochemical systems, OC: Fe_R values should only be interpreted with these caveats in mind.

In addition to its impact on OC storage in the marine realm, OC- Fe_R bonding also plays an important role in terrestrial OC cycling. Research in soils has been ongoing for many more years than it has in marine sediments, since the development of the technique to extract Fe oxides from soil matrices in the 1950s (Mehra & Jackson, 1958). Most recent estimates suggest that in soils, OC- Fe_R may account for 40% of the total carbon

inventory (Chen et al., 2020; Wagai & 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 & Syers, 1976).

Similar processes to those that occur in marine sediments drive OC-Fe_R interactions in terrestrial environments, but the dominant mechanisms depend more strongly on the climatic conditions and associated differences in, for example, 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 temperate forest topsoils (Kaiser & Guggenberger, 2003). In systems with high OC:Fe ratios such as peatlands, co-precipitation likely dominates OC-Fe_R interactions (Joss et al., 2022; Patzner et al., 2020; Riedel et al., 2013), while complexation is important in thawing permafrost soils (Monhonval et al., 2022). Terrestrial environments also differ from most marine settings in the regularity and intensity of redox fluctuations, as in the association with wetting and drying cycles that can act to break down OC-Fe_R (Bhattacharyya et al., 2018). However, preferential preservation of OC-Fe_R relative to the bulk organic matter pool is still observed in terrestrial settings, with mineral-bound carbon observed 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 bonding and transformation mechanisms taking place in marine and terrestrial environments, OC-Fe_R 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 survive through the oxic zone, below which oxidation and OC breakdown occur at much slower rates (Hartnett et al., 1998; Henrichs, 1992). Hence, the OC-Fe_R coupling serves as a protective mechanism for the shuttling of OC across the layers of most active remineralization in sediments and soils. As mentioned above, the amount of OC associated with Fe_R (fOC-Fe_R) is between 10% and 80% in marine sediments, but the most frequently mentioned value is around 20%. Since the initial publication of Lalonde et al. (2012), a number of studies have estimated the fOC-Fe_R in a range of new locations and depositional environments, highlighting the OC-Fe variability in marine (e.g., Faust et al., 2020; Salvadó et al., 2015; Shields et al., 2016) and terrestrial systems (e.g., C. Mu et al., 2020; Huang et al., 2021; Joss et al., 2022). However, no comprehensive effort has been made to collate and evaluate these new data. Here, we provide a new assessment of global OC-Fe_R burial rates in a variety of marine and terrestrial environments, using published estimates of fOC-Fe_R, OC burial, and probabilistic modeling to re-evaluate the size of the “rusty carbon sink” (Eglinton, 2012) and outline the contributions of individual Earth surface environments to this estimate.

2. Material and Methods

2.1. Qualifying OC-Fe_R Extraction Methodologies

The standard method for assessing the amount of OC associated with Fe_R in marine 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 & Jackson, 1958), with widespread application to OC-Fe_R in marine sediments since the study of Lalonde et al. (2012). For the Fe_R extraction, dry and homogenized sediment samples are subjected to a short (15 min) high temperature (80°C) leach in buffered 0.1 M sodium dithionite (Fisher et al., 2021). Despite concerns regarding the capacity 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 as the standard (Fisher et al., 2020). 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 most studies that present an estimate of OC-Fe_R via the CBD method in marine sediments (see Table S1). Historically, quantification of mineral phases associated with OC in terrestrial settings has more commonly deployed methods based on dispersion and density fractionation (Kögel-Knabner et al., 2008). However, the classical CBD method for direct quantification of fOC-Fe_R 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 hr vs. 15 min), reducing temperature (room temperature vs. 80°C) and omitting citrate from the extraction buffer (Coward et al., 2017; Wagai & Mayer, 2007; Wagai et al., 2013). This methodological variation includes a weak HCl rinse following dithionite extraction to redissolve Fe precipitated as acid-volatile sulfides and associated OC (Coward et al., 2017; Wagai & Mayer, 2007;

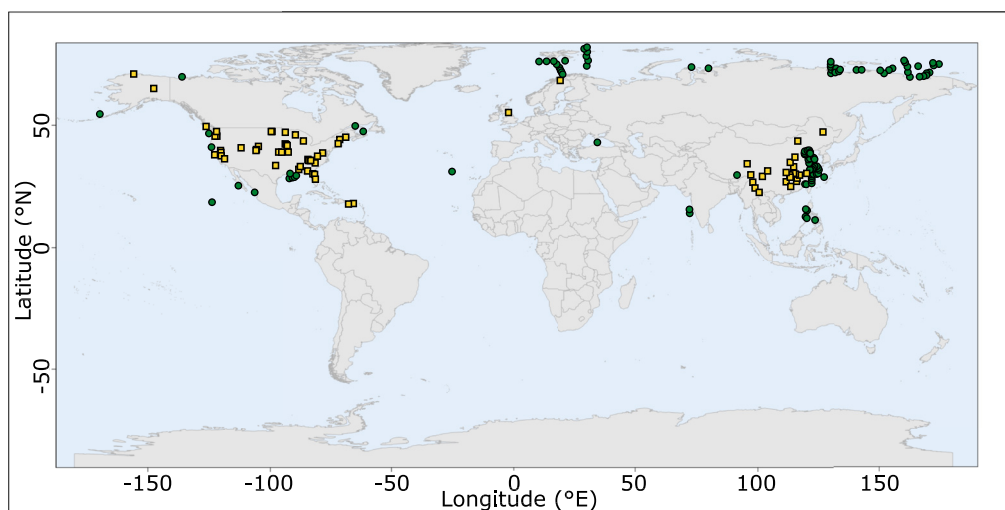


Figure 1. Map with indication of all study locations used in this work. Marine sites are highlighted with green circles, whilst terrestrial sites are indicated with yellow squares.

Wagai et al., 2013). 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 OC composition. However, the benefit of extending the extraction time under oxic conditions has been questioned (Fisher et al., 2021). Other works have therefore opted to use anoxic conditions when extending the extraction period (Joss et al., 2022; Patzner et al., 2020). Such comparative studies suggest that the highlighted methodological variations have minimal influence on quantification of OC-Fe_R itself, and we therefore include all currently existing studies utilizing (variations of) the dithionite-based method in our compilation for terrestrial environments.

2.2. Statistical Analysis

We collate all individual results of fOC-Fe_R and group them by marine depositional environment (Figure 1, Table S1). The grouping is intentionally broad, as this allows for variability in environmental factors within the group to be accounted for by the Monte Carlo statistics. All continental shelf and slope sediments are represented in one group (Shelves and Slopes), with a second group representing all estuarine/deltaic sediments (Deltaic), a third for anoxic and euxinic environments (Anoxic) and a final group representing deep-sea environments (Abyssal). We use the classification of Hedges and Keil (1995) to determine deltaic sediments, which accounts for input of riverine material onto shelves and slopes. We also include groups on fjord sediments, tephra, mangroves, salt marshes and seagrass, to highlight their potential importance as OC burial locations (C. M. Duarte et al., 2005; Longman et al., 2019; Smith et al., 2015). In the absence of directly observed fOC-Fe_R, Fe_R in fjord sediments is assumed to have the same fOC-Fe_R values as continental shelves (as the OC retained in these environments is a mix of terrigenous and marine OC, similar to shelf sediment; Faust & Knies, 2019), whilst the fOC-Fe_R in salt marshes and seagrass is assumed to be similar to mangrove sediments. For each of these groups we use the individual fOC-Fe_R measurements to derive averages and standard deviation values that we use in further modeling (Table 1). All individual studies used, all raw data and an indication of groups are in Table S1, with locations in Figure 1.

To estimate the size of the “rusty carbon sink” in marine environments, we use the data collated in combination with estimates of total OC burial in each location (Figures 3 and 4). To estimate the OC burial represented by each group, we use the yearly OC burial estimates of Hedges and Keil (1995). For the group Shelves and Slopes we combine shelf and slope estimates of carbon burial from the groups “Shelves and upper slopes,” “Biogenous sediments” (representing high productivity regions of the shelves), and “Shallow-water carbonates” (representing OC associated with the burial of inorganic carbonate). For the Deltaic group, we use the estimate of “Terrigenous deltaic-shelf sediments” from Hedges and Keil (1995). For the Anoxic group we use the “Anoxic basins” designation, and for the abyssal group we combine the estimates of “pelagic Biogenous sediments”

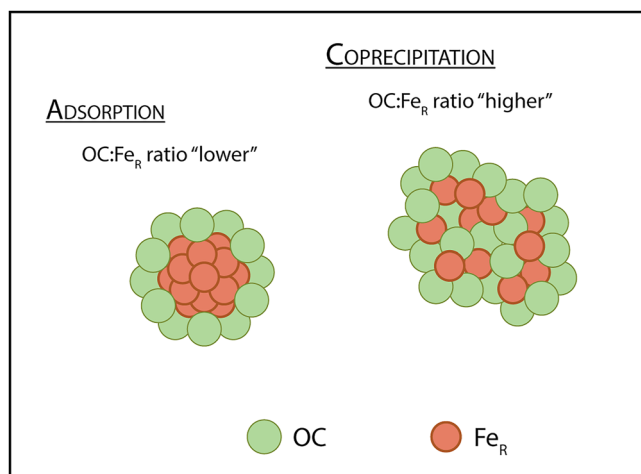


Figure 2. Illustration of the two types of binding mechanism discussed in this work. First is adsorption, whereby organic carbon (OC) compounds adhere to the reactive Fe surfaces, a process that results in lower OC:Fe_R ratios. Second is co-precipitation, whereby OC and Fe_R precipitate at the same time, and result in higher OC:Fe_R ratios.

and “Pelagic sediments” (Hedges & 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, Gernon, Palmer, & Manners, 2021), an estimate of 1 km³ deposited per year (Pyle, 1995) and a density of 1,400 kg/m³ (Gudmundsson et al., 2012). For mangroves, salt marsh and seagrass sediment, we use previously published estimates (C. M. Duarte et al., 2005). Despite only having fOC-Fe_R estimates for mangrove sediments, we consider all three locations separately, to highlight their potentially large carbon sequestration capacity. All marine carbon burial estimates may be found in Table 1. For each location in the marine environment, we develop a range of estimates of this value, which we term the OC-Fe_R burial rate. This term represents a value of OC buried in concert with Fe_R, which does not consider future processing of the OC which may occur after burial.

