



Interactions between organic matter and Fe oxides at soil micro-interfaces: Quantification, associations, and influencing factors

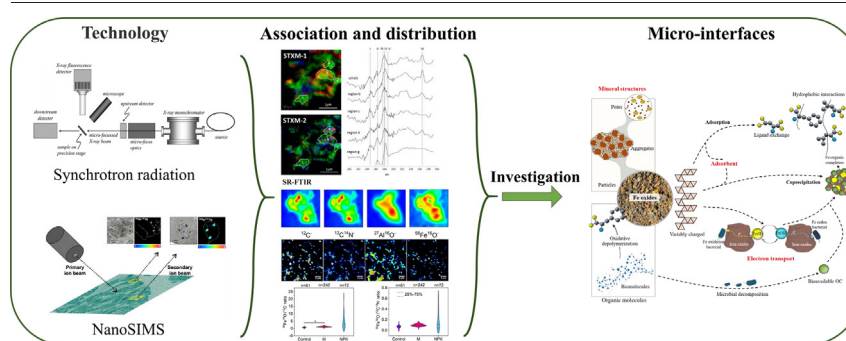


Qi Li, Weifang Hu, Linfeng Li, Yichun Li *

Guangdong Key Laboratory of Nutrient Cycling and Farmland Conservation, Guangzhou 510640, China

GRAPHICAL ABSTRACT

- The mechanisms and processes related to OM transformation dynamics occurring at mineral-organic interfaces is complex.
- Functional and spatial complexity need to be considered in soil environments where Fe-OC interactions occur.
- Multiple combinations of technology provide *in situ* molecular interactions between Fe oxides and OC at soil micro-interfaces.



ABSTRACT

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Influential factors

Iron (Fe) oxides are widely recognized to prevent the degradation of organic matter (OM) in environments, thereby promoting the persistence of organic carbon (OC) in soils. Thus, discerning the association mechanisms of Fe oxides and OC interactions is key to effectively influencing the dynamics and extent of organic C cycling in soils. Previous studies have focused on i) quantifying Fe oxide-bound organic carbon (Fe-OC) in individual environments, ii) investigating the distribution and adsorption capacity of Fe-OC, and iii) assessing the redox cycling and transformation of Fe-OC. Furthermore, the widespread application of high-tech instrumentation and methods has greatly contributed to a better understanding of the mechanism of organic mineral assemblages in the past few decades. However, few literature reviews have comprehensively summarized Fe-OC distributions, associations, and characteristics in soil-plant systems. Here, studies investigating the Fe-OC contents among different environments are reviewed. In addition, the mechanisms and processes related to OM transformation dynamics occurring at mineral-organic interfaces are also described. Recent studies have highlighted that diverse interactions occur between Fe oxides and OC, with organic compounds adhering to Fe oxides due to their huge specific surfaces area and active reaction sites. Moreover, we also review methods for understanding Fe-OC interactions at micro-interfaces. Lastly, developmental prospects for understanding coupled Fe-OC geochemical processes in soil environments at molecular- and nano-scales are outlined. The summary suggests that combined advanced techniques and methods should be used in future research to explore micro-interfaces and in situ descriptions of organic mineral assemblages. This review also suggests that future studies need to consider the functional and spatial complexity that is typical of soil/sediment environments where Fe-OC interactions occur.

* Corresponding author at: Institute of Agricultural Resources and Environment, Guangdong Academy of Agricultural Sciences, Guangzhou 510640, China.
E-mail address: vichunli@gdaas.cn (Y. Li).

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1. Introduction

The vast majority of organic carbon (OC) in the biosphere is predominantly present at solid earth interfaces in close spatial proximity to minerals (Paustian et al., 2016; Kramer and Chadwick, 2018; Churchman et al., 2020; Grant et al., 2022). Consequently, carbon (C) flowing through the biosphere will inevitably contact mineral surfaces as it is subjected to diverse transformations inherent to carbon turnover, and organic-mineral phases interactions have been the subject of scientific investigation for many years. For example, the majority of soil organic carbon (SOC) is associated with colloidal-sized minerals (Kleber et al., 2015; Lugato et al., 2021; Georgiou et al., 2022), leading to early suggestions that these associations are crucial for soil fertility and plant nutrients and, by extension, ‘vital to health’ (Burgeon et al., 2021; Cui et al., 2022; Gerke, 2022). Furthermore, scientific studies have increasingly focused on sequestering superfluous atmospheric carbon by soils (Yu et al., 2021; Ye et al., 2022), resulting in in-depth research into the mechanisms that govern the formation, strength, and stability of organic-mineral assemblages (Chen and Thompson, 2021; Kleber et al., 2021). Thus, understanding the interactions between organic matter (OM) and Fe oxides at soil micro-interfaces is critical for OC sequestration applications and the projection of future climate scenarios.

Numerous studies have investigated OC sequestration in soil systems to understand the mechanisms and drivers of OC stability (Chen et al., 2014a; Hicks Pries et al., 2017; Kögel-Knabner, 2017; Lehmann et al., 2020; Angst et al., 2021). Traditionally, the formation of chemical compounds resistant to microbial degradation has been assumed to be particularly important for soil organic matter (SOM) stabilization. However, these persistent humic substances do not appear to form based on available evidence (Dungait et al., 2012; Lehmann and Kleber, 2015). Rather, increasing evidence points to the significance of organo-mineral assemblages in protecting OM, in addition to blocking OM, leading to the physical inaccessibility of microbial activity (Hemingway et al., 2019; Kopittke et al., 2020; Kleber et al., 2021; Lugato et al., 2021; Rowley et al., 2021). Organo-mineral associations form via surface interactions between OM and minerals, and critically influence the provisioning and accumulation of nutrients in soils (Kögel-Knabner et al., 2008; Kleber et al., 2015; Jilling et al., 2018; Xue et al., 2019a), as well as the stabilization and binding of OC. The persistence of mineral-associated organic matter (MAOM) has been attributed to the ability of OM to form strong chemical bonds with minerals, as well as its physical protection within microaggregates or co-precipitates

(Tamrat et al., 2019; Possinger et al., 2020; Burgeon et al., 2021; Liu et al., 2021). Once OM is initially associated with minerals, soil structural characteristics (e.g., aggregate formation and stability in addition to the percentage of large pores) can further isolate and compartmentalize OM from decomposing organisms, while also limiting oxygen (O₂) diffusion, thereby further protecting SOM from decomposition (Asano and Wagai, 2014; Totsche et al., 2018). These dynamics result in slower MAOM turnover than particulate OM (Poeplau et al., 2018; Cotrufo et al., 2019), and may also explain the estimated residence times of MAOM ranging from centuries to millennia (Schmidt et al., 2011). Nevertheless, the complex nature of both mineral and organic phases has hindered the investigation of organo-mineral assemblages and their roles in stabilizing OC.

