The effect of iron on the preservation of organic carbon in marine sediments and its implications for carbon sequestration

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Abstract   Marine sediments are the most significant reservoir of organic carbon (OC) in Earth′s surface system. Iron, a crucial component of the marine biogeochemical cycle, has a considerable impact on marine ecology and carbon cycling. Understanding the effect of iron on the preservation of OC in marine sediments is essential for comprehending biogeochemical processes of carbon and climate change. This review summarizes the methods for characterizing the content and structure of iron-bound OC and explores the influencing mechanism of iron on OC preservation in marine sediments from two aspects: the selective preservation of OC by reactive iron minerals (iron oxides and iron sulfides) and iron redox processes. The selective preservation of sedimentary OC is influenced by different types of reactive iron minerals, OC reactivity, and functional groups. The iron redox process has dual effects on the preservation and degradation of OC. By considering sedimentary records of iron-bound OC across diverse marine environments, the role of iron in long-term preservation of OC and its significance for carbon sequestration are illustrated. Future research should focus on identifying effective methods for extracting reactive iron, the effect of diverse functional groups and marine sedimentary environments on the selective preservation of OC, and the mediation of micro-organisms. Such work will help elucidate the influencing mechanisms of iron on the long-term burial and preservation of OC and explore its potential application in marine carbon sequestration to maximize its role in achieving carbon neutrality.

Keywords   Marine sedimentary organic carbon, Reactive iron minerals, Iron-bound organic carbon, Selective preservation, Carbon sequestration

1.   Introduction

Marine sedimentary organic carbon (OC) is the principal storage system that extracts carbon from the atmosphere and buries it for long-term stability, serving as the largest OC reservoir in Earth's surface system (Hedges and Keil, 1995; Falkowski et al., 2000; Berner, 2003; Jiao et al., 2016).

Various factors affect the burial and preservation of marine sedimentary OC, including OC activity (Canfield et al., 1993; Asaoka et al., 2020), sedimentary dynamic processes (Keil et al., 1994; Lückge et al., 1996; Schubert and Stein, 1996; Goñi et al., 2005), oxygen exposure time (Suess, 1980; Hartnett et al., 1998; Burdige, 2007), and mineral protection (Müller and Suess, 1979; Hemingway et al., 2019; Cui et al., 2022). Among them, stable terrestrial OC input, high sedimentation rates, and short-term oxygen exposure are con-

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ducive to OC preservation, although these factors have noticeable regional constrains. Contrarily, as minerals and OC are the fundamental components of marine sediments, mineral adsorption and its protection of OC are widespread across various regions of the world's ocean (Lalonde et al., 2012). These aspects dominate the long-term preservation of OC (Hemingway et al., 2019), and are vital mechanisms for OC burial and geological storage.

Iron and clay minerals are the two most reactive minerals types in the marine environment, contributing significantly to the adsorption of OC (Mayer, 1994; Keil and Mayer, 2014). Compared with clay minerals, iron minerals are affected substantially by redox conditions, and the effect of iron on OC preservation varies noticeably across different marine environments. Additionally, iron cycling is intrinsically linked to the biogeochemical cycling of OC (Ma et al., 2018; Faust et al., 2021). Recently, the importance of the interaction between OC and minerals, particularly the interaction between OC and iron minerals, has attracted wide attention. Researchers have demonstrated that iron, acting as an "effective rusty carbon sink", effectively associate with sedimentary OC from various sources in the marine environment, enhancing OC burial and preservation in sediments (as shown in Figure 1) (Eglinton, 2012; Lalonde et al., 2012; Roy et al., 2013; Shields et al., 2016; Tagliabue et al., 2017; Zhao et al., 2018; Sun et al., 2020; Faust et al., 2021, 2023; Ma et al., 2022).

However, the mechanisms and capacities of iron oxide binding to OC are not uniform; they are affected by the species of iron oxide (e.g., goethite, hematite, and ferrihydrite), type of OC (e.g., polysaccharides and proteins), and

functional group (e.g., carboxyl, and hydroxyl), resulting in selective preservation of OC (Raiswell and Canfield, 2012; Keil and Mayer, 2014). On the other hand, reduced iron minerals, such as iron sulfides (e.g., mackinawite and pyrite), may also play a critical role in the long-term preservation of OC (Picard et al., 2019; Ma et al., 2022; Nabeh et al., 2022; Tétrault and Gélinas, 2022). In addition, microbial processes that utilize reactive iron minerals for respiratory metabolism significantly affect the preservation of sedimentary OC (Weber et al., 2006; Melton et al., 2014; Shi et al., 2016; Zhang et al., 2022). Therefore, understanding the effect and control mechanisms of iron on OC preservation in marine sediments is vitally important for the comprehension of the carbon burial capacity of the ocean, the associated long-term carbon storage mechanisms, and its role in dealing with climate change.

This review summarizes the methods for characterizing iron-bound OC in sediments, highlighting the influencing mechanisms of selective preservation and redox conditions on the association between reactive iron and OC. Besides, the article reviews the sedimentary records and controlling factors of iron-bound OC across various marine environments, and offers a perspective on potential future research directions.