For terrestrial carbon, we use published estimates of OC stocks and fOC-Fe_R for a range of locations (Figures 2 and 4). As with marine environments, we use broad groupings and divide the terrestrial carbon stock into five categories. The first group is “Forest Soils” which combines estimates of temperate, boreal and tropical forest soils to make a single estimate of the entire OC stock (Table 1). For grasslands, we use the published values of White et al. (2000), and for croplands we take the recent estimate by Zomer et al. (2017). The fourth group, “peatlands,” uses estimates of global OC stock in peatlands from Yu et al. (2010) and contains data on fOC-Fe_R collected from

bogs and fens in China (Huang et al., 2021) as well as selected data from bogs and fens in northern Sweden (Patzner et al. (2020), excluding samples from permafrost-supported palsas included in that data set). The fifth group, “thermokarst regions,” collates fOC-Fe_R estimates from the northern circumpolar permafrost region (Joss

Table 1
Average Fractions of Organic Carbon Associated With Reactive Iron (fOC-Fe_R) and Molar Ratio of OC to Iron (OC:Fe) for All Environments Considered Here

	Average fOC-Fe _R ± 1 SD (%)	Average annual OC burial ± 1 SD (Mt/yr)	Average OC:Fe ± 1 SD (molar ratio)	Average annual OC-Fe _R burial (Mt/yr)	<i>n</i>	References for OC burial
<i>Marine sediments</i>						
Shelves and slopes	18.59 ± 9.44	89 ± 16.99	3.6 ± 2.7	16.99	225	Hedges and Keil (1995)
Deltaic	15.34 ± 13.88	70 ± 10.73	2.1 ± 1.8	10.73	102	Hedges and Keil (1995)
Anoxic	24.67 ± 3.86	1 ± 0.25	14.3 ± 7.9	0.25	7	Hedges and Keil (1995)
Abyssal	13.27 ± 8.73	8 ± 1.15	7.3 ± 4.5	1.15	13	Hedges and Keil (1995)
Fjords	18.59 ± 9.44	19.4 ± 3.4	3.6 ± 2.7	3.40		Cui et al. (2016)
Tephra	79.02 ± 12.92	3.6 ± 2.79	3.7 ± 1.1	2.79	14	Longman, Mills, et al. (2021)
Mangroves	14.5 ± 4.99	26.1 ± 3.81	7.9 ± 4.8	3.81	6	Duarte et al. (2005)
Seagrass	14.5 ± 4.99	60.4 ± 8.76	7.9 ± 4.8	8.76		Duarte et al. (2005)
Salt marshes	14.5 ± 4.99	27.4 ± 3.97	7.9 ± 4.8	3.97		Duarte et al. (2005)
Total marine	20.22 ± 15.52	304.9 ± 15	3.8 ± 2.6	51.85	406	
<i>Terrestrial sediments</i>						
Peatlands	9.51 ± 9.67	n/a	5.75 ± 5.78	n/a	17	n/a
Thermokarst	16.54 ± 12.61	n/a	3.05 ± 3.68	n/a	90	n/a
Forests	12.63 ± 14.96	783 ± 157	5.23 ± 8.45	45.96	52	Pan et al. (2011)
Grasslands	5.26 ± 3.74	500 ± 100	5.32 ± 12.25	120.69	9	Scurlock and Hall (1998)
Croplands	22.45 ± 14.44	1,375 ± 950	6.36 ± 12.66	279.48	18	Zomer et al. (2017)
Total terrestrial	14.9 ± 13.41	2,658 ± 402	3.86 ± 8.08	446.13	186	

Note. The average fOC-Fe_R values, and the standard deviations presented alongside were used for Monte Carlo simulation of the total OC-Fe_R sink (see Section 2). This was completed using the estimates of carbon burial presented here, along with the publications from which they were taken.

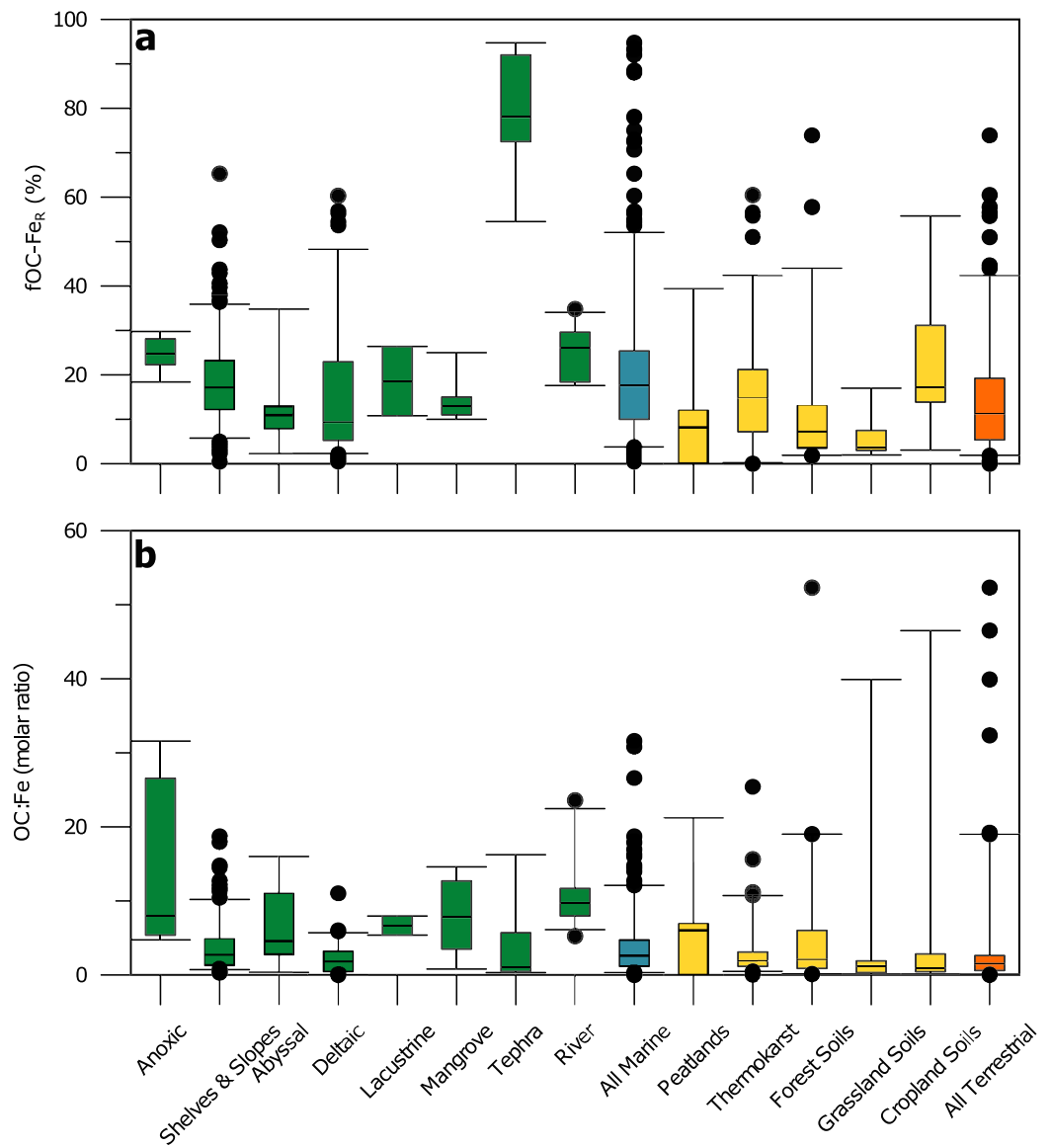


Figure 3. Box plots of collated fraction of organic carbon stock associated with Fe_R (fOC-Fe_R) (a) and OC:Fe molar ratio (b) data from marine environments. For both panels, all marine settings are highlighted in green, with the combined values for the marine realm in blue. All individual settings in the terrestrial environment are in yellow, with the combined estimates in orange.

et al. (2022) and selected data from Patzner et al. (2020)), as well as from permafrost regions in the Qinghai–Tibet Plateau (C. C. Mu et al., 2016; C. Mu et al., 2020; Liu et al., 2022). The estimate of global carbon stock in these regions combines an estimate of carbon stored in thermokarst areas of the northern circumpolar permafrost region (Olefeldt et al., 2016), as well as estimates of the permafrost carbon stock in the Tibetan Plateau (Ding et al., 2016). This estimate does not account for total Fe_R-OC in permafrost as data is only available from areas with thermokarst features and not the large areas of continuous permafrost of the northern hemisphere or deep permafrost deposits (e.g., the Yedoma domain). However, given that around 50% of peatland carbon in the northern hemisphere overlies permafrost (Hugelius et al., 2020) it is expected that a significant fraction of the peatland pool may be vulnerable to transformation during permafrost thaw.

For environments where rates of annual carbon accumulation were reliably available (all except thermokarst and peatland regions), we could also estimate the annual burial rate of OC-Fe_R for certain terrestrial environments as we have done for the marine realm (forests, grasslands, and croplands). This approach uses the burial estimates of

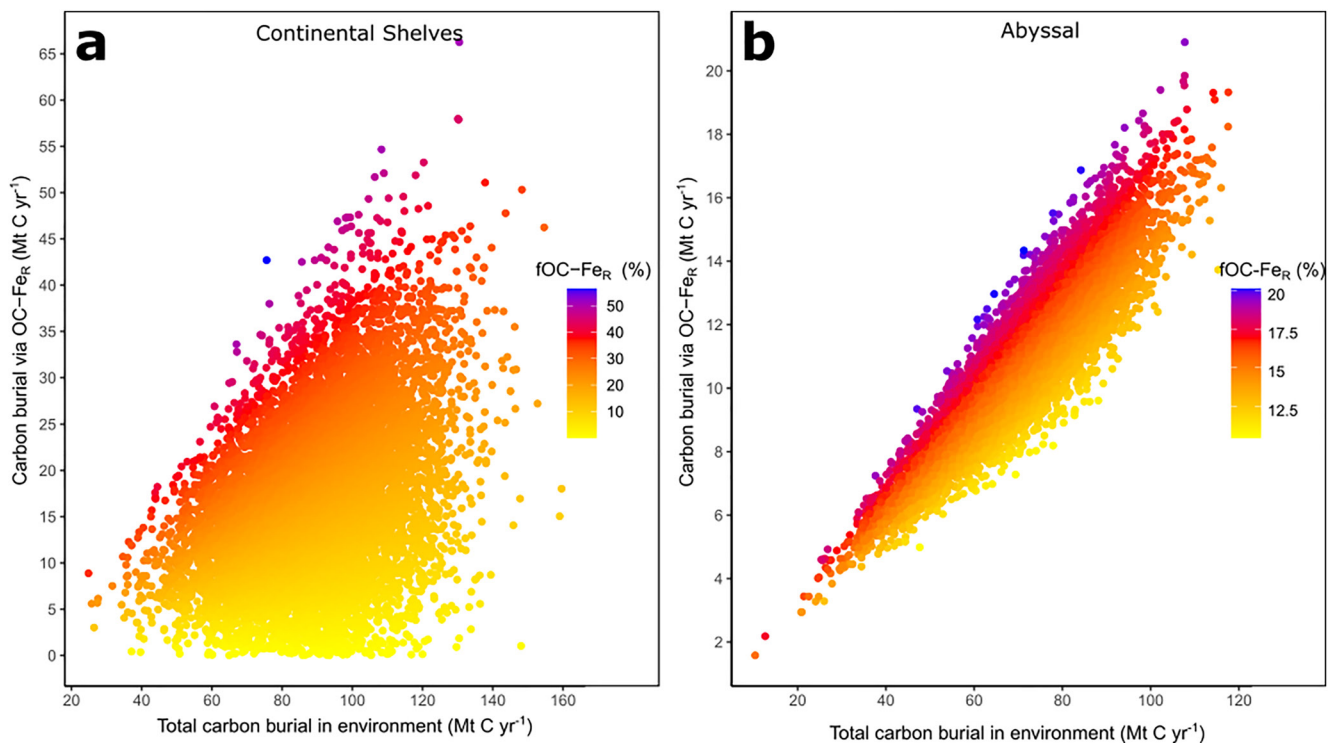


Figure 4. Example outputs of Monte Carlo modeling, displaying impact of fraction of organic carbon stock associated with Fe_R ($fOC-Fe_R$) (color of points) on total carbon burial in the specific environment via $OC-Fe_R$ (y-axis) when compared to total carbon burial in that environment (x-axis). Panel (a) shows the modeling for continental shelves while panel (b) is the modeling for deep-sea abyssal environments.

the period 2000–2007 from soils in forest environments (Pan et al., 2011). For grasslands, we use the published values of Scurlock and Hall (1998); for croplands we take the recent estimate by Zomer et al. (2017). The distinction of burial rates and total stocks is important in the terrestrial environment as the timescales of turnover in terrestrial environments can vary greatly, for example, decadal timescales in forest soils compared to thousands of years in peatlands and permafrost-impacted regions.

To make a most likely estimate of the amount of OC burial in each environment, we use a Monte Carlo based approach (see Longman, Gernon, Palmer, Jones, et al., 2021). For this, the average and standard deviations of the $fOC-Fe_R$ values for each environment were calculated (Figures 2 and 3). For OC burial, we use average and standard deviations of published estimates. For environments where data are not available, we apply an artificial 20% standard deviation for modeling purposes (Table 1). We use Rstudio and the package *rtruncnorm* to perform 10,000 iterations of each variable. For each iteration, we multiply the OC burial value by the $fOC-Fe_R$ estimate to attain a single estimate of $OC-Fe_R$ burial. We then 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 (Figure 5).