Iron (Fe) minerals are associated with a large portion of MAOM via adsorption or co-precipitation and form refractory organic-mineral complexes (Wagai and Mayer, 2007; Zhao et al., 2016) that can serve as efficient ‘rusty sinks’ that increase the stability of OC and represent an important mechanism of OC storage (Shields et al., 2016; Han et al., 2019; Duan et al., 2020; Che et al., 2021). Adsorption on Fe oxide surfaces primarily occurs due to ligand exchange of the organic groups, such as the hydroxyl and carboxyl groups (Wiseman and Püttmann, 2006; Kida and Fujitake, 2020). Co-precipitation occurs when another substance precipitates by inclusion, occlusion, or adsorption when the pH and/or redox potential changes (Wagai and Mayer, 2007; Fritzsche et al., 2015; Possinger et al., 2021). In comparison to adsorption, co-precipitation results in higher soil C content (~130 mg g⁻¹ C difference) (Chen et al., 2014b). Furthermore, considering the same C/Fe ratio, the co-precipitation of Fe-OC is more difficult than adsorbed Fe-OC (Mikutta et al., 2014; Zhang et al., 2022). Chemical functional groups in certain compounds may be responsible for binding iron oxides and forming a highly stable organic carbon pool with long turnover times, while other compounds may exist in aggregate pores as particulate OM (Adhikari and Yang, 2015; Adhikari et al., 2016; Kleber et al., 2021). The distribution, adsorption capacity and molecular composition of OC on Fe oxides have been abundantly investigated in recent studies within both, artificial composites, as well as natural samples.

Different OM forms may exhibit fine-scale differences at the nanometer scale, making determining their chemical species challenging (Lehmann et al., 2008; Dwivedi et al., 2019; Sharma et al., 2021). In turn, if there are systematic differences among OM forms variably located in soil matrix, only investigating the forms of OM in the whole soil or not identifying specific spatial localizations of individual biopolymer types will lead to

loss of important information. Thus, instrumental analysis methods have been extensively used for investigating spatial heterogeneity of soil Fe-OC associations at the fine-scale. For example, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), scanning transmission X-ray microscopy (STXM), and nano-secondary ion mass spectroscopy (NanoSIMS) offer valuable insights into OC associations with Fe oxides at soil micro-interfaces (Li et al., 2018; Qu et al., 2019; Li et al., 2020; Li et al., 2022a; Yu and Liu, 2022). Nevertheless, these analytical techniques have low detection limits and soil samples have high homogeneity. Furthermore, the extremely low and uneven levels of OC adsorbed on diverse soil components, necessitating high-resolution analytical instruments.

To evaluate OC behavior in multi-component soil systems, numerous analytical techniques including chemical and spectroscopic approaches, have been abundantly used and expanded. Yet, these analytical techniques are very expensive and provide limited information at the molecular- and nano-scale, particularly for natural soils with low OC concentrations (Schlüter et al., 2018; Hu et al., 2020; Li et al., 2022b). These individual methods, therefore, cannot be applied in large-scale practical applications. The interaction between OC and Fe oxides at micro-interfaces has not been systematically summarized. Hence, the current knowledge of the sequestration of OC by Fe oxides at micro-scale interfaces is outlined in this review. Additional discussion is also devoted to target research areas involving the influences of soil properties and environmental factors on Fe-OC. Furthermore, advanced analytical methods for exploring the micro-interfaces and in situ characteristics of OC and Fe oxides are also discussed.

2. Associations of Fe oxides and OC

2.1. Storage of Fe-associated OC

Iron oxides have consequently been widely observed to play important roles in preserving OC in soils (Zhao et al., 2016; Ma et al., 2018). Nano-scale Fe oxides are redox sensitive and have a strong affinity for OC (Coward et al., 2017; Xue et al., 2019b; Krause et al., 2020), leading to the formation of stable Fe-OC assemblages that can permanently exist for thousands of years. These particles have high surface area-to-volume ratios and easily bind OC and increase its stability (Mueller et al., 2017; Hall et al., 2018). The maximum sorption capacity of Fe oxides for naturally occurring OC is 0.14 g OC g⁻¹ Fe oxide (Tipping, 1981; Kaiser and Guggenberger, 2007), which is higher than that of montmorillonite by approximately one order of magnitude (Chorover and Amistadi, 2001). Recent quantitative characterizations revealed that 6.2–31.2 % of SOC was trapped by Fe oxides in 12 arable soils (Wan et al., 2019), and 19.5 ± 12.3 % of SOC was bound to Fe oxides in the Qinghai-Tibet Plateau permafrost, China (Mu et al., 2016; Fang et al., 2019; Table 1). Patzner et al. (2020) showed that OC is primarily associated with reactive Fe in the transition region between organic and mineral horizons (9.9–14.8 % of the total SOC) across a thaw gradient in Abisko (Sweden). As much as 40 % of the total C in a given soil may be associated with Fe oxides based on selective extractions, indicating a significantly important role of Fe-OC in regulating biogeochemical C cycles (Mikutta et al., 2014; Zhao et al., 2016; Ye et al., 2022; Zhang et al., 2022).

2.2. Fe-OC association mechanisms

The importance of ligand exchange between OM and reactive Fe has been recently highlighted in the stabilization of OM in marine sediments. Specifically, marine researchers have adapted an Fe reduction method previously used in soils (Mehra and Jackson, 1958; Wagai and Mayer, 2007), revealing that approximately 21 % of OC is directly associated with reactive Fe oxides and trapped as a result of its interaction with Fe in the Mexican and Indian margins, the Southern Ocean, the St. Lawrence estuary and gulf, and the Black Sea (Lalonde et al., 2012). Subsequent research further demonstrated that 26–63 % of the total reactive Fe is bound to OC directly through inner-sphere complexations via ligand exchange in coastal sediments (Barber et al., 2017). These OM-Fe interactions may likely lead

Table 1

Percentage of Fe-OC to OC in natural soil and sediment environments.