2. Methods for characterizing iron-bound OC: From content to structure

Recent progress in characterization techniques such as spectroscopy, mass spectrometry, and electron microscopy,
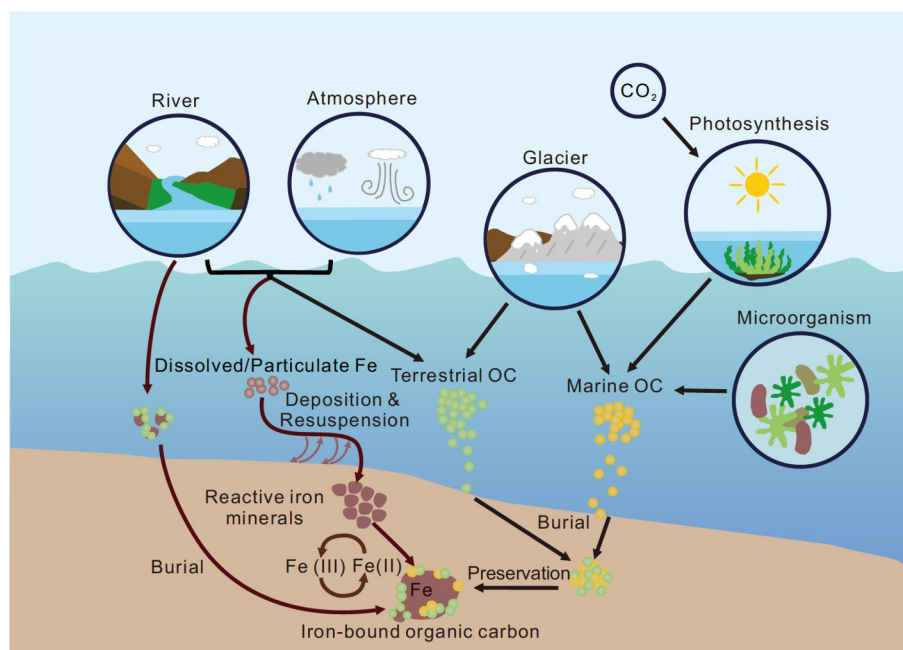
Figure 1 The effect and mechanism of iron on the burial and preservation of OC in marine environments (Raiswell, 2006; Lenstra et al., 2019; Fisher et al., 2020).

coupled with geochemical analytical methods, has significantly deepened our understanding of iron-bound OC in sedimentary environments. The iron content of marine sediments serves as the foundation for the preservation of iron-bound OC, and a higher iron content is generally accepted to provide more opportunities for OC to bind with iron (Boudot et al., 1989; Mikutta et al., 2014; Ma et al., 2018; Faust et al., 2021). Previously, colorimetric methods were typically used to determine the total iron content of sediments (Baas Backing and Moore, 1959). However, this method exhibited low sensitivity and high requirements for the sample matrix. Technological advances have led to the use of atomic absorption spectroscopy (AAS), X-ray fluorescence spectroscopy (XRF), inductively coupled plasma-atomic/optical emission spectroscopy (ICP-AES/OES), microwave plasma-atomic emission spectroscopy (MP-AES) (Jilbert et al., 2018; Sirois et al., 2018), and inductively coupled plasma-mass spectrometry (ICP-MS) to analyze the occurrence of iron in different media (Table 1) (Haese et al., 1997; Nickel et al., 2008; Gelting et al., 2010; Roy et al., 2013; Salvadó et al., 2015; Ma et al., 2018; Faust et al., 2020, 2021; Longman et al., 2021).

Currently, the citrate-bicarbonate-dithionite (CBD) treatment method is commonly employed to reduce iron oxides, thereby releasing the bound OC. Elemental analyzer-isotope ratio mass spectrometry is then used to determine the content and isotopic composition of OC in sediments before and after extraction, with the iron-bound OC content and isotopic composition calculated based on the difference. However, the CBD treatment method is applicable only to the extraction of iron oxide-bound OC and not to the extraction of iron sulfide-bound OC. Beyond iron minerals, clay minerals are the most abundant inorganic components that bind with OC in marine sediments. Future work should aim to identify more efficient experimental methods for the extraction of clay and iron mineral-bound OC separately or sequentially to enable the comprehensive evaluation of interactions between OC and minerals and their effect on OC preservation (Vosteen et al., 2022).

With the advancement of research, it has become evident that simple content determination cannot reflect the binding modes and existence states of reactive iron minerals and OC. Consequently, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are employed to characterize the crystal structure of various types of reactive iron mineral and the surface morphology of iron-bound OC (Ransom et al., 1997; Lalonde et al., 2012; Cismasu et al., 2016; Lv et al., 2016; Barber et al., 2017). Paired with energy dispersive spectrometry (EDS), these methods enable the observation of the morphology of iron-bound OC and component analysis, to provide a comprehensive understanding of the binding mechanism between OC and reactive iron minerals (Adhikari and Yang, 2015; Picard et al., 2019).

In addition to surface morphology, techniques such as Fourier transform infrared spectroscopy (FTIR), X-ray absorption spectroscopy (XAS), and Mössbauer spectroscopy can be utilized to characterize the internal structure of iron-bound OC (Table 1) and reveal the binding mechanisms between different types of OC and various reactive iron minerals. For instance, FTIR can offer insights into the characteristics and relative abundance of chemical groups (e. g., carboxyl, aromatic, and aliphatic) in OC (Lv et al., 2016). Recently, this method was used to characterize the surface sorption of polysaccharide-rich hydroxylated OC on mackinawite (FeS; Figure 2a) (Tétrault and Gélinas, 2022).

XAS can be divided into two parts: near-edge X-ray absorption fine structure spectroscopy (NEXAFS) and X-ray absorption near-edge spectroscopy (XANES). NEXAFS can aid the identification of the local structure of iron-bound OC, and distinction of various types of reactive iron mineral and OC (Charette and Sholkovitz, 2002; O'Day et al., 2004; Ma et al., 2022). For example, Picard et al. (2019) utilized it to investigate the association of FeS with microbial OC under anoxic conditions, determining that FeS principally associates with proteinaceous OC (Figure 2b). XANES, on the other hand, aids the determination of the valence of iron, the mineral type, and the three-dimensional structure of iron-bound OC (O'Day et al., 2004; Picard et al., 2019; Ghaisas et al., 2021). It has unique advantages for the analysis of variation in the Fe(II) or Fe(III) content of sediments under differing redox conditions (Figure 2c) (Ghaisas et al., 2021). In addition, Mössbauer spectroscopy plays an important role in characterizing the valence state, coordination number, distribution of iron ions in crystals, and magnetic properties of materials (Haese et al., 1997; van der Zee et al., 2003; Eusterhues et al., 2008; Zhai and Zhou, 2014; Jilbert et al., 2018; Zhao et al., 2018). Room-temperature ^{57}Fe Mössbauer spectroscopy has been used to estimate the relative proportions of Fe(II) and Fe(III) in samples and infer the occurrence states of iron minerals and their associations with OC in sediments [e.g., Fe(II) complex with organic matter and phosphates; Figure 2d] (Jilbert et al., 2018). Recently, a combination of scanning transmission X-ray microscopy (STXM) and NEXAFS spectroscopy was applied to analyze the mechanism of iron oxide-OC association and to simultaneously acquire the solid-phase occurrence characteristics of iron oxides and OC (Curti et al., 2021).