2.3. Assumptions Used in the Calculations

Burial rates of OC as presented by Hedges and Keil (1995) are a simplification of the true marine carbon cycle. These OC burial rates do not consider variability in sediment type, oxidation state of sediment, proportions of terrestrial versus marine OC, the rate of lithogenic input to the location, and the proportion of allochthonous versus autochthonous OC content, all variables which may impact the local $fOC-Fe_R$ of a sediment package (Faust et al., 2021; Lalonde et al., 2012; Longman, Gernon, Palmer, & Manners, 2021). However, these burial rate estimates provide a first and first order estimation of how much OC may be buried in certain locations, and they provide a means to compare previously published results more systematically across diverse environments.

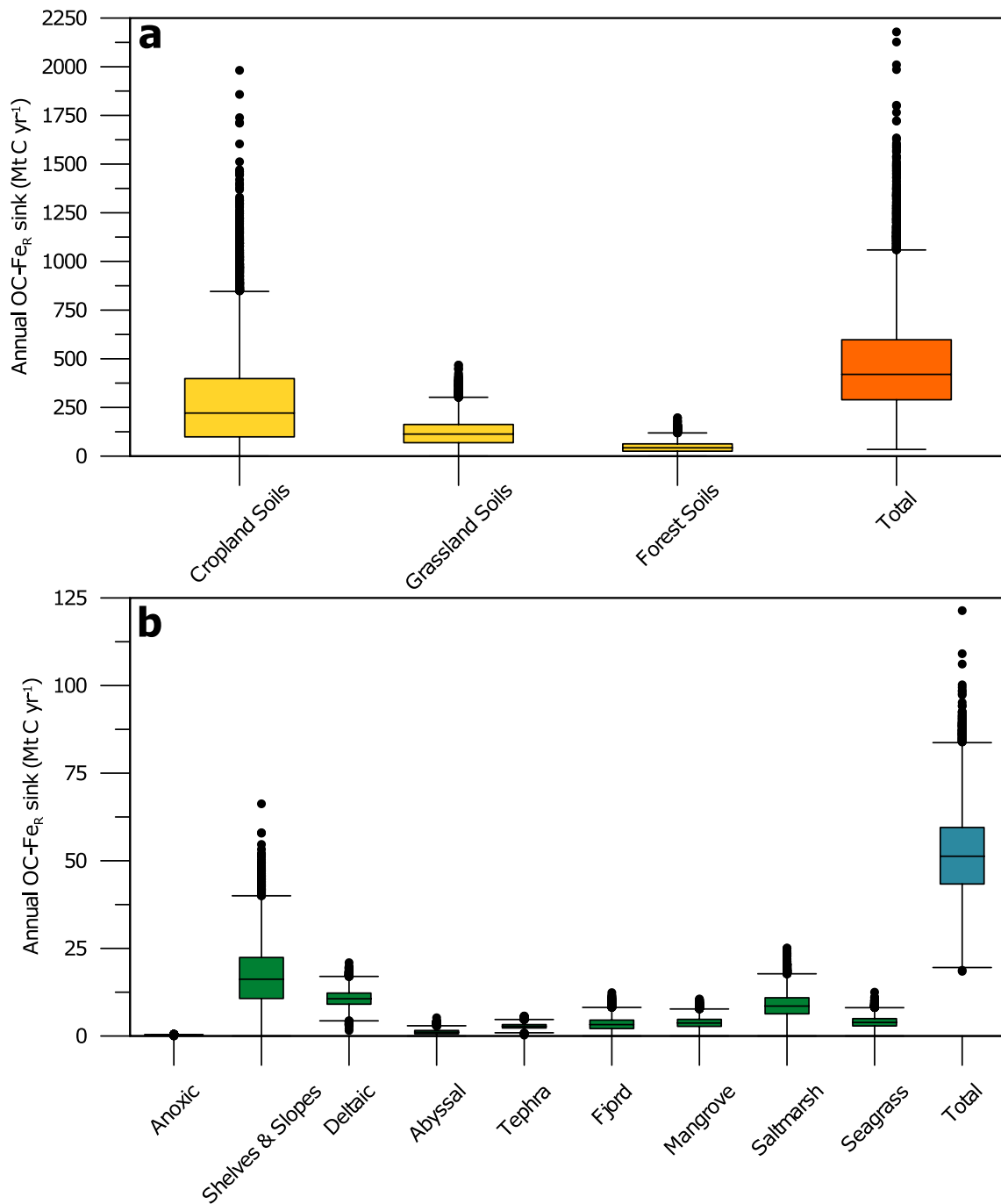


Figure 5. Outputs of Monte Carlo modeling exercise for marine sedimentary environments. Displayed here are the range of possible C burial values for each of the environments considered. Panel (a) shows box plots for each of the individual terrestrial environments (in yellow), with the synthesis of terrestrial C burial in orange. In panel (b), individual box plots for each of the marine environments are displayed in green, with the synthesis of the “rusty carbon sink” in marine sediments in blue.

Because of the simplified methodology, our approach makes the following assumptions: First, that the location of OC-Fe_R bond formation does not impact our estimates. Whether OC-Fe_R bonds present in marine sediments were formed in a terrestrial environment and then transferred into the ocean, or formed in a marine sediment itself is not something our method can distinguish, and so we assume it is not significant in large-scale OC burial estimates. Second, we assume that OC-Fe_R is no more susceptible to decomposition in anoxic conditions than typical OC, a conclusion supported by the fOC-Fe_R values of anoxic basins being similar to oxic locations (Lalonde et al., 2012). Finally, as we develop estimates of annual OC-Fe_R burial, we do not consider the impact

of further burial and changing redox conditions in the sediment column through diagenesis on the sink of carbon. It has been shown that OC-Fe_R bonds persist through early diagenesis and burial (Faust et al., 2021; Longman, Gernon, Palmer, & Manners, 2021), but studies on this topic are in their infancy and many data are lacking, so it is possible that changing porewater Eh and pH conditions during burial may reduce the stability of OC-Fe_R bonds.

We account for the inherent uncertainties in our burial assumptions by using a Monte Carlo based approach to estimate the burial of OC with Fe_R that considers the error terms—those that provide a range of burial rates above and below the mean estimates of Hedges and Keil (1995) to represent a realistic range of possible OC burial values. As a result, we do not present our model outputs as single average data values, but as most likely ranges.

3. Results and Discussion

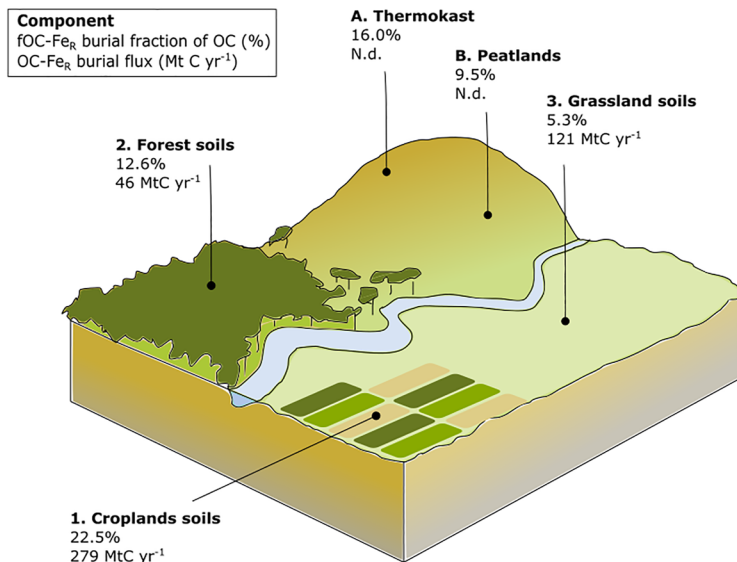
3.1. New Estimates of fOC-Fe_R

Our compilation of data from marine locations yields an overall fOC-Fe_R of 20.22% ± 15.52% (1 SD, *n* = 406). This fraction of OC bound to reactive Fe 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 study sites, indicating the comparability of their initial approach and the robustness of their earlier conclusions. The present compilation, however, affords a new perspective on how global OC burial is influenced by Fe_R to greater and lesser extents across many depositional environments (Table 1).

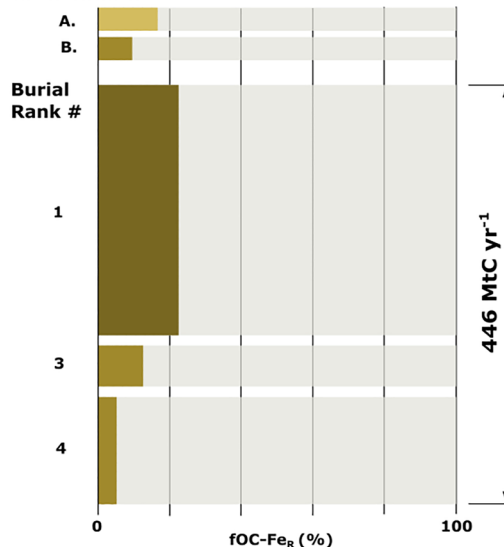
For oxic continental shelves and slopes, fOC-Fe_R (18.59% ± 9.44%, 1 SD, *n* = 225) was very similar to Lalonde et al. (2012), who derived an estimate of 18.41% ± 9.37% (1 SD, *n* = 12). However, for other environments, we estimate average fOC-Fe_R values that are distinct from previous work (Table 1). For example, abyssal sediments were previously thought to contain fOC-Fe_R of 20.89% ± 9.38% (1 SD, *n* = 5), but our expanded data compilation suggests a lower value of 13.72% ± 8.73% (1 SD, *n* = 13). We make a similar revision to lower average values of fOC-Fe_R in deltaic environments, from 21.66% ± 7.55% (1 SD, *n* = 16) to 15.34% ± 13.88% (1 SD, *n* = 102) (Figure 3). This diminished fOC-Fe_R 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 & Keil, 1995). This revision does not reduce the importance of deltaic locations for OC burial, but demonstrates that OC-Fe_R burial is not as dominant as in other locations. In contrast, high fOC-Fe_R values for a range of new environments were found, such as marine tephra deposits, which are thought to be potentially important settings for OC burial (Longman et al., 2019). Indeed, the estimates of fOC-Fe_R from these locations are the highest recorded (average 79.02% ± 12.92%, 1 SD, *n* = 14), suggesting that OC-Fe_R bonding is potentially most prevalent in marine locations with regular deposition of chemically unweathered, fine-grained volcanogenic material (Longman, Gernon, Palmer, & Manners, 2021). We also considered other OC-rich peripheral marine environments in this study, such as mangroves, seagrass meadows and salt marshes (Figure 3). For these environments, we use the fOC-Fe_R of mangrove sediments (average 14.50% ± 13.00%, 1 SD, *n* = 6), as we assume this to be similar in other peripheral locations of high OC burial. These locations are known to be extremely efficient locations for OC burial (C. M. Duarte et al., 2005; Fourqurean et al., 2012; Pendleton et al., 2012).

We provide the first estimates of fOC-Fe_R across a diverse range of terrestrial environments. In terrestrial soils, our compilation indicates an average fOC-Fe_R of 14.84% ± 13.46% (1 SD, *n* = 191). Previous estimates across all terrestrial environments are not available for comparison, but this value for terrestrial soils is considerably lower than often-cited values of up to 40% (Chen et al., 2020; Zhao et al., 2016), and most similar to our revised estimate for deltaic environments. As we found for marine sediment, fOC-Fe_R values also vary between the terrestrial environments studied here, from cropland with the highest average fOC-Fe_R (22.45% ± 14.44%; 1 SD, *n* = 18) to grassland with the lowest: 5.26% ± 3.86% (1 SD, *n* = 15). Peatlands show an average fOC-Fe_R of 9.95% ± 9.67% (1 SD, *n* = 17), with thermokarst environments containing an average fOC-Fe_R of 16.54% ± 12.61% (1 SD, *n* = 90). 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_R in mediating the size and long-term stability of these OC sinks (Lovelock & Duarte, 2019; Pendleton et al., 2012).