Site or type	Percentage of Fe-OC to OC	Reference
Discontinuous permafrost region in Sweden	9.9–14.8 %	Patzner et al., 2020; Patzner et al., 2022
Peatlands in China	1.64–5.94 %	Huang et al., 2021a
Mangrove soils in the Philippines	~15 %	Dicen et al., 2019
Changjiang estuary sediments in China	7.4 ± 3.5 %	Zhao et al., 2018
Marine sediments in Mexican and Indian margins, the Southern Ocean, the St. Lawrence estuary and gulf, and the Black Sea	21.5 ± 8.6 %	Lalonde et al., 2012
Permafrost soils in northern Alaska	13.68 ± 2.31 %	Joss et al., 2022
Permafrost soils in the Qinghai-Tibetan Plateau	19.5 ± 12.3 %	Mu et al., 2016
Meadow soils in the Qinghai-Tibetan Plateau	4.1–25.6 %	Mu et al., 2020
Saanich, Arabian Sea, Mexican margin, and St. Lawrence estuary	25.7–62.6 %	Barber et al., 2017
Tibetan alpine grasslands in China	15.8 ± 12.0 %	Fang et al., 2019
East China Sea sediments	2.77–31.5 %	Ma et al., 2018
Arable soils in China	6.2–31.2 %	Wan et al., 2019
Forest soils in the USA	37.8 %	Zhao et al., 2016
Wax Lake Delta sediments in the USA	~15.0 %	Shields et al., 2016

to long-term OM preservation in marine sediments due to strong and irreversible inner-sphere complexation. Similarly, reactive Fe plays important roles in OM stabilization in estuarine sediments (Peter and Sobek, 2018; Zhao et al., 2018). Shields et al. (2016) observed that approximately 15.0 % of OC integrated with reactive Fe oxides in the Wax Lake Delta sediments in the USA. Following these studies, Dicen et al. (2019) reported for the first time that Fe-OC accounted for approximately 15 % of the OC pool in mangrove soils, corroborating similar results in estuarine and marine sediments. These findings are contrary to intuitive expectations because ligand exchange is inhibited by sulfate (SO₄²⁻) that is abundant in seawater (0.03 M), and because Fe can be reductively dissolved as Fe(II) in reducing environments, resulting in interrupted Fe-OC interactions (Chen et al., 2020; Huang et al., 2020a; Yu and Kuzakov, 2021). Under natural conditions, these Fe oxides and OC interactions must actually be irreversible to explain the persistence of reactive OC, since reversible binding ultimately results in the solubilization of OC, eventually leading to its biodegradation and enzymatic hydrolysis. However, the long-term stability of these Fe-OC interactions in the face of global environmental change has not been thoroughly explored and requires further investigation.

As a sorbent and structural component in soil, Fe may increase soil C storage by reducing OM availability to extracellular enzymes and heterotrophic microorganisms (Kleber et al., 2015; Totsche et al., 2018; Jeewani et al., 2021a; Song et al., 2022; Fig. 1). Fe(III) can behave as a connective cement to couple minerals and OM together into nano-, micro-, and macro-aggregates (Barral et al., 1998; Asano et al., 2018; Rabot et al., 2018; Totsche et al., 2018). In addition, OM has the potential to adsorb or co-precipitate with Fe minerals or its surface coatings (Kleber et al., 2015; Adhikari et al., 2019; Bao et al., 2021). Adsorption and co-precipitation experiments confirmed that Fe oxides are preferentially able to associate organic functional groups or compounds of dissolved organic carbon (DOC) (Eusterhues et al., 2014; Han et al., 2019). A generally recognized mechanism for the formation of MAOM is through adsorption or co-precipitation via dissolved organic matter (DOM) from plant or microbial origin (Roth et al., 2019) with existing and de novo minerals (Kaiser and Guggenberger, 2003; Chen et al., 2014b; Adhikari et al., 2019). The molar ratio of C and Fe points to the dominance of co-precipitation over adsorption as the primary process that controls associations of Fe oxides and OC (Wagai and Mayer, 2007; Mikutta et al., 2014; Han et al., 2019). The molar ratio of C and Fe serves as an indicator of the association mechanism of OC and Fe oxides. An OC:Fe molar ratio >1.0 suggests dominant sorption effects, whereas a ratio of >6–10 implies the dominance of co-precipitation or complexation interactions (Wagai and Mayer, 2007; Wang et al., 2017). Duan et al. (2020) found that the molar ratios of C