3. Selective preservation of OC by reactive iron minerals

The selective preservation of OC by reactive iron minerals hinges on various factors. On one hand, the distinct types of reactive iron mineral present in the ocean display considerable differences in particle size, specific surface area, and

Table 1   Methods used to characterize iron-bound OC in marine sediments

Content	Methods		Advantages	Disadvantages	References
Iron contents	Colorimetry		Simple operation; high-speed analysis	Low sensitivity; a high sample purity is required.	Baas Backing and Moore, 1959
	AAS		Lower detection limit; higher sensitivity	Limited identification of known elements	Nickel et al., 2008; Faust et al., 2020, 2021
	ICP-AES/OES		Mature technology; wide application	Sample destruction; complex pretreatment; inability to analyze isotopes	Haese et al., 1997; Gelting et al., 2010; Roy et al., 2013; Ma et al., 2018; Jilbert et al., 2018; Wang et al., 2019; Ghaisas et al., 2021
	ICP-MS		Lowest detective limit; satisfactory result; minor sample requirement	Poor salt tolerance; complex operation; generally used for standard measurement	Salvadó et al., 2015; Barber et al., 2017; Sirois et al., 2018; Zhao et al., 2018; Longman et al., 2021
	XRF		Simple pretreatment; low cost; wide application	Higher detection limit; it is limited to elements and cannot be applied to compounds.	Faust et al., 2020, 2021
	MP-AES		Lower cost than ICP-MS; no combustible gas	The detetctive limit is higher than that of ICP-MS.	Jilbert et al., 2018; Sirois et al., 2018
Surface morphology/ parameters of iron-bound organic carbon	TEM		Non-conductive sample; high resolution; ability to observe crystal structure	Complex pretreatment; the 3D perception is inferior to that of SEM.	Ransom et al., 1997; Lalonde et al., 2012; Barber et al., 2017
	SEM		Observation of surface morphology and change; 3D image	Lower resolution than TEM; conductive sample	Lv et al., 2016; Picard et al., 2019
	EDS		High-speed anlaysis; it conducts qualitative and untargeted quantitative analysis simultaneously.	Complex pretreatment; it is limited to obtain the contents of elements.	Adhikari and Yang, 2015; Picard et al., 2019
	BET method		Better accurancy; high recognition	long-term consumption	Mayer, 1994; Ransom et al., 1997; Keil and Cowie, 1999; Curti et al., 2021; Ma et al., 2022
Internal structure/ parameters of iron-bound organic carbon	FTIR		No sample destruction; assessment of the chemical bonds strength; identificaion of organic functional groups	Limited identification of species; inability to achieve quantitative analysis at the molecular level	Gu et al., 1994, 1995; Lv et al., 2016
	XAS	NEXAFS	Identification of the local structure and mineral species; measurement of bond length or coordination number	Complex pretreatment; interference of impurity; lower sensitivity	Charette and Sholkovitz, 2002; O'Day et al., 2004; Ma et al., 2022
		XANES	Identification of the element valence, mineral types, and the 3D structure of complexes		O'Day et al., 2004; Picard et al., 2019; Ghaisas et al., 2021
	Mössbauer Spectroscopy		No sample destruction; anti-interference	High-cost pretreatment with extremely low iron content; applicable to nuclei exhibiting a strong Mössbauer effect	Haese et al., 1997; van der Zee et al., 2003; Eusterhues et al., 2008; Jilbert et al., 2018; Zhao et al., 2018

crystallinity, all of which affect their reactivity and ability to bind and interact with OC. On the other hand, the type and functional group of OC also significantly affect its association with iron minerals.

From a mineralogical standpoint, reactive iron minerals in marine sediments comprise primarily amorphous iron hydroxides (e.g., ferrihydrite), various iron oxides (e.g., goethite, hematite, and magnetite), and iron sulfides (e.g., mackinawite and pyrite) (Haese et al., 1997; Raiswell and