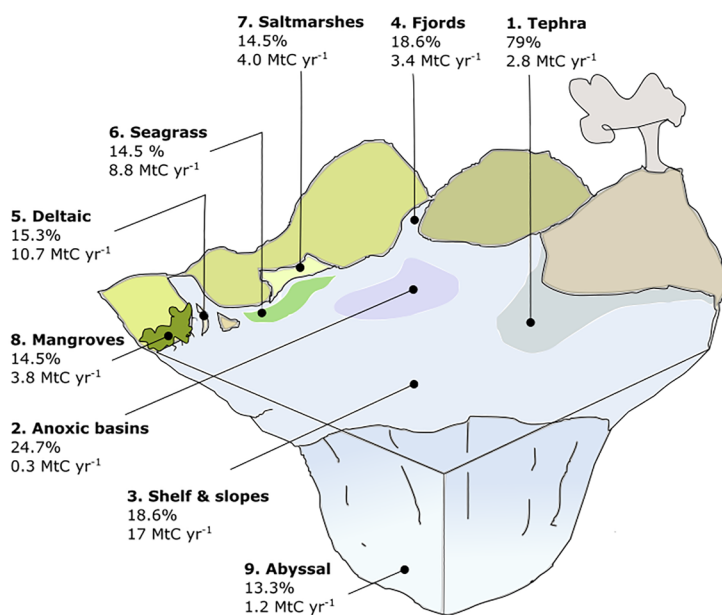
(a) Terrestrial soil OC-Fe_R



Other Stocks.



(b) Marine sedimentary OC-Fe_R



Burial Rank #

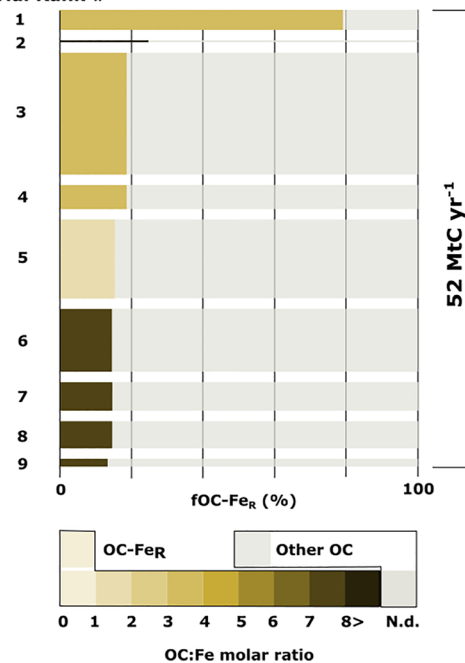


Figure 6. Ranked variable contributions of reactive iron (Fe_R) to the storage and burial of organic carbon (OC) in the soils and sediments of (a) terrestrial and (b) marine environments. To the left, idealized diagrams depict component storage and burial of OC via interactions with Fe_R in terrestrial and marine environments. Burial rates (OC-Fe_R, Mt C yr⁻¹) and fractions (fOC-Fe_R) are derived from the average outputs of Monte Carlo model simulations. To the right, stacked area charts depict the ranked order of components within which the fraction of OC stock attributed to Fe_R (fOC-Fe_R) is highest relative to other OC burial mechanisms. A color scale denotes the molar ratio of OC:Fe within the OC-Fe_R pools. Y-axis labels correspond to the components environments denoted in the idealized diagrams. Component bar thickness is proportional to the OC-Fe_R burial rate relative to the summed total in the marine or terrestrial environment.

3.2. OC:Fe_R Molar Ratio as an Indicator of Bond Type

In addition to estimates of fOC-Fe_R, our synthesis provides the OC:Fe molar ratio in each environment (where available; Figures 2b and 6, Table 1). This ratio has been used in the past to infer predominant bonding styles, with low values (below 1) indicating mono-layer adsorption, and higher values indicative of co-precipitation (Faust

et al., 2021; Wagai & Mayer, 2007). The overall averages for both marine (3.82 ± 4.25 m/m, 1 SD, $n = 338$) and terrestrial (3.86 ± 8.08 m/m, 1 SD, $n = 131$) OC:Fe are remarkably similar, which might imply overall similar processes dictating OC-Fe_R bonding on land and in the ocean, and that coprecipitation is the predominant mechanism responsible for creating OC-Fe_R associations observed across Earth's surface environments. However, individual environments show considerable deviation from this average (Figure 2). In marine environments, OC:Fe is notably lowest in estuarine/deltaic (2.12 ± 1.89 m/m, 1 SD, $n = 79$), shelves and slopes (3.60 ± 3.21 m/m, 1 SD, $n = 215$), and tephra-rich locations (3.68 ± 4.89 m/m, 1 SD, $n = 14$). This is consistent with a supply of OC-Fe_R derived from the terrestrial environment, in which sorption is the dominant bonding mechanism (Faust et al., 2021; Shields et al., 2016). In other environments, such as anoxic (14.33 ± 10.14 m/m, 1 SD, $n = 7$) and abyssal sites (7.32 ± 5.12 m/m, 1 SD, $n = 13$), co-precipitation of Fe_R and OC seems to be dominant, as suggested by Lalonde et al. (2012). Mangrove sediments show some of the highest values (7.87 ± 4.83 m/m, 1 SD, $n = 13$), indicating that such sediments, which are often anoxic at shallow sediment depth (Clark et al., 1998; Noël et al., 2015), are sustaining co-precipitation of Fe and OC. Terrestrial environments show an overall much greater spread of data, with the ranges of grasslands (5.32 ± 12.25 m/m, 1 SD, $n = 9$) and croplands (6.36 ± 12.66 m/m, 1 SD, $n = 18$) being especially variable. The generally low average values, however, do support previous work indicating that sorption of OC to Fe_R primarily occurs on land (Wagai & Mayer, 2007).

3.3. Re-Assessment of Global OC Preservation by Reactive Fe

We use a Monte Carlo based approach to estimate the stock of OC associated with Fe_R, based on new estimates of fOC-Fe_R across the full range of marine and terrestrial carbon-accumulating environments and previous estimates of their total OC accumulation rates (Figures 3 and 4).

In the oceans, we find a most likely range for the OC-Fe_R sink of 31–70 Mt C yr⁻¹ (5th–95th percentile), with an average of 52 Mt C yr⁻¹ (Figure 5). This estimate is roughly 25% of the total global marine sedimentary OC sink (200 Mt C yr⁻¹; 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_R-associated sink of OC between 171 and 946 Mt C yr⁻¹ (5th–95th percentile) with an average of 472 Mt C yr⁻¹ (Figure 5). This is equivalent to roughly 40% of all carbon sequestered in forest environments worldwide per year (Pan et al., 2011), and around 15% of the entire OC sink on land (3,610 Mt yr⁻¹; Keenan & Williams, 2018). By combining the estimates for marine and terrestrial settings, we yield a total global Fe_R-associated OC burial rate between 222 and 995 Mt C yr⁻¹ (5th–95th percentile), with an average of 524 Mt C yr⁻¹ (Figure 5)—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_R sinks between depositional environments (Figure 6). The most important settings for marine OC-Fe_R accumulation are continental shelves and slopes (average 17 Mg C yr⁻¹) and deltaic/estuarine environments (average 11 Mg C yr⁻¹), accounting for 33% and 21% of the total annual marine OC-Fe_R sink, respectively (Figures 4 and 5). These are the first estimates of OC-Fe_R burial attributed to specific depositional environments of the ocean, and appear to match our understanding that continental shelves and slopes are key settings for marine OC burial in general (Bianchi et al., 2018; Blair & Aller, 2012). We also provide the first estimates for OC-Fe_R burial in fjords (3.4 Mt C yr⁻¹), volcanic tephra (2.8 Mt C yr⁻¹), mangroves (3.6 Mt C yr⁻¹), salt marshes (8.8 Mt C yr⁻¹), and seagrass sediment (4 Mt C yr⁻¹); see Figure 6. Our findings illustrate the comparative roles each of these environments play in contributing to the burial of OC via Fe_R. For example, despite having one of the smallest burial rates of OC, the extremely high fOC-Fe_R in tephra deposits ($79.02\% \pm 12.92\%$; Longman, Mills, et al., 2021) indicates that, gram for gram, volcanic tephra provides the most efficient OC burial via Fe_R in marine sediments (Figure 6).

OC-Fe_R 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 grasslands and croplands accumulate more carbon each year through OC-Fe_R bonding than any other terrestrial environment. Croplands appear to be the most important single terrestrial environment for OC-Fe_R stocks (average 279 Mt C yr⁻¹), followed by grasslands (average 121 Mt C yr⁻¹), with these settings accounting for 59% and 26% of the terrestrial stock of OC-Fe_R, respectively. In addition to previous work which has displayed that higher environmental resilience promotes grassland stability (Dass et al., 2018), we propose that this stability may also relate to the large fOC-Fe_R in grassland soils.

Explicit in our findings is that the OC-Fe_R sink on land is greater than in the ocean; average OC-Fe_R burial rates in ocean sediments are estimated to be 52 Mt yr⁻¹ compared to 472 Mt yr⁻¹ on land. However, it is important to recognize that OC reservoirs on land are smaller with comparatively shorter residence times than in the ocean (Carvalhais et al., 2014), and it is ultimately the size of these OC reservoirs, and not their annual turnovers, that will impact the global carbon cycle on geological timescales (Table 1). Nonetheless, there is an important gap in our understanding of the linkages between terrestrial and marine OC-Fe_R stocks: the extent to which Fe_R-associations may facilitate the transfer of terrigenous OC into marine reservoirs is still unknown, but there are many indications that terrestrial OC-Fe_R enters the marine realm. Salvadó et al. (2015) found carbon isotope values were indicative of both substantial marine and terrestrial Fe-OC inputs to Arctic shelf surface sediments relative to typical shelves. Elsewhere, deep ocean relationships between dissolved Fe and electroactive humic substances have been used to suggest land-sea transfer of OC may be a regulatory feedback to the ocean's iron inventory and gross primary production (Whitby et al., 2020).

Our findings incorporate most previously published OC-Fe_R data to date, as outlined above, and encourage future scientific endeavors to better understand OC-Fe_R burial rates, by continuing to characterize the mechanisms that regulate the formation and fate of OC-Fe_R. That is, to understand under exactly which conditions OC transformations and protective bonds are formed with Fe (oxyhydr)oxides, and how these may alter or persist within and between depositional environments over time.

3.4. Implications for the Geological Past

With recent evidence indicating the long-term preservation of OC-Fe_R interactions (Faust et al., 2021; Longman, Gernon, Palmer, & Manners, 2021), the scale of the OC-Fe_R sink in marine sediments highlights OC-Fe_R bonding as an important component of the long-term carbon cycle. The capability of these bonds to survive for hundreds of thousands of years, at least in marine sediments, means that changes in the OC-Fe_R sink may have implications for carbon storage and global biogeochemical cycles on geological timescales (Faust et al., 2021; Longman, Gernon, Palmer, & Manners, 2021). For example, it is plausible that during periods in which intense OC-Fe_R coupling occurred, such as due to enhanced tephra deposition, OC preservation partially accounted for lowered pCO₂ and global cooling (Longman et al., 2019).