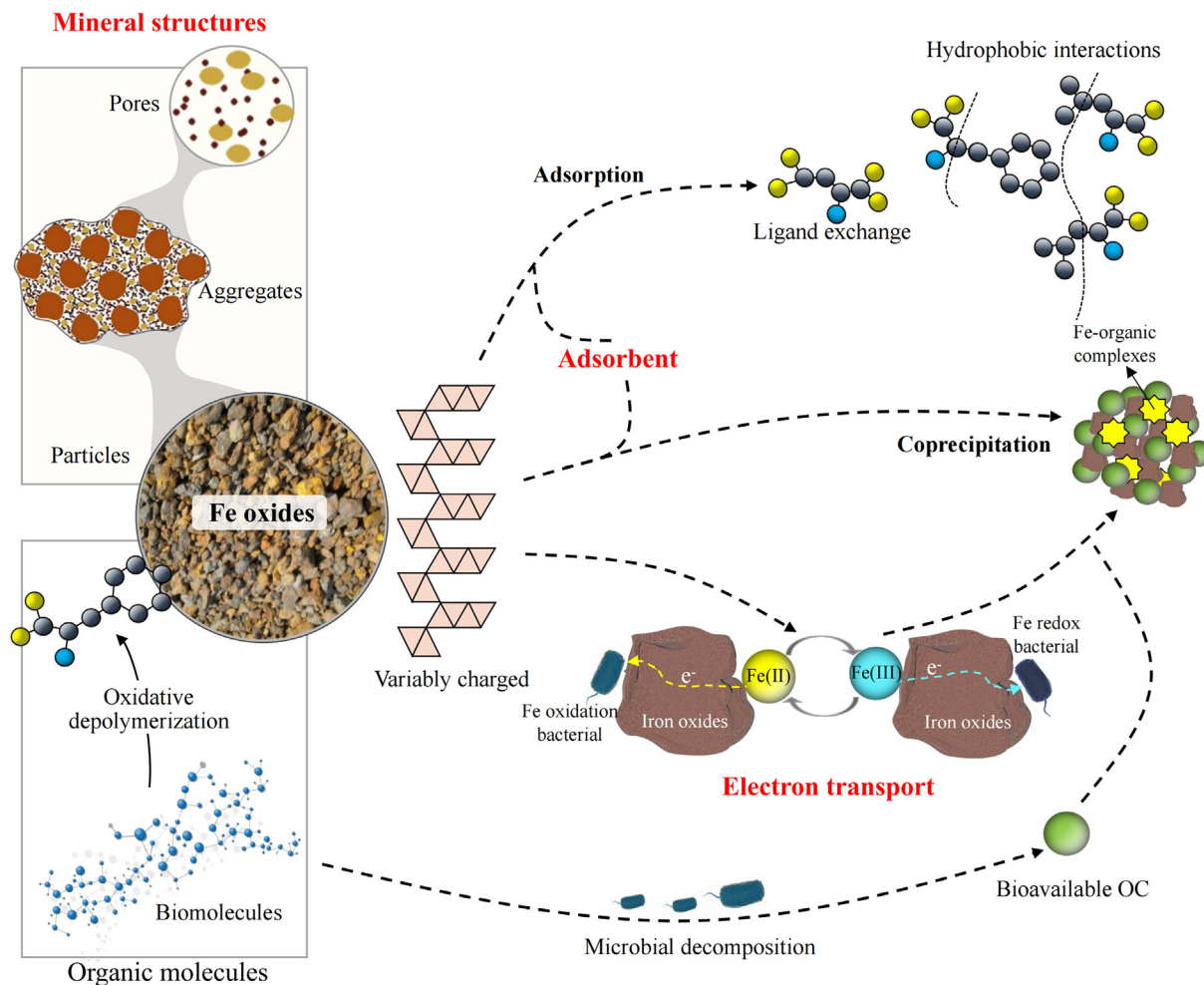


Fig. 1. The association process of Fe oxides and OC at the soil micro-scale interfaces. Mineral interfaces occur at various spatial scales and topography in soils, where diverse, primarily low-molecular-weight, amphiphilic organic ligands may reach solid–solution interfaces. Once proximal, ligands can bind to mineral surfaces through one or multiple complexation mechanisms that are based on structural reactivity, adsorbing dynamics, and electron transport.

and Fe in wetland rhizosphere soils ranged from 8 to 11, indicating that Fe oxides protect OC in these soils primarily via co-precipitation (Wan et al., 2019). Recently, Zong et al. (2021) also reported that soil amorphous Fe oxides directly promoted SOC accumulation, which may be attributable to two mechanisms related to aggregation and association. First, Fe oxide concentrations in soils affect the conversion of SOC, because Fe oxides contribute to soil aggregate formation (Zhang et al., 2018). Because of their larger surface areas, aggregates can absorb and combine more readily with OC to form OM-complexed (Fe_p), which is a primary driver of Fe migration and transformations in soils (Wiesmeier et al., 2019). Second, Fe oxides in soils form strong chemical bonds that adsorb DOC. These processes lead to co-precipitation as insoluble organic compounds (Wang et al., 2018), in addition to flocculation and decreasing the surface area available for OM adsorption (Six et al., 2004; Oloibiri et al., 2017), representing critical mechanisms of SOM preservation. Nevertheless, additional research is required to explore the chemical characteristics of associated OC to determine its refractory characteristics and lability.

2.3. Effects of Fe on OC sequestration and Fe-OC on the immobilization of trace elements

Fe plays dual roles as a terminal electron acceptor for microbial OC mineralization and as chemical protection against degradation when associated with OC (Mejia et al., 2018; Kappler et al., 2021). Redox processes, wherein Fe(III) accepts electrons from microorganisms or

electron shuttles (De-Campos et al., 2012; Wang et al., 2017; Bai et al., 2021) or Fe(II) donates electrons to diverse oxidants like O_2 , NO_3^- , or H_2O_2 (Poggenburg et al., 2018; Chen et al., 2020; Yu and Kuzyakov, 2021), are especially observed in paddy soils or anaerobic compartments within soil aggregates (Xu et al., 2019; Li et al., 2021; Joss et al., 2022). A extremely important pathway of MAOM formation is the oxidation of Fe(II) to Fe(III) at redox interfaces, followed by its rapid hydrolysis to short-range-ordered (SRO) Fe(III) oxides that co-precipitate with DOM (Riedel et al., 2013). Anoxic solutions containing Fe(II) may facilitate this reaction whenever they come into contact with O_2 , such as in aggregates of upland soils at redox potential gradients or in periodically flooded soil horizons (Cismasu et al., 2011; Keiluweit et al., 2017). In addition, dissimilatory Fe reduction by the bacterium, *Shewanella oneidensis* MR-1, has been shown to liberate C from its associated forms (Pan et al., 2016). In anoxic environments, microbial-mediated Fe reduction is the primary mechanism of Fe reduction that can decrease dissolved or solid Fe(III) to Fe(II) while coupling the oxidation of organic compounds substances (Honetschlagerová et al., 2018; Su et al., 2020; Kirsten et al., 2021). Microbial Fe reduction only changes the forms and distributions of Fe and OM in environments, but also considerably impacts the migration and transformation of phosphorus, arsenic, cadmium, manganese, and certain organic contaminants (Lee et al., 2012; Ventura et al., 2015; Dai et al., 2018; Herndon et al., 2019). In most cases, the accumulation and stabilization of SOM by Fe in soils is the result of combined abiotic and biotic processes. Therefore, to understand Fe-OC relationships, microbially-mediated processes and

functions must be considered, since these can significantly affect OC transformation, storage, and cycling in soil environments.