Canfield, 2012) (Table 2). Studies suggest that the abundance of poorly crystalline minerals, particularly those characterized by surface hydroxylation (e.g., ferrihydrite), partly dictates the ability of mineral matrix to preserve OC (Kleber et al., 2005). Numerous studies have determined that nanogoethite is the dominant reactive iron phase in marine sediments (van der Zee et al., 2003) playing a crucial role in the association and preservation of OC (Ghaisas et al., 2021). Compared to goethite and hematite, ferrihydrite demon-
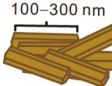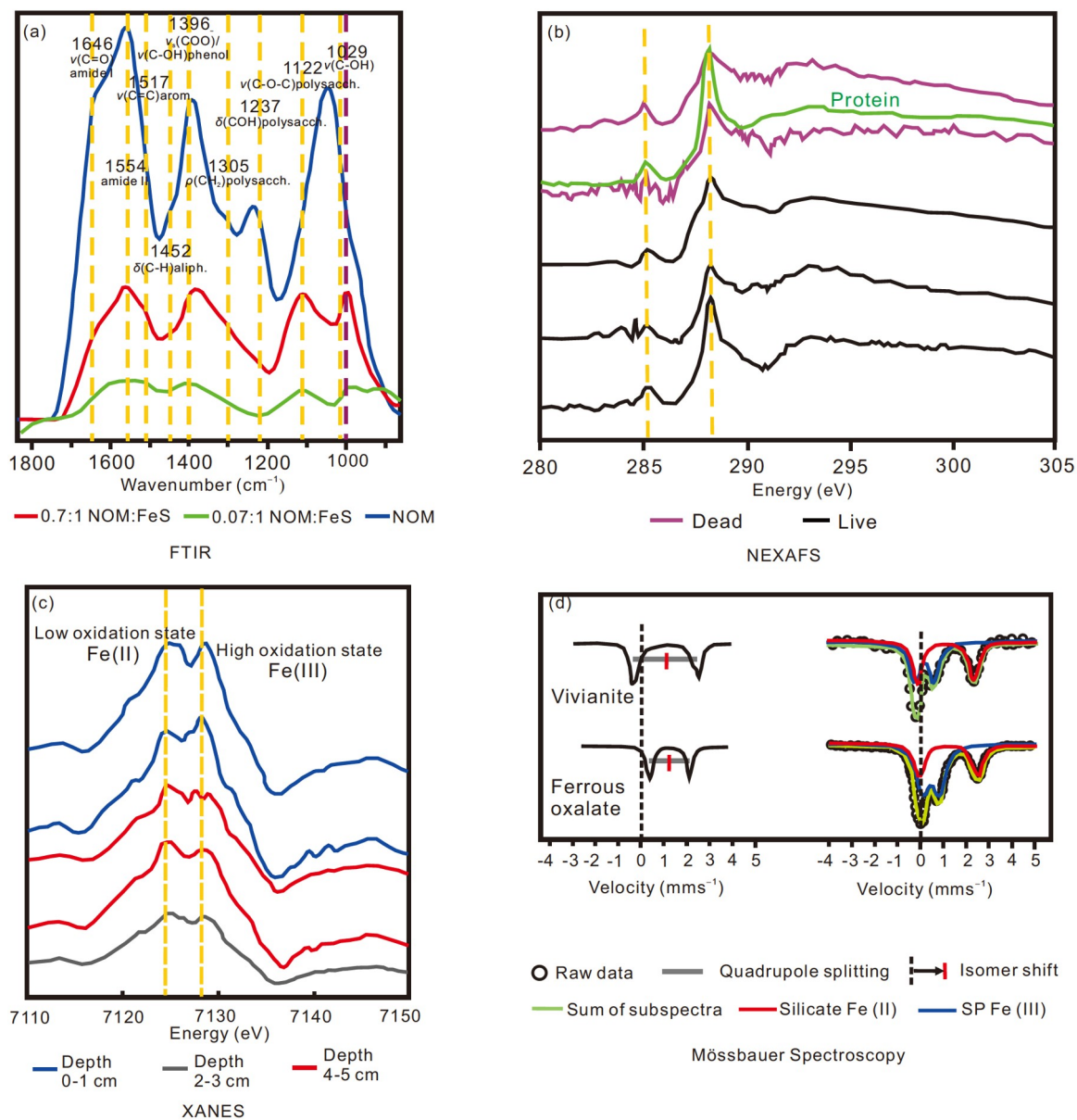
Figure 2 Representative spectra acquired with various methods for the characterization of iron-bound OC. (a) FTIR (Tétrault and Gélinas, 2022); (b) NEXAFS (Picard et al., 2019); (c) XANES (Ghaisas et al., 2021); (d) Mössbauer spectroscopy (Jilbert et al., 2018).

strates properties such as nanoscale particle sizes, high specific surface areas, and high reactivities (Kaiser and Guggenberger, 2000; Henneberry et al., 2012; Barber et al., 2014; Cismasu et al., 2016), making it more effective in adsorbing OC via ligand exchange and thus promoting its preservation. Beyond iron oxides, recent studies have demonstrated that iron sulfides, specifically FeS, possess the potential to stabilize and preserve OC under anoxic conditions (Picard et al., 2019; Wang et al., 2019; Ma et al., 2022). Generally, reactive iron minerals undergo transformation over time and under shifting environmental conditions. However, when associated with OC, FeS is less affected by mineral phase transformation and can effectively protect OC (Nabeh et al., 2022). This ability suggests the potential of iron sulfides to

stabilize and preserve OC in fluctuating environments.

Current research suggests that ligand exchange is the most important mechanism for the adsorption of OC by reactive iron minerals in marine sediments (Figure 3) (Parfitt et al., 1977; Gu et al., 1995; Adhikari and Yang, 2015). More specifically, ligand exchange involves the exchange of hydroxyl (e.g., carboxyl and phenolic hydroxyl) functional groups from OC with hydroxyl groups on iron oxides, leading to the formation of inner-sphere complexes (Bao et al., 2021). Besides, reactive iron minerals can also bind with OC through various adsorption mechanisms, including cation bridging and weak interactions (e.g., van der Waals forces, hydrophobic interactions, and hydrogen bonding) (Figure 3) (Arnarson and Keil, 2000; Keil and Mayer, 2014;
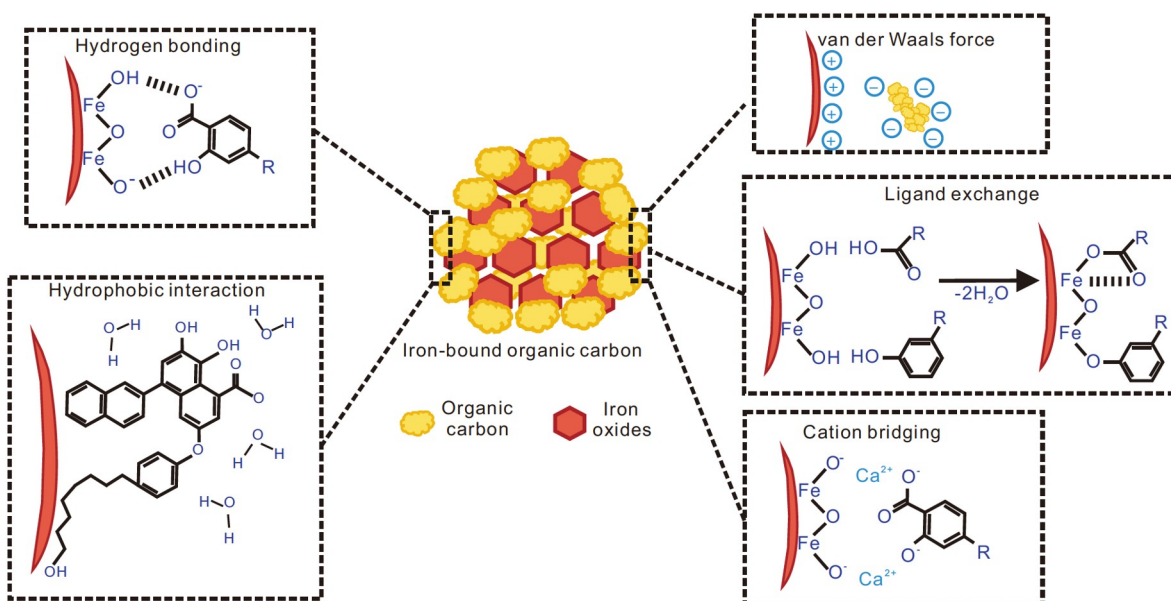
Table 2   Reactive iron minerals in marine sediments[a]

Mineral type	Molecular formula	Size and shape
Iron oxides	Ferrihydrite $Fe_4OH_8 \cdot 4H_2O$	~3–5 nm
	Goethite $\alpha\text{-FeOOH}$	100–300 nm ~50–100 nm
	Hematite Fe_2O_3	~50–100 nm
Iron sulfides	Mackinawite FeS	~5–10 nm
	Pyrite FeS_2	~3–5 nm

a) Li et al., 2014; Bolney et al., 2021; Kleber et al., 2021.