Our findings reinforce the fact that continental shelves and slopes are key components of the OC-Fe_R sink. Modern continental configurations provide a shelf area which is small compared to periods of, for example, the Early Cretaceous (around 100 Ma) and Late Ordovician (around 440 Ma). At these times, shelf areas were more than double in size than the modern situation (Harrison et al., 1983; Walker et al., 2002). As such, these environments were likely even more important for OC-Fe_R burial in the past than today. This is an example of how OC-Fe_R stock could change considerably with changing continental configurations (Bernier & 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 fjords is considered. But, reconstructing the size of these environments in geological time is complicated by the challenges of paleo-shoreline reconstruction (Heine et al., 2015). Ultimately, the global burial of OC results from the balance of OC regeneration and burial across all Earth surface environments. As such, the effect that changes in one aspect of one OC-Fe_R sink may have on other OC-Fe_R sinks is not yet understood. For example, as continental shelves and their OC-Fe_R sink increase, the consequent decrease in peripheral vegetation may offset changes to the net burial of OC. Thus, to accurately account for changes in specific environments, paleoenvironmental reconstructions should aim to consider system changes to the carbon 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 today (Lee et al., 2018; McKenzie et al., 2016; Mills et al., 2014). If these volcanic systems produced large amounts of volcanic ash, as occurred in the Cretaceous and Ordovician (Lee et al., 2018; Longman, Mills, et al., 2021), it is possible the size of the ash-related OC-Fe_R burial rate was far greater than we report here for modern sediments. Estimates place the current annual production of ash at around 1 km³ yr⁻¹ (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 >1,000 km³ of ash. Other studies indicate these were not isolated events (Bryan et al., 2010; Ernst et al., 2021). Considering that tephra and tephra-hosting sediments contain the

highest fOC-Fe_R values, these periods likely had the potential to preserve more OC-Fe_R in marine sediments, considering that there was sufficient OC available to be paired with this increased Fe_R supply. For example, if we assume each 1,000 km³ tephra deposition event had an ash density of 1,400 kg/m³ (Gudmundsson et al., 2012) and buried 0.1 wt% OC and 80% fOC-Fe_R (Longman, Gernon, Palmer, & Manners, 2021), it would lead to the sequestration of 1,120 Mt C—equivalent to >20 times the annual C burial represented by OC-Fe_R interactions in the modern Earth system. This regardless of the impact of dispersed ash, which appears to lead to ~10% increase in fOC-Fe_R in sediments surrounding ash (Longman, Gernon, Palmer, & Manners, 2021), and would have led to a second considerable carbon sink. The impact of volcanic material, however, is also highly dependent on the specific location of volcanoes (i.e., are they located close to an environment with high OC supply), and numerous features of the volcanism itself such as tephra chemistry, which dictates proportions of Fe oxides, and total Fe content.

The rate of carbon turnover in soils (average of 23 years for complete turnover; 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, with the high fOC-Fe_R values contributing to high OC burial rates which are a feature of rapid burial to below the oxic zone. The formation of coal beds from ancient peatlands might attest to this (Dai et al., 2020), with peatlands proposed to have acted as important carbon sinks in the Pliocene and Paleocene (Kurtz et al., 2003; Panitz et al., 2016), although a link to Fe_R-related protection has not yet been demonstrated. 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_R sink in these settings would have been 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_R sink and the anoxic carbon sink. It is widely understood that anoxic conditions favor the preservation of OC in marine sediments because they do not sustain OC remineralization rates found in oxygen-replete environments (Demaison & 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_R values, and result in low total OC burial via OC-Fe_R. In oxygen-replete settings, the availability of OC could become the limiting resource for OC-Fe_R burial. For example, in regions where high tephra or terrigenous Fe deposition support comparatively high fOC-Fe_R, it could be the supply of OC that ultimately limits the capacity of Fe_R to increase OC-Fe_R burial rates. For these reasons, the significant potential of Fe_R supply to regulate a fraction of OC burial is clear, but its quantitative impact on the global carbon cycle requires further examination.

3.5. How Will the OC-Fe_R Sink Change Due To Anthropogenic Climate Change?

Our work has outlined the scale of the OC-Fe_R 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 settings, and reduce it in others (Barange et al., 2014), meaning that the overall impact of shelf-sea productivity variations on OC preservation by Fe_R is unclear. It is likely that a series of impacts will be driven by sea-level rise 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. For example, increased aridification and decreased fluvial discharge across North America appears to be a trend set to continue (Overpeck & 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 seagrass and mangroves, due to the combined effects of acidification, warming and rising sea levels (B. Duarte et al., 2018; Gilman et al., 2008; Lovelock & 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 Fe(III)-reducing bacteria, which act to dissolve Fe_R phases. However, the potential for such states of anoxia to alter efficacy of mineral-organic preservation, and how this relates more generally to the reduced oxygen exposure time of OC, is 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 and co-precipitation of OC (Riedel et al., 2013). So despite zones of persistent ocean anoxia expanding as a result

of rising global temperatures (Altieri & Gedan, 2015), the impact of OC-Fe_R as a component of net OC burial is unclear. Climate models also 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 Fe_R minerals which could release solubilized iron minerals and associated OC as dissolved OC in these areas (Barcellos et al., 2018), enhancing the seaward transfer of these dissolved phases from the continents.

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_R (Patzner et al., 2020), although the extent of this loss varies between vegetation types (C. 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_R. Projected increases in soil acidification associated with nitrogen fertilization (Tian & 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_R abundance in terrestrial soils, suggesting any future decreases in soil pH may increase OC-Fe_R.

4. Conclusions, Caveats, and Outlook

Our work shows that in the marine environment, as much as 52 Mt C yr⁻¹ is buried as OC-Fe_R, with the primary settings of burial being the continental shelves, slopes and deltaic environments. In terrestrial environments, the annual burial rate of OC-Fe_R is estimated to be 446 Mt C yr⁻¹—an order of magnitude more than the OC-Fe_R buried per year in marine sediments—with as much as half of this terrestrial accumulation attributed to cultivated cropland soils. The significant size of these terrestrial stocks, 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_R needs to be better understood and monitored.

The conclusions presented here must be caveated by the fact that large areas of the globe are not well represented in our data sets (Figure 1). There are zero data available from south of the equator. We have no data from Africa as a continent, or from Australasia, and in the marine realm, no data are available for the southern Pacific, Atlantic and Indian Oceans. The data presented here should therefore be considered a starting point, as it is clear that more widespread data collection is next required to ensure conclusions drawn from the existing data are not biased by the skewed representation of Earth's surface environments. In spite of these caveats, however, we find that OC-Fe_R is an integral component of OC stocks across all of Earth's surface environments studied so far, and suggest it ought to be considered as such in future carbon accounting and sequestration strategies within critical zones on land and the closely connected marine realm.

Data Availability Statement

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 <https://doi.org/10.6084/m9.figshare.19691905>.

References

- Altieri, A. H., & Gedan, K. B. (2015). Climate change and dead zones. *Global Change Biology*, 21(4), 1395–1406. <https://doi.org/10.1111/gcb.12754>
- Barange, M., Merino, G., Blanchard, J. L., Scholtens, J., Harle, J., Allison, E. H., et al. (2014). Impacts of climate change on marine ecosystem production in societies dependent on fisheries. *Nature Climate Change*, 4(4), 211–216. <https://doi.org/10.1038/nclimate2119>
- Barber, A., Brandes, J., Leri, A., Lalonde, K., Balind, K., Wirick, S., et al. (2017). Preservation of organic matter in marine sediments by inner-sphere interactions with reactive iron. *Scientific Reports*, 7(1), 366. <https://doi.org/10.1038/s41598-017-00494-0>
- Barcellos, D., O'connell, C. S., Silver, W., Meile, C., & Thompson, A. (2018). Hot spots and hot moments of soil moisture explain fluctuations in iron and carbon cycling in a humid tropical forest soil. *Soil Systems*, 2(4), 59. <https://doi.org/10.3390/SOILSYSTEMS2040059>
- Berner, R. A. (1973). Phosphate removal from sea water by adsorption on volcanogenic ferric oxides. *Earth and Planetary Science Letters*, 18(1), 77–86. [https://doi.org/10.1016/0012-821X\(73\)90037-X](https://doi.org/10.1016/0012-821X(73)90037-X)
- Berner, R. A., & Canfield, D. E. (1989). A new model for atmospheric oxygen over Phanerozoic time. *American Journal of Science*, 289(4), 333–361. <https://doi.org/10.2475/AJS.289.4.333>
- Bhattacharyya, A., Campbell, A. N., Tfaily, M. M., Lin, Y., Kukkadapu, R. K., Silver, W. L., et al. (2018). Redox fluctuations control the coupled cycling of iron and carbon in tropical forest soils. *Environmental Science & Technology*, 52(24), 14129–14139. https://doi.org/10.1021/ACS.EST.8B03408/SUPPL_FILE/ES8B03408_SI_001.PDF