In ternary systems of Fe oxide, OM, and metal, OM negatively affects the metal's adsorption onto Fe oxides by forming soluble metal-OM complexes that are resilient to precipitation or compete with metals for reactive surface sites (Tang et al., 2014; Du et al., 2018). For example, Xue et al. (2019a) showed that the co-precipitation of HA with ferrihydrite decreased both As(III) and As(V) adsorption because HA reduced the available adsorption sites at the ferrihydrite surfaces and generated a higher negative surface charge that was unfavorable for negatively charged As(III) and As(V) to be sorbed by positively charged ferrihydrite. Moreover, Du et al. (2021a) suggested that Cd-As co-adsorption behaviors on ferrihydrite-organocomposites are different from those on pure minerals, and the presence of bacteria/HA can significantly affect metals speciation, distribution, and ternary interactions. The adsorption capacity of metals by Fe-OM associations cannot solely be shown by the sum of the adsorption capacity of the two pure phases (Du et al., 2018), and both the solution condition and OM species are factors that affect metal adsorption. Overall, the interactions between Fe oxides and OM are supposed to play critical roles on the migration and fate of metals in natural environments by changing the structure and surface properties of Fe oxides or by competing with metals for adsorption sites (Verbeeck et al., 2017; Xue et al., 2019a; Du et al., 2020).

2.4. Molecular composition of Fe-OC

OC speciation reflects the ecological properties of SOM (Schmidt et al., 2011; Cotrufo et al., 2015) and the influences of organo-Fe oxide interactions (Chassé et al., 2015). Specific OC components (O/N-alkyl C and O-alkyl C groups of polysaccharides) are preferentially stabilized by associations with Fe oxides (Schöning et al., 2005; Spielvogel et al., 2008). Fe oxide surfaces or co-precipitates are rich in aliphatic C derived from microbial lipids and amide C groups from bacterial proteins (Keiluweit et al., 2012). In comparison to hematite-bound aromatic organic compounds, aliphatic-Fe complexes exhibit greater resistance to reductive dissolution (Adhikari and Yang, 2015). Moreover, amorphous ferrihydrite has been shown to preferentially adsorb aromatic and carboxylic compounds (Adhikari et al., 2017; Mejia et al., 2018; Han et al., 2019), while crystalline hematite preferentially stabilizes aliphatic compounds in humic acids (Adhikari et al., 2016). The differing affinities of SOM functional groups towards Fe oxides may critically affect OC stabilization. Investigating the mechanisms underlying organo-mineral interactions between specific organic compounds and Fe oxides is an important future research area.

To investigate the molecular composition of Fe-OC, Huang et al. (2021a) examined the isotopic composition of Fe-OC, observing that Fe-OC was comparatively enriched in ^{13}C in most peat soils, consistent with other results from central and eastern Chinese arable soils (Wan et al., 2019), forest soils from the USA (Zhao et al., 2016), and sediments from Mexican and Indian margins, the Southern Ocean, the St. Lawrence estuary and gulf, and the Black Sea (Lalonde et al., 2012). Natural organic compounds that are enriched in O and N, like proteins and carbohydrates, are particularly depleted in ^{13}C , while lipid fractions are comparatively enriched in ^{13}C (Wang et al., 1998; Six et al., 2001; Schnecker et al., 2016). Likewise, an isotopic analysis of specific compounds has indicated that ^{13}C -enrichment in compounds like cellulose, hemicellulose, and amino acids that are oxygen- and nitrogen-rich (Glaser, 2005). Organic compounds enriched in nitrogen and oxygen are beneficial for forming inner-sphere complexes with Fe oxides (McKnight et al., 1992; Lalonde et al., 2012). Studies have found that deep peat contains significant amounts of protein and carbohydrate compounds (Segnini et al., 2013; Tfaily et al., 2014). Incorporating protective mechanisms with minerals may lead to the production of the aforementioned complexes. Laboratory studies have indicated that Fe oxides are preferentially associated with terrestrial lignin-derived OC compared to labile polysaccharide-derived OC because lignin-derived OC contains more carboxylic and aromatic C that readily complex with reactive Fe (Kaiser and Guggenberger, 2000; Zhao et al., 2018). Thus, relatively unstable compounds could be bound

to Fe oxides via adsorption and/or co-precipitation that would improve their chemical stability, further implicating the importance of Fe oxides in OC sequestration.

Co-precipitation models based on the 'layer-by-layer onion' theory suggest that preferentially-protected aromatic groups shape the initial inner layer of the 'onion' through strong specific interactions with Fe oxides, thereby providing an absorbing surface to enable association of phenolic and aliphatic compounds and forming alternating layers in Fe-OC colloids (Sollins et al., 2006; Yu et al., 2017; Han et al., 2019; Duan et al., 2020; Zhang et al., 2021). Herein, upon the reduction of dissimilatory Fe, the entire outer layer consisting of phenolic and aliphatic compounds is released from the inner layer containing Fe oxides and bound aromatic compounds. Consequently, aromatic groups remain exposed on the surface of the Fe oxides, as observed in other cases (Mikutta et al., 2014; Poggenburg et al., 2018; Han et al., 2019). The Fe(III)-bearing minerals thus significantly influence the order where the multi-layer complex liberates OC compounds. For example, hematite-OC complexes release aromatic OC faster than ferrihydrite-OC complexes when Fe(III) is reduced (Adhikari and Yang, 2015; Adhikari et al., 2017).

3. Effects of environmental factors on Fe-OC

In addition to C composition, the stability of soil Fe-OC generally depends on the environmental conditions being considered, which may lead to the difference of Fe-OC association and biological sources (Fig. 2). Initial decomposition rates of plant residues roughly reflect their bulk chemical compositions, while environmental conditions likely determine the stability of Fe-OC residence times that vary from decades to millennia (Schmidt et al., 2011; Dungait et al., 2012; Minasny et al., 2017; Zong et al., 2021). Studies of soils have focused on OM stabilization for many years, leading to the identification of common mechanisms underlying OM stabilization in these respective environments.