Lv et al., 2016; Yang et al., 2016). However, these binding mechanisms are comparatively weak and cannot guarantee the long-term stability of OC. In addition to adsorption at the iron mineral interface, OC can bind with reactive iron through multilayer adsorption. For example, Chen et al. (2014) found that when OC is saturated on the surface and in the pores of iron minerals, adsorption between OC molecules becomes dominant, offering a new focus for future research on adsorption mechanisms. Environmental changes in pH (Evans and Russell, 1959; Davis, 1982; Evanko and Dzombak, 1998; Filius et al., 2000; Wagai and Mayer, 2007) and temperature (Islam et al., 2020) significantly affect the ability of reactive iron minerals to adsorb and preserve OC. In particular, pH changes affect the adsorption of OC by altering the protonation of surface hydroxyl groups on iron

oxides. At lower pH, iron oxides are neutral or positively charged, making surface hydroxyl groups more prone to undergo ligand exchange with carboxyl and hydroxyl groups on OC. Conversely, at higher pH, the surfaces of iron oxides are negatively charged, with oxygen atoms tightly bound to iron, rendering ligand exchange reactions less likely (Evanko and Dzombak, 1998). Additionally, the adsorption of OC onto iron oxides generally increases with temperature (Islam et al., 2020). Although research on the adsorption mechanisms and capacities of iron minerals for OC under environmental influences has focused primarily on soil environments, these changes are also common in marine sediments. Therefore, future studies should explore iron mineral-OC binding mechanisms and capacities under various environmental conditions.

Among OC types, certain carbohydrates (e.g., polysaccharides) and proteins (including specific enzymes) can readily form inner-sphere surface complexes with iron atoms on mineral surfaces (Weisseborn et al., 1995; Wang et al., 1998). Experimental simulations carried out by Eusterhues et al. (2011, 2014) to examine associations between sugars and iron oxides, demonstrated that iron oxides preferentially bind with mannose and glucose through coprecipitation. This process slows degradation rate and forms coprecipitation products with non-crystalline structural characteristics, such as larger lattice spacings, fewer crystal planes, and smaller particles. However, their protective effect on OC is not as robust as that of adsorption products (Mikutta et al., 2014; Zhao et al., 2016; Chen and Sparks, 2018; Chen et al., 2020). Moreover, biogenic iron sulfide (FeS) has been observed to potentially protect proteins (Picard et al., 2019; Nabeh et al., 2022). In addition to carbohydrates and proteins, terrestrial lignin derivatives containing aromatic carbon and phenolic

Figure 3   Adsorption mechanisms of iron-bound OC in marine sediments (Philippe and Schaumann, 2014; Bao et al., 2021).

acids in sediments can be preferentially adsorbed by reactive iron minerals. This process forms a substrate conducive to the accumulation of more terrestrial OC (Shields et al., 2016; Zhao et al., 2018).

The binding of different types of OC with reactive iron minerals is related to functional groups, such as carboxyl and aromatic carbon, which are more easily preserved by iron (Gu et al., 1995; Reiller et al., 2006; Keiluweit and Kleber, 2009; Lv et al., 2016). Curti et al. (2021) found that an increase in the number of carboxyl groups enhances their ligand exchanges on the surface of iron oxides, thereby improving the effectiveness of iron oxides in preserving OC. Sowers et al. (2019) found that bacteriogenic iron oxides selectively stabilize various aromatic and carboxyl carbons. Upon the reduction of iron oxides in soil, aromatic carbon in the complexed organic matter is released more easily and aliphatic carbon is better preserved (Adhikari and Yang, 2015). Recent studies have revealed that ferrihydrite and goethite also selectively preserve carboxyl carbon (Ma et al., 2022); goethite, in particular, is more inclined to preserve active polysaccharide-rich natural OC, while displaying weaker preservation of carboxyl-rich aromatic materials in lignin degradation products (Tétrault and Gélinas, 2022). Terrestrial OC entering the sea usually contains more carboxyl and aromatic carbon, which is more easily adsorbed on the surfaces of reactive iron minerals (Kaiser and Guggenberger, 2000; Zhao et al., 2016; Dicen et al., 2019). Overall, current research on the selective preservation of OC functional groups remains insufficient and has consisted primarily of laboratory simulation experiments. Future research efforts should focus on the analysis of actual samples to better understand the influence of differences in OC functional groups on its selective preservation.

4. The effect of redox processes on the preservation of iron-bound OC

Iron, being a multivalent element, plays vital roles in balancing primary productivity and degrading OC (Zhang et al., 2023). The supply of iron significantly regulates the oceanic carbon cycle, and redox processes linked to iron crucially effect on the preservation of iron-bound OC. In oxygenated bottom waters, iron exists predominantly in its oxidized state [Fe(III)] (Martin, 1990). Conversely, in pore-water of sediments, iron is present primarily as Fe(II), which migrates into the redox interface (i.e., the sediment interface making the transition from an anoxic to an oxic environment) through sedimentary processes and pore water movement, subsequently coprecipitating with OC (Hedges et al., 1997; Bianchi, 2011; Henneberry et al., 2012; Riedel et al., 2013; Lv et al., 2016; Linkhorst et al., 2017). The frequent shifts in the redox environment at the interface can foster the asso-