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- Bianchi, T. S., Cui, X., Blair, N. E., Burdige, D. J., Eglinton, T. I., & Galy, V. (2018). Centers of organic carbon burial and oxidation at the land-ocean interface. *Organic Geochemistry*, *115*, 138–155. <https://doi.org/10.1016/j.ORGEOCHEM.2017.09.008>
- Bjerrum, C. J., Bendtsen, J., & Legarth, J. J. F. (2006). Modeling organic carbon burial during sea level rise with reference to the Cretaceous. *Geochemistry, Geophysics, Geosystems*, *7*(5), 5008. <https://doi.org/10.1029/2005GC001032>
- Blair, N. E., & Aller, R. C. (2012). The fate of terrestrial organic carbon in the Marine environment. *Annual Review of Marine Science*, *4*(1), 401–423. <https://doi.org/10.1146/annurev-marine-120709-142717>
- Bryan, S. E., Peate, I. U., Peate, D. W., Self, S., Jerram, D. A., Mawby, M. R., et al. (2010). The largest volcanic eruptions on Earth. *Earth-Science Reviews*, *102*(3–4), 207–229. <https://doi.org/10.1016/j.EARSCIREV.2010.07.001>
- Burdige, D. J. (2007). Preservation of organic matter in marine sediments: Controls, mechanisms, and an imbalance in sediment organic carbon budgets? *Chemical Reviews*, *107*(2), 467–485. <https://doi.org/10.1021/cr050347q>
- Calvert, S. E., & Pedersen, T. F. (1992). Organic carbon accumulation and preservation in marine sediments: How important is anoxia? In J. Whelan & J. Farrington (Eds.), *Organic matter: Productivity, accumulation, and preservation in recent and ancient sediments* (pp. 231–263). Columbia University Press.
- Canadell, J. G., Monteiro, P. M. S., Costa, M. H., Cunha, L. C. D., Cox, P. M., Eliseev, A. V., et al. (2021). Chapter 5: Global carbon and other biogeochemical cycles and feedbacks. In V. Masson-Delmotte, P. Zhai, A. Pirani, S. L. Connors, C. Péan, S. Berger, et al. (Eds.), *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change* (p. 221). Cambridge University Press.
- Carvalho, N., Forkel, M., Khomik, M., Bellarby, J., Jung, M., Migliavacca, M., et al. (2014). Global covariation of carbon turnover times with climate in terrestrial ecosystems. *Nature*, *514*(7521), 213–217. <https://doi.org/10.1038/nature13731>
- Chen, C., Dynes, J. J., Wang, J., & Sparks, D. L. (2014). Properties of Fe-organic matter associations via coprecipitation versus adsorption. *Environmental Science & Technology*, *48*(23), 13751–13759. https://doi.org/10.1021/ES503669U/SUPPL_FILE/ES503669U_SI_001.PDF
- Chen, C., Hall, S. J., Coward, E., & Thompson, A. (2020). Iron-mediated organic matter decomposition in humid soils can counteract protection. *Nature Communications*, *11*(1), 1–13. <https://doi.org/10.1038/s41467-020-16071-5>
- Chen, C., & Sparks, D. L. (2018). Fe(II)-induced mineral transformation of ferrihydrite-organic matter adsorption and co-precipitation complexes in the absence and presence of As(III). *ACS Earth and Space Chemistry*, *2*(11), 1095–1101. https://doi.org/10.1021/ACSEARTHSPACECHEM.8B00041/SUPPL_FILE/SP8B00041_SI_001.PDF
- Clark, M. W., McConchie, D., Lewis, D. W., & Saenger, P. (1998). Redox stratification and heavy metal partitioning in Avicennia-dominated mangrove sediments: A geochemical model. *Chemical Geology*, *149*(3–4), 147–171. [https://doi.org/10.1016/S0009-2541\(98\)00034-5](https://doi.org/10.1016/S0009-2541(98)00034-5)
- Coward, E. K., Thompson, A. T., & Plante, A. F. (2017). Iron-mediated mineralogical control of organic matter accumulation in tropical soils. *Geoderma*, *306*, 206–216. <https://doi.org/10.1016/j.GEODERMA.2017.07.026>
- Cui, X., Bianchi, T. S., Savage, C., & Smith, R. W. (2016). Organic carbon burial in fjords: Terrestrial versus marine inputs. *Earth and Planetary Science Letters*, *451*, 41–50. <https://doi.org/10.1016/j.EPSL.2016.07.003>
- Curti, L., Moore, O. W., Babakhani, P., Xiao, K.-Q., Woulds, C., Bray, A. W., et al. (2021). Carboxyl-richness controls organic carbon preservation during coprecipitation with iron (oxyhydr)oxides in the natural environment. *Communications Earth & Environment*, *2*(12), 1–13. <https://doi.org/10.1038/s43247-021-00301-9>
- Dai, S., Bechtel, A., Eble, C. F., Flores, R. M., French, D., Graham, I. T., et al. (2020). Recognition of peat depositional environments in coal: A review. *International Journal of Coal Geology*, *219*, 103383. <https://doi.org/10.1016/j.COAL.2019.103383>
- Dass, P., Houlton, B. Z., Wang, Y., & Warlind, D. (2018). Grasslands may be more reliable carbon sinks than forests in California. *Environmental Research Letters*, *13*(7), 074027. <https://doi.org/10.1088/1748-9326/aacb39>
- Demaison, G. J., & Moore, G. T. (1980). Anoxic environments and oil source bed genesis. *The American Association of Petroleum Geologists Bulletin*, *64*, 1179–1209. <https://doi.org/10.1306/2F91945E-16CE-11D7-8645000102C1865D>
- Dicen, G. P., Navarrete, I. A., Rallos, R. V., Salmo, S. G., & Garcia, M. C. A. (2019). The role of reactive iron in long-term carbon sequestration in mangrove sediments. *Journal of Soils and Sediments*, *19*(1), 501–510. <https://doi.org/10.1007/S11368-018-2051-Y/FIGURES/3>
- Ding, J., Li, F., Yang, G., Chen, L., Zhang, B., Liu, L., et al. (2016). The permafrost carbon inventory on the Tibetan Plateau: A new evaluation using deep sediment cores. *Global Change Biology*, *22*(8), 2688–2701. <https://doi.org/10.1111/GCB.13257>
- Duarte, B., Martins, I., Rosa, R., Matos, A. R., Roleda, M. Y., Reusch, T. B. H., et al. (2018). Climate change impacts on seagrass meadows and macroalgal forests: An integrative perspective on acclimation and adaptation potential. *Frontiers in Marine Science*, *5*, 190. <https://doi.org/10.3389/FMARS.2018.00190/BIBTEX>
- Duarte, C. M., Middelburg, J. J., & Caraco, N. (2005). Major role of marine vegetation on the oceanic carbon cycle. *Biogeosciences*, *2*, 1–8. <https://doi.org/10.5194/bg-2-1-2005>
- Dunne, J. P., Sarmiento, J. L., & Gnanadesikan, A. (2007). A synthesis of global particle export from the surface ocean and cycling through the ocean interior and on the seafloor. *Global Biogeochemical Cycles*, *21*(4), GB4006. <https://doi.org/10.1029/2006GB002907>
- Eglinton, T. I. (2012). A rusty carbon sink. *Nature*, *483*(7388), 165–166. <https://doi.org/10.1038/483165a>
- Ernst, R. E., Bond, D. P. G., Zhang, S., Buchan, K. L., Grasby, S. E., Youbi, N., et al. (2021). Large igneous province record through time and implications for secular environmental changes and geological time-scale boundaries. In *Large igneous provinces: A driver of global environmental and biotic changes* (pp. 1–26). <https://doi.org/10.1002/9781119507444.ch1>
- Eusterhues, K., Rennert, T., Knicker, H., Kögel-Knabner, I., Totsche, K. U., & Schwertmann, U. (2011). Fractionation of organic matter due to reaction with ferrihydrite: Coprecipitation versus adsorption. *Environmental Science & Technology*, *45*(2), 527–533. https://doi.org/10.1021/ES1023898/SUPPL_FILE/ES1023898_SI_001.PDF
- Falkowski, P., Scholes, P. J., Boyle, E., Canadell, J., Canfield, D., Elser, J., et al. (2000). The global carbon cycle: A test of our knowledge of Earth as a system. *Science*, *290*(5490), 291–296. <https://doi.org/10.1126/science.274.5291.1346>
- Fang, K., Qin, S., Chen, L., Zhang, Q., & Yang, Y. (2019). Al/Fe mineral controls on soil organic carbon stock across Tibetan alpine grasslands. *Journal of Geophysical Research: Biogeosciences*, *124*(2), 247–259. <https://doi.org/10.1029/2018JG004782>
- Faust, J. C., & Knies, J. (2019). Organic matter sources in North Atlantic fjord sediments. *Geochemistry, Geophysics, Geosystems*, *20*(6), 2872–2885. <https://doi.org/10.1029/2019GC008382>
- Faust, J. C., Stevenson, M. A., Abbott, G. D., Knies, J., Tessin, A., Mannion, I., et al. (2020). Does Arctic warming reduce preservation of organic matter in Barents Sea sediments? *Philosophical Transactions of the Royal Society A*, *378*(2181), 20190364. <https://doi.org/10.1098/RSTA.2019.0364>
- Faust, J. C., Tessin, A., Fisher, B. J., Zindorf, M., Papadaki, S., Hendry, K. R., et al. (2021). Millennial scale persistence of organic carbon bound to iron in Arctic marine sediments. *Nature Communications*, *12*(1), 1–9. <https://doi.org/10.1038/s41467-020-20550-0>

- Feely, R. A., Trefry, J. H., Massoth, G. J., & Metz, S. (1991). A comparison of the scavenging of phosphorus and arsenic from seawater by hydrothermal iron oxyhydroxides in the Atlantic and Pacific Oceans. *Deep-Sea Research, Part A: Oceanographic Research Papers*, 38(6), 617–623. [https://doi.org/10.1016/0198-0149\(91\)90001-V](https://doi.org/10.1016/0198-0149(91)90001-V)
- Feng, X., Thompson, S. E., Woods, R., & Porporato, A. (2019). Quantifying Asynchronicity of precipitation and potential evapotranspiration in mediterranean climates. *Geophysical Research Letters*, 46(24), 14692–14701. <https://doi.org/10.1029/2019GL085653>
- Fisher, B. J., Faust, J. C., Moore, O. W., Peacock, C. L., & März, C. (2021). Technical note: Uncovering the influence of methodological variations on the extractability of iron-bound organic carbon. *Biogeosciences*, 18(11), 3409–3419. <https://doi.org/10.5194/bg-18-3409-2021>
- Fisher, B. J., Moore, O. W., Faust, J. C., Peacock, C. L., & März, C. (2020). Experimental evaluation of the extractability of iron bound organic carbon in sediments as a function of carboxyl content. *Chemical Geology*, 556, 119853. <https://doi.org/10.1016/j.chemgeo.2020.119853>
- Fourqurean, J. W., Duarte, C. M., Kennedy, H., Marbà, N., Holmer, M., Mateo, M. A., et al. (2012). Seagrass ecosystems as a globally significant carbon stock. *Nature Geoscience*, 5(7), 505–509. <https://doi.org/10.1038/ngeo1477>
- Friedlingstein, P., O'Sullivan, M., Jones, M. W., Andrew, R. M., Hauck, J., Olsen, A., et al. (2020). Global carbon budget 2020. *Earth System Science Data*, 12(4), 3269–3340. <https://doi.org/10.5194/essd-12-3269-2020>
- Gilman, E. L., Ellison, J., Duke, N. C., & Field, C. (2008). Threats to mangroves from climate change and adaptation options: A review. *Aquatic Botany*, 89(2), 237–250. <https://doi.org/10.1016/j.aquabot.2007.12.009>
- Giosan, L., Syvitski, J., Constantinescu, S., & Day, J. (2014). Climate change: Protect the world's deltas. *Nature*, 516(7529), 31–33. <https://doi.org/10.1038/516031a>
- Greb, S. F., DiMichele, W. A., & Gastaldo, R. A. (2006). Evolution and importance of wetlands in Earth history. *Special Papers – Geological Society of America*, 399, 1–40. [https://doi.org/10.1130/2006.2399\(01\)](https://doi.org/10.1130/2006.2399(01))
- Gudmundsson, M. T., Thordarson, T., Höskuldsson, Á., Larsen, G., Björnsson, H., Prata, F. J., et al. (2012). Ash generation and distribution from the April–May 2010 eruption of Eyjafjallajökull, Iceland. *Scientific Reports*, 2(1), 572. <https://doi.org/10.1038/srep00572>
- Guo, J. H., Liu, X. J., Zhang, Y., Shen, J. L., Han, W. X., Zhang, W. F., et al. (2010). Significant acidification in major Chinese croplands. *Science*, 327(5968), 1008–1010. <https://doi.org/10.1126/SCIENCE.1182570>
- Harrison, C. G. A., Miskell, K. J., Brass, G. W., Saltzman, E. S., & Sloan, J. L. (1983). Continental hypsography. *Tectonics*, 2(4), 357–377. <https://doi.org/10.1029/TC0021004P00357/FORMAT/PDF>
- Hartnett, H. E., Keil, R. G., Hedges, J. I., & Devol, A. H. (1998). Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. *Nature*, 391(6667), 572–575. <https://doi.org/10.1038/35351>
- Hedges, J. I., & Keil, R. G. (1995). Sedimentary organic matter preservation: An assessment and speculative synthesis. *Marine Chemistry*, 49(2–3), 81–115. [https://doi.org/10.1016/0304-4203\(95\)00008-F](https://doi.org/10.1016/0304-4203(95)00008-F)
- Heine, C., Yeo, L. G., & Müller, R. D. (2015). Evaluating global paleoshoreline models for the Cretaceous and Cenozoic. *Australian Journal of Earth Sciences*, 62, 275–287. <https://doi.org/10.1080/08120099.2015.1018321>
- Henrichs, S. M. (1992). Early diagenesis of organic matter in marine sediments: Progress and perplexity. *Marine Chemistry*, 39(1–3), 119–149. [https://doi.org/10.1016/0304-4203\(92\)90098-U](https://doi.org/10.1016/0304-4203(92)90098-U)
- Homoky, W. B., Conway, T. M., John, S. G., König, D., Deng, F. F., Tagliabue, A., & Mills, R. A. (2021). Iron colloids dominate sedimentary supply to the ocean interior. *Proceedings of the National Academy of Sciences of the United States of America*, 118(13), e2016078118. <https://doi.org/10.1073/PNAS.2016078118>
- Huang, X., Liu, X., Liu, J., & Chen, H. (2021). Iron-bound organic carbon and their determinants in peatlands of China. *Geoderma*, 391, 114974. <https://doi.org/10.1016/j.geoderma.2021.114974>
- Hugelius, G., Loisel, J., Chadburn, S., Jackson, R. B., Jones, M., MacDonald, G., et al. (2020). Large stocks of peatland carbon and nitrogen are vulnerable to permafrost thaw. *Proceedings of the National Academy of Sciences of the United States of America*, 117(34), 20438–20446. https://doi.org/10.1073/PNAS.1916387117/SUPPL_FILE/PNAS.1916387117.SD06.XLSX
- Joss, H., Patzner, M. S., Maisch, M., Mueller, C. W., Kappler, A., & Bryce, C. (2022). Cryoturbation impacts iron-organic carbon associations along a permafrost soil chronosequence in northern Alaska. *Geoderma*, 413, 115738. <https://doi.org/10.1016/j.geoderma.2022.115738>
- Kaiser, K., & Guggenberger, G. (2003). Mineral surfaces and soil organic matter. *European Journal of Soil Science*, 54(2), 219–236. <https://doi.org/10.1046/J.1365-2389.2003.00544.X>
- Keenan, T. F., & Williams, C. A. (2018). The terrestrial carbon sink. *Annual Review of Environment and Resources*, 43(1), 219–243. <https://doi.org/10.1146/ANNUREV-ENVIRON-102017-030204>
- Keil, R. G., & Mayer, L. M. (2014). Mineral matrices and organic matter. In *Treatise on geochemistry: Second edition* (pp. 337–359). <https://doi.org/10.1016/B978-0-08-095975-7.01024-X>
- Keil, R. G., Montluçon, D. B., Prahl, F. G., & Hedges, J. I. (1994). Sorptive preservation of labile organic matter in marine sediments. *Nature*, 370(6490), 549–552. <https://doi.org/10.1038/370549a0>
- Kleber, M., Bourg, I. C., Coward, E. K., Hansel, C. M., Myneni, S. B., & Nunan, N. (2021). Dynamic interactions at the mineral-organic matter interface. *Nature Reviews Earth & Environment*, 2(6), 402–421. <https://doi.org/10.1038/s43017-021-00162-yf>
- Kögel-Knabner, I., Guggenberger, G., Kleber, M., Kandeler, E., Kalbitz, K., Scheu, S., et al. (2008). Organo-mineral associations in temperate soils: Integrating biology, mineralogy, and organic matter chemistry. *Journal of Plant Nutrition and Soil Science*, 171(1), 61–82. <https://doi.org/10.1002/JPLN.200700048>
- Kremlin, H. N., Santos Ferreira, C. S., Destouni, G., Keesstra, S. D., Salvati, L., & Kalantari, Z. (2021). Arctic wetland system dynamics under climate warming. *Wiley Interdisciplinary Reviews: Water*, 8(4), e1526. <https://doi.org/10.1002/WAT2.1526>
- Kurtz, A. C., Kump, L. R., Arthur, M. A., Zachos, J. C., Paytan, A., & Kurtz, C. (2003). Early Cenozoic decoupling of the global carbon and sulfur cycles. *Paleoceanography*, 18(4), 1090. <https://doi.org/10.1029/2003PA000908>
- Lalonde, K., Mucci, A., Ouellet, A., & Gélinas, Y. (2012). Preservation of organic matter in sediments promoted by iron. *Nature*, 483(7388), 198–200. <https://doi.org/10.1038/nature10855>
- Lee, C.-T. A., Jiang, H., Ronay, E., Minisini, D., Stiles, J., & Neal, M. (2018). Volcanic ash as a driver of enhanced organic carbon burial in the Cretaceous. *Scientific Reports*, 8(1), 4197. <https://doi.org/10.1038/s41598-018-22576-3>
- Liu, L., Zhuang, Q., Zhao, D., Zheng, D., Kou, D., & Yang, Y. (2022). Permafrost degradation diminishes terrestrial ecosystem carbon sequestration capacity on the Qinghai-Tibetan Plateau. *Global Biogeochemical Cycles*, 36(2), e2021GB007068. <https://doi.org/10.1029/2021GB007068>
- Longman, J., Gernon, T. M., Palmer, M. R., Jones, M. T., Stokke, E. W., & Svensen, H. H. (2021). Marine diagenesis of tephra aided the Paleocene-Eocene Thermal Maximum termination. *Earth and Planetary Science Letters*, 571, 117101. <https://doi.org/10.1016/j.epsl.2021.117101>
- Longman, J., Gernon, T. M., Palmer, M. R., & Manners, H. R. (2021). Tephra deposition and bonding with reactive oxides enhances burial of organic carbon in the Bering Sea. *Global Biogeochemical Cycles*, 35(11), e2021GB007140. <https://doi.org/10.1029/2021GB007140>