3.1. Redox conditions

Redox state is an important environmental factor that controls the Fe-OC distribution across sediment and paddy soil environments (Zhao et al., 2017; Yu et al., 2019; Chen et al., 2021). OC binds to Fe(III) oxides under oxic conditions that then promote aggregation and sedimentation of the complex (Lalonde et al., 2012; Giannetta et al., 2022), protecting it from microbial degradation (Young et al., 2008; Zhong et al., 2017; Angst et al., 2021). However, this Fe(III)-bearing OC pool can also be reactivated under anoxic conditions by reductively dissolving Fe and simultaneously releasing OC (Han et al., 2019; Ma et al., 2022). Interestingly, OC can be released by reducing Fe oxides, breaking down Fe-OC associations (Adhikari and Yang, 2015; Chen and Sparks, 2015). Because the associations between Fe-OC may be reversible, Fe reduction caused by microorganisms is triggered by the supply of labile marine OC and may stimulate terrestrial OC release (Linkhorst et al., 2017). In addition, a recent study in a boreal estuary demonstrated that the flocculation of Fe and terrestrial OC was decoupled during sedimentation, leading to labile Fe accumulation that exists in the form of ferrihydrite and Fe-OC complexes (Jilbert et al., 2018). Furthermore, OM precipitates on Fe oxide surfaces (Riedel et al., 2013), forming highly stable Fe-OC assemblages that are extremely recalcitrant under anaerobic or intermittent anaerobic conditions (Huang et al., 2021a; Wang et al., 2021). However, the exterior portion of the Fe-OC assemblage structures loosely attached to the mineral matrix preferentially degraded upon long-term exposure to aerobic environments, resulting in an extremely low molar ratio of OC:Fe (Lalonde et al., 2012; Melton et al., 2014).

OC bound to Fe oxides is liberated under oxygen-limited conditions as a consequence of dissimilatory Fe reduction mediated by Fe reducing bacteria (Arnason and Keil, 2007; Pan et al., 2016). A recent isotope experiment confirmed these observations, demonstrating that Fe(III) protected OC by preventing microbial access to OC, while increasing mineralization of SOC and DOC by 32–41 % and 74 %, respectively, under anaerobic conditions (Chen et al., 2020). Fe oxides do not intrinsically protect OM due to

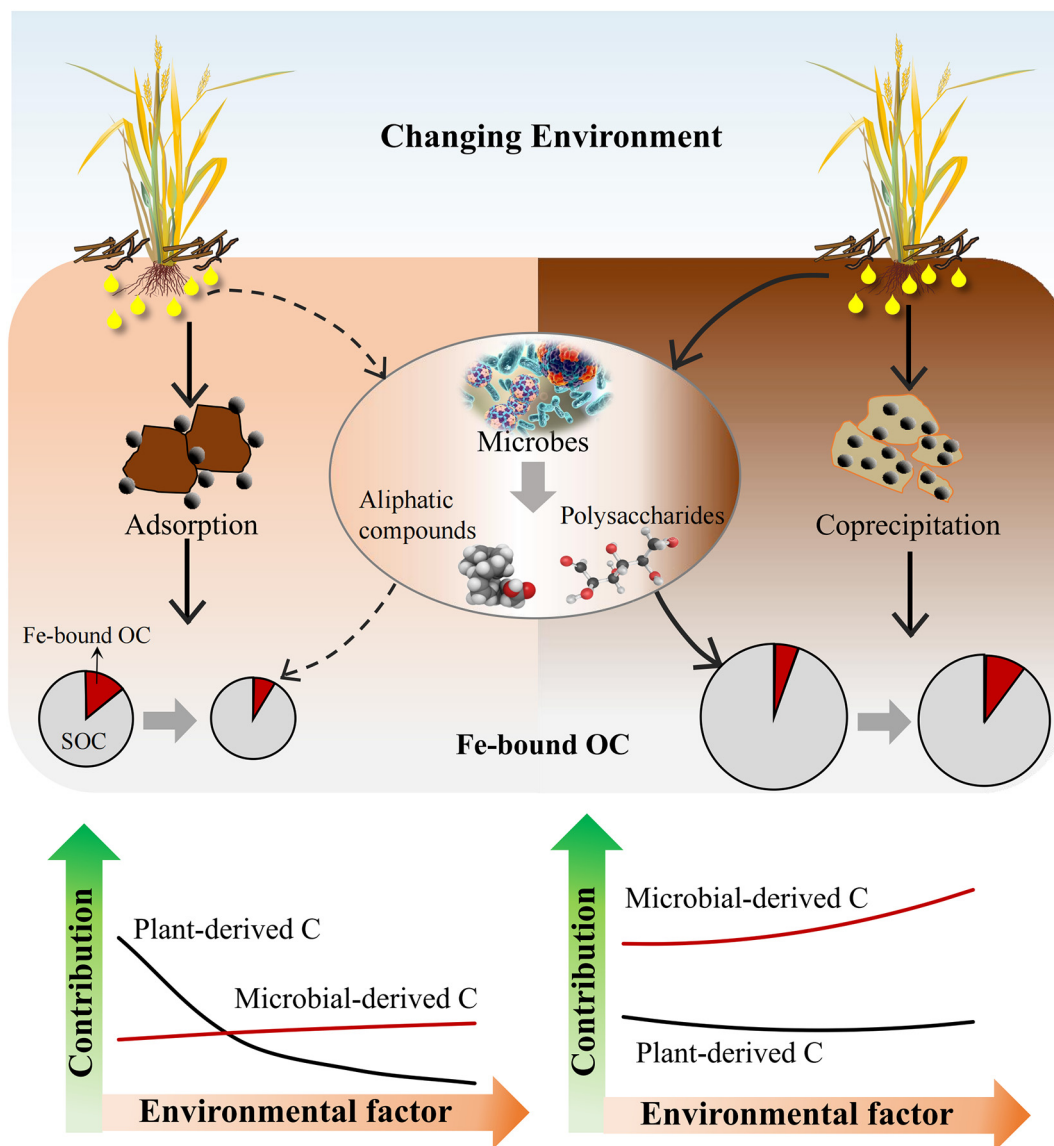


Fig. 2. The potential impact of changes in the environmental factors on the Fe-OC association (adsorption or coprecipitation) and biological sources (plant-derived C or microbial-derived C).

periodic oxygen limitation in humid soils. Rather, reactive Fe phases need their own physicochemical protection to facilitate the persistence of OM. Thus, given the dual role of iron phases in accelerating and inhibiting OM decomposition, biological and geochemical contexts are important for elucidating the turnover of Fe-associated OC due to climate change (Chen et al., 2020; Patzner et al., 2020). Consequently, redox conditions are critical controlling factors of Fe-OC distribution across sediment and paddy soil systems (Zhao et al., 2017; Yu et al., 2019; Chen et al., 2021; Giannetta et al., 2022). Overall, additional studies are required to better clarify these associations of Fe-OC in soils and sediments, especially in highly dynamic systems.