ciation between reactive iron and terrestrial OC, and limit the delivery of specific types of terrestrial OC into the ocean (Riedel et al., 2013). Poorly crystalline Fe(III)-containing iron minerals, such as ferrihydrite, in sediments can adsorb or coprecipitate with OC. These processes result in the formation of OC-Fe(III) oxide complexes (Figure 4), which can retard or inhibit their own aging into crystalline iron minerals (e.g., hematite and goethite) (Cornell and Schwertmann, 1979) while concurrently preserving OC. During the transition from an oxidizing environment to a reducing setting, ferrihydrite bound to OC ages and reduces to form iron carbonate minerals and sulfides. During this transformation, the composition and quantity of OC also undergo significant alterations. The relative proportion of reduced carbon forms (e.g., aromatic, olefinic, and aliphatic carbon) diminishes gradually while that of amide/carboxyl functional groups increases (Cismasu et al., 2016). For example, in estuary and nearshore sediments, periodic redox cycles may occur due to frequent physical reworking, causing the continuous disruption of the association between iron oxides and OC, decomposition of OC, and preservation of predominantly older terrestrial OC. Simultaneously, the iron oxides undergo continuous aging, leaving behind mainly minerals of high crystallinity (e.g., hematite) (Zhao B et al., 2023). On the Eurasian Arctic Shelf, where permafrost is melting, reactive iron minerals associate mainly with older terrestrial OC (Salvadó et al., 2015).

Aside from preserving OC, iron can act as an electron shuttle for oxygen and OC in sediments (Burdige, 1993). For example, under anaerobic conditions, Fe(III) serves as an electron acceptor for the metabolism of glucose and other organic compounds (Lovley, 1991) (Figure 4). The resulting reduced state [Fe(II)] is mobile. Upward-migrating Fe(II) is oxidized by O_2 and NO_3^-, and continues to associate with OC in the form of reactive iron minerals, a process more common in nearshore sediments with vigorous sedimentary hydrodynamics (Canfield et al., 1993; Aller, 2004). However, this swift iron redox cycle may inhibit the association of iron oxides with OC, leading to intermittent OC release (Adhikari et al., 2016; Zhao et al., 2018). For instance, simulation experiments performed by Chen et al. (2020) revealed that iron oxides hinder OC mineralization under static oxic conditions only when exogenous iron and OC are supplied concurrently. When Fe(II) is added alone, the iron oxides formed by oxygen content fluctuations fail to protect OC.

On the other hand, Fe(II) may react with hydrogen sulfide (H_2S) in the sulfate reduction zone to form iron sulfides (Figure 4) (Wijsman et al., 2002; Huang and Wang, 2009; Liu and Yan, 2011). Meanwhile, sulfate reduction can effectively mineralize OC (Jørgensen, 1982; Nickel et al., 2008; Friese et al., 2021). Mackinawite (FeS) can form stable complex with OC through adsorption and coprecipitation, facilitating OC storage in anoxic environments (Picard et al.,
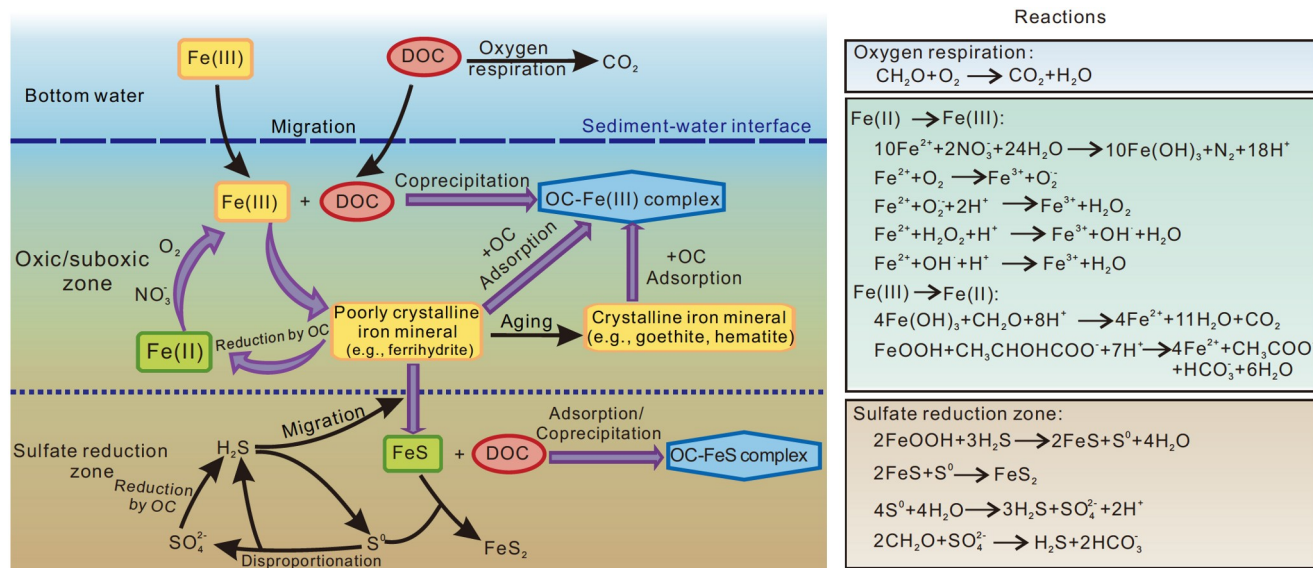
Figure 4 The interplay between iron redox and OC cycling. The reaction schemes are adapted from Zabel and Horst (2000).

2019). This becomes a significant "black sink" for OC re-sequestration (Ma et al., 2022). Simulation experiments have demonstrated that the association of Fe(III) with reducible natural organic matter protects Fe(III) from being oxidized to Fe(II) (Daugherty et al., 2017; Wang et al., 2019; Chen and Thompson, 2021). However, in natural anoxic sediments, reduced iron predominantly exists as pyrite (FeS_2), which is relatively more stable than mackinawite. Currently, research on the association between pyrite and OC is limited (Tribovillard et al., 2022). The two are known to be positively correlated in reducing marine environments (Berner, 1984; Liu et al., 2021), which may be related to microbial sulfate reduction processes. Similarly, microbially mediated processes may be among the critical aspects to be explored in future studies on OC-iron complexation (Melton et al., 2014).