- Longman, J., Mills, B. J. W., Manners, H. R., Gernon, T. M., & Palmer, M. R. (2021). Late Ordovician climate change and extinctions driven by elevated volcanic nutrient supply. *Nature Geoscience*, *14*(12), 924–929. <https://doi.org/10.1038/s41561-021-00855-5>
- Longman, J., Palmer, M. R., Gernon, T. M., & Manners, H. R. (2019). The role of tephra in enhancing organic carbon preservation in marine sediments. *Earth-Science Reviews*, *192*, 480–490. <https://doi.org/10.1016/j.earscirev.2019.03.018>
- Longman, J., Palmer, M. R., Gernon, T. M., Manners, H. R., & Jones, M. T. (2022). Subaerial volcanism is a potentially major contributor to oceanic iron and manganese cycles. *Communications Earth & Environment*, *3*(1), 1–8. <https://doi.org/10.1038/s43247-022-00389-7>
- Lovelock, C. E., & Duarte, C. M. (2019). Dimensions of blue carbon and emerging perspectives. *Biological Letters*, *15*(3), 23955–26900. <https://doi.org/10.1098/RSL.2018.0781>
- Lützow, M. V., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., & Flessa, H. (2006). Stabilization of organic matter in temperate soils: Mechanisms and their relevance under different soil conditions – A review. *European Journal of Soil Science*, *57*(4), 426–445. <https://doi.org/10.1111/j.1365-2389.2006.00809.x>
- Ma, W. W., Zhu, M. X., Yang, G. P., & Li, T. (2018). Iron geochemistry and organic carbon preservation by iron (oxyhydr)oxides in surface sediments of the East China Sea and the south Yellow Sea. *Journal of Marine Systems*, *178*, 62–74. <https://doi.org/10.1016/j.jmarsys.2017.10.009>
- Mayer, L. M. (1994). Relationships between mineral surfaces and organic carbon concentrations in soils and sediments. *Chemical Geology*, *114*(3–4), 347–363. [https://doi.org/10.1016/0009-2541\(94\)90063-9](https://doi.org/10.1016/0009-2541(94)90063-9)
- McKenzie, N. R., Horton, B. K., Loomis, S. E., Stockli, D. F., Planavsky, N. J., & Lee, C.-T. A. (2016). Continental arc volcanism as the principal driver of icehouse-greenhouse variability. *Science*, *352*(6284), 444–447. <https://doi.org/10.1126/science.aad5787>
- Mehra, O. P., & Jackson, M. L. (1958). Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays and Clay Minerals*, *7*(1), 317–327. <https://doi.org/10.1346/CCMN.1958.0070122>
- Mikutta, R., & Kaiser, K. (2011). Organic matter bound to mineral surfaces: Resistance to chemical and biological oxidation. *Soil Biology and Biochemistry*, *43*(8), 1738–1741. <https://doi.org/10.1016/j.soilbio.2011.04.012>
- Mills, B., Daines, S. J., & Lenton, T. M. (2014). Changing tectonic controls on the long-term carbon cycle from Mesozoic to present. *Geochemistry, Geophysics, Geosystems*, *15*(12), 4866–4884. <https://doi.org/10.1002/2014GC005530>
- Milne, E., Banwart, S. A., Noellemeyer, E., Abson, D. J., Ballabio, C., Bampa, F., et al. (2015). Soil carbon, multiple benefits. *Environmental Development*, *13*, 33–38. <https://doi.org/10.1016/j.envdev.2014.11.005>
- Monhonval, A., Strauss, J., Thomas, M., Hirst, C., Titeux, H., Louis, J., et al. (2022). Thermokarst processes increase the supply of stabilizing surfaces and elements (Fe, Mn, Al, and Ca) for mineral–organic carbon interactions. *Permafrost and Periglacial Processes*, *33*(4), 452–469. <https://doi.org/10.1002/PPP.2162>
- Mu, C., Abbott, B. W., Norris, A. J., Mu, M., Fan, C., Chen, X., et al. (2020). The status and stability of permafrost carbon on the Tibetan Plateau. *Earth-Science Reviews*, *211*, 103433. <https://doi.org/10.1016/j.earscirev.2020.103433>
- Mu, C. C., Zhang, T. J., Zhao, Q., Guo, H., Zhong, W., Su, H., & Wu, Q. B. (2016). Soil organic carbon stabilization by iron in permafrost regions of the Qinghai-Tibet Plateau. *Geophysical Research Letters*, *43*(19), 10–286. <https://doi.org/10.1002/2016GL070071>
- Mueller, C. W., Hoeschen, C., Steffens, M., Buddenbaum, H., Hinkel, K., Bockheim, J. G., & Kao-Kniffin, J. (2017). Microscale soil structures foster organic matter stabilization in permafrost soils. *Geoderma*, *293*, 44–53. <https://doi.org/10.1016/j.geoderma.2017.01.028>
- Mueller, C. W., Rethemeyer, J., Kao-Kniffin, J., Löppmann, S., Hinkel, K. M., & Bockheim, J. G. (2015). Large amounts of labile organic carbon in permafrost soils of northern Alaska. *Global Change Biology*, *21*(7), 2804–2817. <https://doi.org/10.1111/GCB.12876>
- Müller, B., Granina, L., Schaller, T., Ulrich, A., & Wehrli, B. (2002). P, As, Sb, Mo, and other elements in sedimentary Fe/Mn layers of Lake Baikal. *Environmental Science & Technology*, *36*(3), 411–420. <https://doi.org/10.1021/ES010940Z>
- Noël, V., Morin, G., Juillot, F., Marchand, C., Brest, J., Bargar, J. R., et al. (2015). Ni cycling in mangrove sediments from New Caledonia. *Geochimica et Cosmochimica Acta*, *169*, 82–98. <https://doi.org/10.1016/j.gca.2015.07.024>
- Olefendt, D., Goswami, S., Grosse, G., Hayes, D., Hugelius, G., Kuhry, P., et al. (2016). Circumpolar distribution and carbon storage of thermokarst landscapes. *Nature Communications*, *7*(1), 1–11. <https://doi.org/10.1038/ncomms13043>
- Overpeck, J. T., & Udall, B. (2020). Climate change and the aridification of North America. *Proceedings of the National Academy of Sciences*, *117*(22), 11856–11858. <https://doi.org/10.1073/PNAS.2006323117>
- Pan, Y., Birdsey, R. A., Fang, J., Houghton, R., Kauppi, P. E., Kurz, W. A., et al. (2011). A large and persistent carbon sink in the world's forests. *Science*, *333*(6045), 988–993. https://doi.org/10.1126/SCIENCE.1201609/SUPPL_FILE/PAPV2.PDF
- Panitz, S., Salzmann, U., Risebrobakken, B., De Schepper, S., & Pound, M. J. (2016). Climate variability and long-term expansion of peatlands in Arctic Norway during the late Pliocene (ODP Site 642, Norwegian Sea). *Climate of the Past*, *12*(4), 1043–1060. <https://doi.org/10.5194/CP-12-1043-2016>
- Patzner, M. S., Mueller, C. W., Malusova, M., Baur, M., Nikeleit, V., Scholten, T., et al. (2020). Iron mineral dissolution releases iron and associated organic carbon during permafrost thaw. *Nature Communications*, *11*(1), 1–11. <https://doi.org/10.1038/s41467-020-20102-6>
- Pendleton, L., Donato, D. C., Murray, B. C., Crooks, S., Jenkins, W. A., Sifleet, S., et al. (2012). Estimating global “blue carbon” emissions from conversion and degradation of vegetated coastal ecosystems. *PLoS One*, *7*(9), e43542. <https://doi.org/10.1371/JOURNAL.PONE.0043542>
- Pyle, D. M. (1995). Mass and energy budgets of explosive volcanic eruptions. *Geophysical Research Letters*, *22*(5), 563–566. <https://doi.org/10.1029/95GL00052>
- Rahmstorf, S. (2007). A semi-empirical approach to projecting future sea-level rise. *Science*, *315*(5810), 368–370. https://doi.org/10.1126/SCIENCE.1135456/SUPPL_FILE/RAHMSTORF.SOM.PDF
- Riedel, T., Zak, D., Biester, H., & Dittmar, T. (2013). Iron traps terrestrially derived dissolved organic matter at redox interfaces. *Proceedings of the National Academy of Sciences of the United States of America*, *110*(25), 10101–10105. <https://doi.org/10.1073/pnas.1221487110>
- Salvadó, J. A., Tesi, T., Andersson, A., Ingri, J., Dudarev, O. V., Semiletov, I. P., & Gustafsson, Ö. (2015). Organic carbon remobilized from thawing permafrost is resequenced by reactive iron on the Eurasian Arctic Shelf. *Geophysical Research Letters*, *42*(19), 8122–8130. <https://doi.org/10.1002/2015GL066058>
- Schrag, D. P., Higgins, J. A., Macdonald, F. A., & Johnston, D. T. (2013). Authigenic carbonate and the history of the global carbon cycle. *Science*, *339*(6119), 540–543. <https://doi.org/10.1126/science.1229578>
- Scurlock, J. M. O., & Hall, D. O. (1998). The global carbon sink: A grassland perspective. *Global Change Biology*, *4*(2), 229–233. <https://doi.org/10.1046/j.1365-2486.1998.00151.x>
- Shen, Y. H. (1999). Sorption of natural dissolved organic matter on soil. *Chemosphere*, *38*(7), 1505–1515. [https://doi.org/10.1016/S0045-6535\(98\)00371-3](https://doi.org/10.1016/S0045-6535(98)00371-3)
- Shields, M. R., Bianchi, T. S., Gélinas, Y., Allison, M. A., & Twilley, R. R. (2016). Enhanced terrestrial carbon preservation promoted by reactive iron in deltaic sediments. *Geophysical Research Letters*, *43*(3), 1149–1157. <https://doi.org/10.1002/2015GL067388>
- Smith, R. W., Bianchi, T. S., Allison, M., Savage, C., & Galy, V. (2015). High rates of organic carbon burial in fjord sediments globally. *Nature Geoscience*, *8*(6), 450–453. <https://doi.org/10.1038/NNGEO2421>