3.2. Freeze thaw

The release of large amounts of OC during high-latitude permafrost thawing will likely contribute to positive feedbacks during climate change. Several studies in permafrost systems have already demonstrated poorly crystalline Fe-OC associations or successfully synthesized them in the lab, identifying its recalcitrance to microbial or chemical reduction (Henneberry et al., 2012; Eusterhues et al., 2014; Coward et al., 2018).

During permafrost thaw, water-logging and oxygen limitation result in reducing conditions and increased abundances of Fe(III)-reducing bacteria that facilitate mineral dissolution and drive Fe and C turnover along thaw gradients (Patzner et al., 2020; Patzner et al., 2022). The presence of terminal electron acceptors leads to the rusty OC sink being readily disrupted along permafrost thaw gradients and the inhibition of OC capture as thaw occurs. In addition, freeze-thawing promotes the transformation of labile Fe oxides into more stable forms (Su and Wang, 2013; Wu et al., 2022). The reactive Fe contents and proportions of poorly crystalline Fe phases are low. As discussed above, it is necessary for Fe(III) phases to exhibit their own physical and chemical protection to ensure OM persistence, and the existence of OM itself can either increase or decrease the stability of Fe(III) minerals, depending on the geochemical conditions (Jones et al., 2009; Chen et al., 2020). However, the presence and extent of reactive Fe phases in redox-dynamic permafrost soils remains unclear, as does their contribution to soil OM persistence. To better predict future greenhouse gas emissions from thawing permafrost soils and improve the accuracy of existing climate models, further investigation is needed to examine Fe(III) reduction rates, the direct contributions of permafrost thaw to CO₂ emissions, and competition with other microbial processes.

3.3. Temperature

Reactive Fe oxides generally have differing thermodynamic properties and reactivities based on their crystal structures (Lv et al., 2016; Hall et al., 2018; Grant et al., 2022). In peatlands, temperature significantly affects TOC and Fe-OC concentrations. Temperature exhibits a positive and linear correlation with TOC and Fe-OC in these environments (Huang et al., 2021a). These results differ from those found in agricultural and

forest soils, where no significant linear relationships were observed between temperature and TOC, Fe-OC, reactive Fe (Zhao et al., 2016; Wan et al., 2019). These differences can be explained by varying characteristics of diverse ecosystems. First, heat and moisture directly influence the generation and growth of peat. Consequently, temperature plays an important role in the emergence and growth of peatlands (Ise et al., 2008; Friesen et al., 2021), and accordingly influences the physicochemical properties of peat soils. Second, differences might be attributed to the various sources of