## 5. Sedimentary records of OC bound to iron in diverse marine environments

By binding with reactive iron, OC in various marine environments can be preserved over long durations (Longman et al., 2022) and documented in the sedimentary record. Figures 5 and 6 show the global distribution and distribution in different marine environments, respectively, of the fraction of iron-bound OC to total OC [f_{Fe-OC} (%)]. Research has shown that river deltas are hotspots for iron-bound OC sink in marine environments, and these complex hydrodynamic environments can speed up the iron redox cycle (Blair and Aller, 2012; Zhao et al., 2018). However, this process is not favorable for the binding of reactive iron and OC (Zhao B et al., 2023), especially in certain mobile mud environments,

where frequent sediment resuspension and movement can hasten iron cycling and accompany the remineralization and decomposition of sedimentary OC (Yao et al., 2014; Xu et al., 2015; Zhao et al., 2018; Song et al., 2022), leading to decreases in OC burial and preservation efficiency. In other environments, such as anoxic zones and deep sea sedimentary environments, where iron cycling is weaker, iron-bound OC can remain relatively stable over extended periods (Lalonde et al., 2012). Globally, the key factors determining f_{Fe-OC} in marine sediments are not the iron and total OC contents, but the sedimentary regimes, OC source, and composition of reactive iron (Zhao B et al., 2023).

Numerous studies have been carried out to examine the iron-bound OC deposition records in the sedimentary environments of coastal estuaries and deltas. Research conducted on the Mississippi River Wax Lake Delta revealed that even in rapidly evolving sedimentary systems, approximately 15% of OC is directly bound to reactive iron, underscoring the crucial role of reactive iron in long-term atmospheric carbon storage (Shields et al., 2016). In a study examine the role of reactive iron in long-term carbon sequestration in mangrove sediment, Dicen et al. (2019) found that the unique pore water conditions and sponge-like characteristics of the mangrove forest floor led to the association of about 15% of reactive iron with OC in the sediment. They suggested that mangrove sediment act as a "giant rusty sponge" for OC (Dicen et al., 2019).

The sedimentary records of iron-bound OC in various continental shelf environments have been examined extensively. A study of surface sediments in the East China and South Yellow Seas revealed that the availability of total OC and reactive iron plays a decisive role in determining the content of iron-bound OC. However, the sediment f_{Fe-OC} is
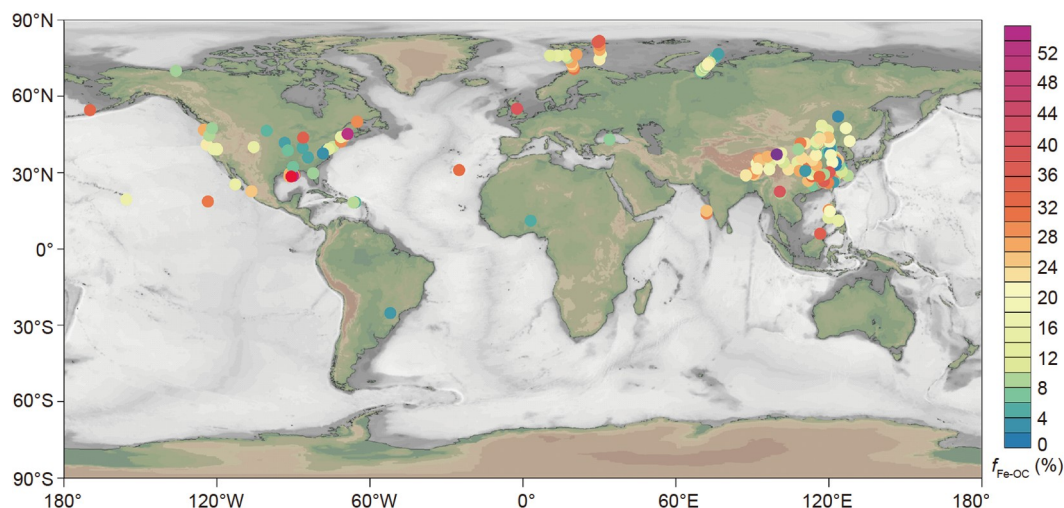
Figure 5 The global distribution of the fractions of iron-bound OC to total OC [f_{Fe-OC} (%)] (Zhao B et al., 2023).
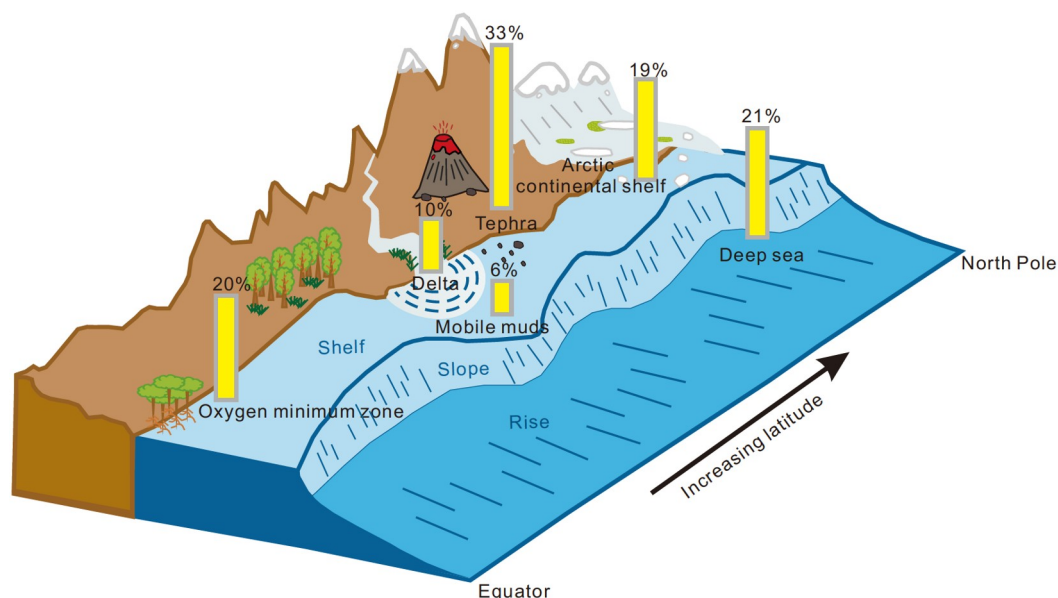
Figure 6 The fractions of iron-bound OC to total OC [f_{Fe-OC} (%)] in different marine environments (Bianchi et al., 2018; Zhao B et al., 2023).