- Su, H., Jiang, J. H., Neelin, J. D., Shen, T. J., Zhai, C., Yue, Q., et al. (2017). Tightening of tropical ascent and high clouds key to precipitation change in a warmer climate. *Nature Communications*, 8(1), 1–9. <https://doi.org/10.1038/ncomms15771>
- Sun, C. H., Zhu, M. X., Ma, W. W., Sun, Z. L., Zhang, X. R., Ding, K. Y., & Liu, S. H. (2020). Examining bulk and iron-associated organic carbon through depth in margin sea sediments (China) under contrasting depositional settings: Chemical and NEXAFS spectral characterization. *Journal of Marine Systems*, 207, 103344. <https://doi.org/10.1016/j.jmarsys.2020.103344>
- Syvitski, J. P. M., Kettner, A. J., Overeem, I., Hutton, E. W. H., Hannon, M. T., Brakenridge, G. R., et al. (2009). Sinking deltas due to human activities. *Nature Geoscience*, 2(10), 681–686. <https://doi.org/10.1038/ngeo629>
- Tian, D., & Niu, S. (2015). A global analysis of soil acidification caused by nitrogen addition. *Environmental Research Letters*, 10(2), 024019. <https://doi.org/10.1088/1748-9326/10/2/024019>
- Torn, M. S., Trumbore, S. E., Chadwick, O. A., Vitousek, P. M., & Hendricks, D. M. (1997). Mineral control of soil organic carbon storage and turnover. *Nature*, 389(6647), 170–173. <https://doi.org/10.1038/38260>
- Vitousek, P. M., Porder, S., Houlton, B. Z., & Chadwick, O. A. (2010). Terrestrial phosphorus limitation: Mechanisms, implications, and nitrogen–phosphorus interactions. *Ecological Applications*, 20(1), 5–15. <https://doi.org/10.1890/08-0127.1>
- Wagai, R., & Mayer, L. M. (2007). Sorptive stabilization of organic matter in soils by hydrous iron oxides. *Geochimica et Cosmochimica Acta*, 71(1), 25–35. <https://doi.org/10.1016/j.gca.2006.08.047>
- Wagai, R., Mayer, L. M., Kitayama, K., & Shirato, Y. (2013). Association of organic matter with iron and aluminum across a range of soils determined via selective dissolution techniques coupled with dissolved nitrogen analysis. *Biogeochemistry*, 112(1–3), 95–109. <https://doi.org/10.1007/s10533-011-9652-5/FIGURES/5>
- Walker, L. J., Wilkinson, B. H., & Ivany, L. C. (2002). Continental drift and Phanerozoic carbonate accumulation in shallow-shelf and deep-marine settings. *The Journal of Geology*, 110(1), 75–87. <https://doi.org/10.1086/324318>
- Walker, T. W., & Syers, J. K. (1976). The fate of phosphorus during pedogenesis. *Geoderma*, 15, 1–19. [https://doi.org/10.1016/0016-7061\(76\)90066-5](https://doi.org/10.1016/0016-7061(76)90066-5)
- Wang, Y., Wang, H., He, J. S., & Feng, X. (2017). Iron-mediated soil carbon response to water-table decline in an alpine wetland. *Nature Communications*, 8(1), 1–9. <https://doi.org/10.1038/ncomms15972>
- Whitby, H., Planquette, H., Cassar, N., Bucciarelli, E., Osburn, C. L., Janssen, D. J., et al. (2020). A call for refining the role of humic-like substances in the oceanic iron cycle. *Scientific Reports*, 10(1), 1–12. <https://doi.org/10.1038/s41598-020-62266-7>
- White, R. P., Murray, S., Rohweder, M., Prince, S. D., & Thompson, K. M. (2000). *Grassland ecosystems* (p. 81). World Resources Institute.
- Ye, C., Huang, W., Hall, S. J., & Hu, S. (2022). Association of organic carbon with reactive iron oxides driven by soil pH at the global scale. *Global Biogeochemical Cycles*, 36(1), e2021GB007128. <https://doi.org/10.1029/2021GB007128>
- Yu, Z., Loisel, J., Brosseau, D. P., Beilman, D. W., & Hunt, S. J. (2010). Global peatland dynamics since the Last Glacial Maximum. *Geophysical Research Letters*, 37(13), L13402. <https://doi.org/10.1029/2010GL043584>
- Zhao, Q., Adhikari, D., Huang, R., Patel, A., Wang, X., Tang, Y., et al. (2017). Coupled dynamics of iron and iron-bound organic carbon in forest soils during anaerobic reduction. *Chemical Geology*, 464, 118–126. <https://doi.org/10.1016/j.chemgeo.2016.12.014>
- Zhao, Q., Poulson, S. R., Obrist, D., Sumaila, S., Dynes, J. J., McBeth, J. M., & Yang, Y. (2016). Iron-bound organic carbon in forest soils: Quantification and characterization. *Biogeosciences*, 13(16), 4777–4788. <https://doi.org/10.5194/bg-13-4777-2016>
- Zomer, R. J., Bossio, D. A., Sommer, R., & Verchot, L. V. (2017). Global sequestration potential of increased organic carbon in cropland soils. *Scientific Reports*, 7(1), 1–8. <https://doi.org/10.1038/s41598-017-15794-8>

References From the Supporting Information

- Bai, J., Luo, M., Yang, Y., Xiao, S., Zhai, Z., & Huang, J. (2021). Iron-bound carbon increases along a freshwater–oligohaline gradient in a subtropical tidal wetland. *Soil Biology and Biochemistry*, 154, 108128. <https://doi.org/10.1016/j.soilbio.2020.108128>
- Chen, J., Hu, Y., Hall, S. J., Hui, D., Li, J., Chen, G., et al. (2022). Increased interactions between iron oxides and organic carbon under acid deposition drive large increases in soil organic carbon in a tropical forest in southern China. *Biogeochemistry*, 158(3), 287–301. <https://doi.org/10.1007/s10533-022-00897-w/FIGURES/4>
- Coward, E. K., Thompson, A., & Plante, A. F. (2018). Contrasting Fe speciation in two humid forest soils: Insight into organomineral associations in redox-active environments. *Geochimica et Cosmochimica Acta*, 238, 68–84. <https://doi.org/10.1016/j.gca.2018.07.007>
- Ghaisas, N. A., Maiti, K., & Roy, A. (2021). Iron-mediated organic matter preservation in the Mississippi River-influenced shelf sediments. *Journal of Geophysical Research: Biogeosciences*, 126(4), e2020JG006089. <https://doi.org/10.1029/2020JG006089>
- Jiang, Z., Liu, Y., Yang, J., Brookes, P. C., & Gunina, A. (2021). Rhizosphere priming regulates soil organic carbon and nitrogen mineralization: The significance of abiotic mechanisms. *Geoderma*, 385, 114877. <https://doi.org/10.1016/j.geoderma.2020.114877>
- Sirois, M., Couturier, M., Barber, A., Gélinas, Y., & Chaillou, G. (2018). Interactions between iron and organic carbon in a sandy beach subterranean estuary. *Marine Chemistry*, 202, 86–96. <https://doi.org/10.1016/j.marchem.2018.02.004>
- Wan, D., Ye, T., Lu, Y., Chen, W., Cai, P., & Huang, Q. (2019). Iron oxides selectively stabilize plant-derived polysaccharides and aliphatic compounds in agricultural soils. *European Journal of Soil Science*, 70(6), 1153–1163. <https://doi.org/10.1111/ejss.12827>
- Wang, D., Zhu, M. X., Yang, G. P., & Ma, W. W. (2019). Reactive iron and iron-bound organic carbon in surface sediments of the river-dominated Bohai Sea (China) versus the Southern Yellow Sea. *Journal of Geophysical Research: Biogeosciences*, 124(1), 79–98. <https://doi.org/10.1029/2018JG004722>
- Wilson, C. A., Cloy, J. M., Graham, M. C., & Hamlet, L. E. (2013). A microanalytical study of iron, aluminium and organic matter relationships in soils with contrasting hydrological regimes. *Geoderma*, 202–203, 71–81. <https://doi.org/10.1016/j.geoderma.2013.03.020>
- Ye, C., Bai, T., Yang, Y., Zhang, H., Guo, H., Li, Z., et al. (2017). Physical access for residue-mineral interactions controls organic carbon retention in an Oxisol soil. *Scientific Reports*, 7(1), 1–9. <https://doi.org/10.1038/s41598-017-06654-6>
- Ye, C., Chen, D., Hall, S. J., Pan, S., Yan, X., Bai, T., et al. (2018). Reconciling multiple impacts of nitrogen enrichment on soil carbon: Plant, microbial and geochemical controls. *Ecology Letters*, 21(8), 1162–1173. <https://doi.org/10.1111/ele.13083>
- Zhao, B., Yao, P., Bianchi, T. S., Shields, M. R., Cui, X. Q., Zhang, X. W., et al. (2018). The role of reactive iron in the preservation of terrestrial organic carbon in estuarine sediments. *Journal of Geophysical Research: Biogeosciences*, 123(12), 3556–3569. <https://doi.org/10.1029/2018JG004649>
- Zong, M., Lin, C., Li, S., Li, H., Duan, C., Peng, C., et al. (2021). Tillage activates iron to prevent soil organic carbon loss following forest conversion to cornfields in tropical acidic red soils. *Science of the Total Environment*, 761, 143253. <https://doi.org/10.1016/j.scitotenv.2020.143253>