governed primarily by the iron redox cycle (Ma et al., 2018). Recent research also indicates that f_{Fe-OC} in different sedimentary environments, such as those of the Yangtze River estuary, South Yellow Sea, and Okinawa Trough do not exhibit significant depth-related changes. This finding suggests that deep reduction processes have minimal effect on the overall stability of iron-bound OC, or even enhance the burial and preservation of OC in marginal seas on a centennial scale (Sun et al., 2020). The distribution of iron-bound OC in modern sediments on the northern Gulf of Mexico Shelf also demonstrate no substantial seasonal or depth-related alternation (Ghaisas et al., 2021). In addition, studies of iron-bound OC in sediments on the East and West Siberian Shelves in the Arctic suggest that the release of

permafrost carbon associated with reactive iron due to climate warming diminishes the decomposition or emission of permafrost carbon into the atmosphere. This factor mitigates the feedback effect of permafrost carbon on Arctic climate warming to certain extent (Salvadó et al., 2015). On a millennial scale, even under the suboxic surface sediments in the Barents Sea, about 19% of total OC remains bound to reactive iron. The substantial input of reactive iron from land does not directly affect f_{Fe-OC}, and coprecipitation at the redox interface is not the primary factor controlling the formation of iron-bound OC (Faust et al., 2021). Moreover, even under conditions with higher fractions of terrestrial OC, fresh marine OC preferentially and rapidly associates with reactive iron (Faust et al., 2023).

On a longer timescale, stable iron-bound OC (constituting up to 33% of total OC) has been identified in tephra depositions dating back over 700,000 years ago (Figure 6). This finding suggests that reactive iron serves as a long-term carbon sink for OC across diverse environments (Longman et al., 2021). The most recent assessment indicates that the global rate of iron-bound OC burial in marine sediments is approximately 52 Mt C yr^{-1}. This rate underscores the importance of reactive iron minerals in the OC burial in the ocean, which forms a carbon sink that is relatively stable over geological timescales (Longman et al., 2022) and could have remarkable responses and feedback effect on global carbon cycling, climate change, and human activities. In addition, earlier studies revealed a close relationship between the ocean's redox conditions and the geochemical cycling of iron throughout geological history, with notable interactions with biological evolution (Anbar and Knoll, 2002; Lyons et al., 2018). For example, the significant increase in iron oxide reservoirs in the Neoarchean correlates well with the rise in atmospheric oxygen content during the same period (Lyons et al., 2014). Such findings may further indicate the role of iron oxides in enhancing OC burial during the evolution of atmospheric oxygen. The ocean-atmosphere oxidation of pyrite in sediments into iron oxides may further facilitate the OC burial, thereby creating a positive feedback mechanism. Thus, the enhancement of OC burial by iron oxides due to changes in the redox state during geological history may have significantly impacted the atmospheric oxygen content and influenced alternations in the marine carbon cycle (Zhao M et al., 2023). These insights highlight the important role of iron cycling in relation to ocean redox conditions at different geological timescales in the marine carbon cycle (Rothman et al., 2003; Lyons et al., 2014, 2021). They have important implications for understanding the geological evolution and carbon sink of the marine biological carbon pump from the perspective of Earth system and sphere interactions (Xie et al., 2022).

6.   Summary and future perspectives

Iron, as a key element in the biogeochemical cycle of marine organisms, greatly affects the preservation of OC in sediment. Research on the processes and controlling mechanisms of this effect is essential for the enhancement of our understanding of the ocean's capacity to sequester carbon and its subsequent climate and environmental impacts. The methods used to characterize reactive iron-OC complexes have evolved from initial spectral qualitative and mass spectrometric quantitative analyses to high-resolution microscopy and synchrotron radiation analysis to determine surface binding characteristics, mineral crystal structure, and internal complex features. Studies have shown that reactive iron

minerals (iron oxides and iron sulfides) selectively preserve OC, with their adsorption capacity significantly affected by the various environments. OC containing protein, polysaccharide, carboxyl, and aromatic carbon groups is more readily preserved by reactive iron. Redox conditions and microbial activity enhance the preservation of OC by iron, but under certain conditions they can also promote its degradation, preferentially associating terrestrial OC in a turbulent oxidizing-reducing environment. Sedimentary records from diverse marine environments illustrate that reactive iron holds substantial potential for the long-term preservation of OC, and the relationship between ocean redox conditions and the iron geochemical cycle is closely tied to geological history. This finding is significantly important for the understanding of the preservation of OC by iron and its role as a carbon sink. Moving forward, the following areas may need further consideration:

(1) As we refine our understanding of iron-bound OC, more effective experimental methods should be developed to distinguish the OC bound to clay and iron minerals and to separate and quantitatively estimate different OC adsorption states. Emphasis should be placed on the understanding of how functional groups, sedimentary environments, and redox conditions affect the selective preservation of OC by reactive iron. It is essential to transit research from laboratory simulations to field studies of natural samples, and emphasize on the role of iron sulfides in the preservation of OC.

(2) The differentiation of abiotic and microbially-mediated iron redox processes and evaluation of their overall contributions to the preservation or degradation of OC associated with reactive iron are needed. It is vital to strengthen research on the burial efficiency and long-term preservation of iron-bound OC in different sedimentary environments, and further assess the evolution of ocean carbon burial capacity and its climate effects. Environmental factors play important regulatory roles in the adsorption of OC by iron, therefore, based on the perspective of interaction of iron-OC-environment, comparative studies of the mechanisms of iron-bound OC and its effect on the OC burial efficiency and long-term preservation in different sedimentary environments OC should be enhanced. Such work will lay the foundation for the evaluation of the evolution of oceanic carbon burial capacity and its controlling mechanisms.

(3) An understanding of the geological evolution and carbon sequestration function of the marine biological carbon pump from the perspective of Earth system and lithosphere interactions requires further research on mineral processes, especially those of iron oxides, that promote the preservation and carbon sequestration pathways involved in OC burial. A deepening of our understanding of the forms, mechanisms, and geological fate of mineral-bound organic matter in the ocean is necessary. It is also crucial to carry out

in-depth research on the effect of iron-related mineral processes on the ocean carbon sink during geological history and related climate-environmental effects.

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