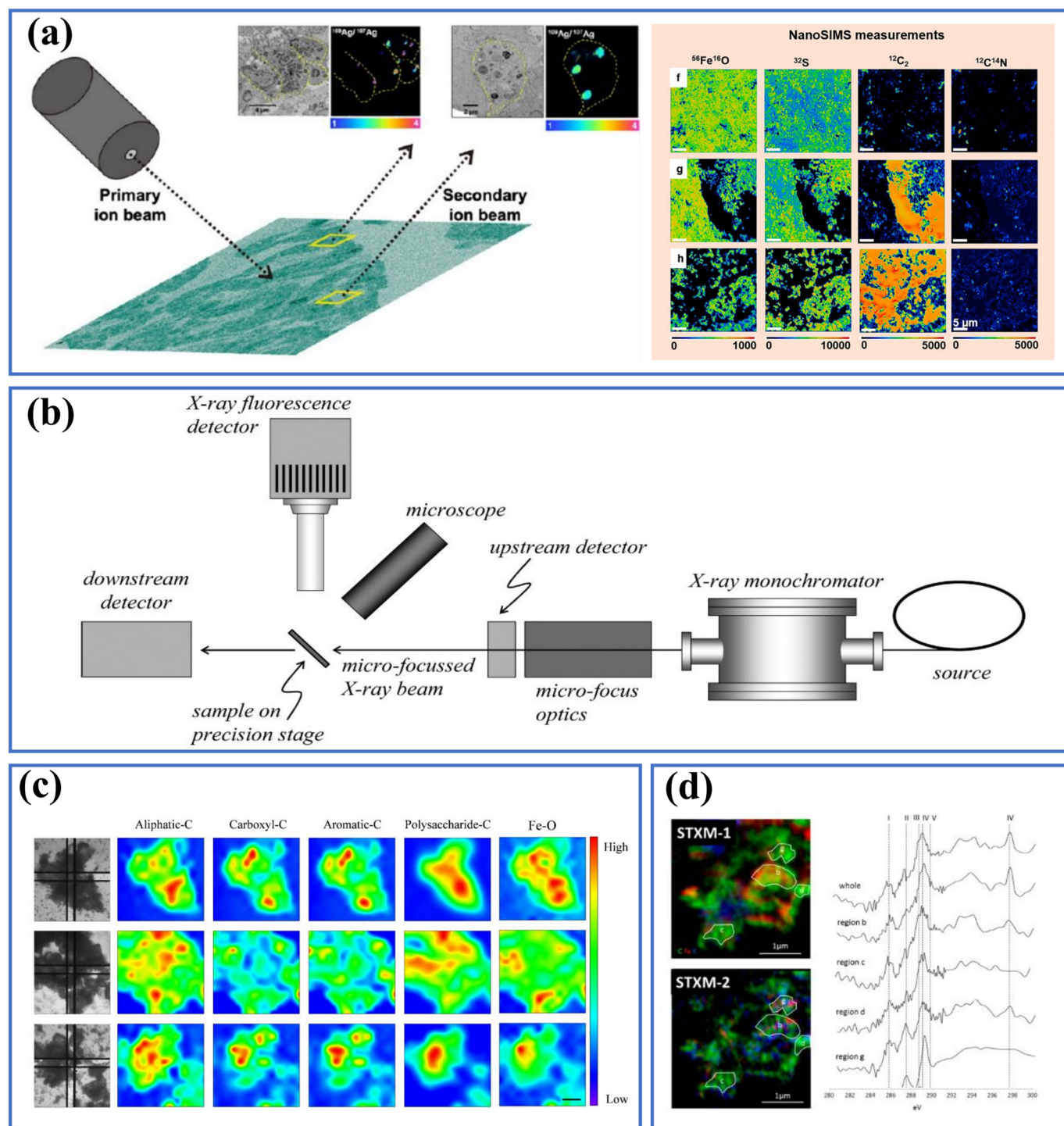


Fig. 3. (a) Schematic overview for mass spectrometry imaging of samples using dynamic SIMS (Shao et al., 2020) and NanoSIMS measurements of $^{12}\text{C}^{14}\text{N}$, ^{32}S , $^{12}\text{C}_2$, and $^{56}\text{Fe}^{16}\text{O}$ (Pohl et al., 2021), (b) Highly simplified and schematic view of the apparatus for conducting X-ray imaging experiments (Pushie et al., 2014), (c) SR-FTIR images showing the distribution of aliphatic C, carboxyl C, aromatic C, polysaccharide C, and Fe-O compounds in soils (unpublished data), (d) STXM-based C 1s NEXAFS analysis of selected regions within an aggregate and that of model compounds (Asano et al., 2018).

Fe minerals that could affect the crystal structures of Fe oxides that depend on temperature (Zhao et al., 1994; Amelung et al., 1997; Schwertmann et al., 1999; Nguyen et al., 2019; Wu et al., 2019). For example, amorphous ferrihydrite can bind greater levels of carbon than other crystalline Fe oxides due to their huge specific surfaces area and active reaction sites in addition to their greater adsorption capacity (Kaiser et al., 2007; Cismasu et al., 2016; Huang et al., 2021a). As a result of temperature changes, Fe oxides can be transformed from amorphous to crystalline forms (Schwertmann et al., 1999; Nguyen et al., 2018), in turn affecting the Fe-OC content. Third, temperature can affect soil OC content and its chemical composition (Amelung et al., 1997; Rovira et al., 2008; Liu et al., 2019). Fe minerals associate with aromatic and carboxyl compounds more readily than other OC components (Gu et al., 1995; Swenson et al., 2015; Adhikari et al., 2017; Mejia et al., 2018; Han et al., 2019). Consequently, changes in soil OC composition can result in different Fe-OC concentrations. The combined effects of temperature on Fe mineral phase transition and OC turnover yields a general relationship summarizing the temperature-dependence of Fe-OC. This implies that temperature indirectly affects Fe oxide mineral properties. Nevertheless, further research is needed to demonstrate their coupled mechanisms.

4. Methods for understanding Fe oxides and OC interactions at micro-interfaces

Identifying the role of Fe-OC in soil functioning and evaluating the intricate pathways leading to its presence in soils requires consideration of numerous biotic and abiotic factors (Wu et al., 2019; Giannetta et al., 2022). Investigations of mineral-associated OC fate are limited to bulk analyses performed on the physical fractions that are operationally defined. These methods highlight Fe-organic associations with specific characteristics, such as increased radiocarbon age and increased proportion of microbially-produced OM in fractions with higher density (Derrien et al., 2006; Grandy and Neff, 2008). Nevertheless, all operationally fractionation techniques involve some disturbance with the spatial integrity of soil micro-environments, despite the growing awareness that the physical structure of mineral matrices is strongly influenced by the intensity of geochemical processes. Consequently, understanding micro-scale complexity poses importance challenges for using these traditional bulk methods in heterogeneous soil systems.

The combined use of observational studies, laboratory experiments, and a suite of advanced analytical techniques enables the characterization of Fe-OC and its functional groups, representing a promising approach to mechanistically understand the processes that lead to Fe-OC incorporation into soil aggregates (Lehmann et al., 2007; Keiluweit et al., 2012; Xiao et al.,

2018; Wan et al., 2019; Fig. 3). For example, the use of FTIR and XPS can help identify many association mechanisms at soil micro-interfaces (Arnarson and Keil, 2001; Hall et al., 2018; Stuckey et al., 2018). Yet, these analytical techniques have relatively low detection limits, and soil samples exhibit generally high homogeneity. An increase in the use of synchrotron radiation and advanced surface analytical techniques in soil sciences has been observed in recent years (Table 2). Further, developing micrometer to nanoscale analytical techniques opens new avenues in exploring elemental, isotopic, and molecular characterization at relevant scales that will provide new insights into organo-Fe associations. More recently, synchrotron-based approaches, such as Fourier transform infrared spectromicroscopy (SR-FTIR), STXM, and near-edge X-ray absorption fine structure (NEXAFS) have enabled the investigation of OC distribution and speciation in situ (Lehmann et al., 2009; Lehmann and Solomon, 2010; Chen and Sparks, 2015; Hernandez-Soriano et al., 2018; Sowers et al., 2020). In particular, NanoSIMS is significantly being employed to investigate soils and identify elemental and isotopic maps of OC at mineral particle surfaces at spatial resolutions <100 nm, permitting the tracking of isotopically labeled substrates applied to soils (Keiluweit et al., 2012; Remusat et al., 2012; Vogel et al., 2014; Schweizer et al., 2018; Li et al., 2020; Du et al., 2022; Li et al., 2022a).

4.1. SR-FTIR

Ongoing efforts to develop in situ methods of analyzing OM are providing new insights into the sequestration and turnover of OC on Fe oxides within soils. SR-FTIR enables the effective examination of both mineral and organic functional groups in soil aggregates (Lehmann et al., 2007; Lehmann and Solomon, 2010), thereby allowing the interfacial study of organic-mineral assemblages. Micro-scale samples have been widely analyzed by SR-FTIR follow its development 20 years ago (Luo et al., 2014; Hernandez-Soriano et al., 2018; Sun et al., 2019; Du et al., 2021b). Further, SR-FTIR can be used to obtain high-quality single spectra but can also be used for chemical composition mapping and assessing the spatial distribution of specific soil components in soil aggregate samples (Xiao et al., 2018; Wan et al., 2019). An additional study by Wan et al. (2019) revealed that the binding strength aliphatic compounds and polysaccharides bound Fe oxides more strongly than those for polypeptides, carboxylic acids, and lignin compounds, suggesting that Fe oxides primarily selectively fix fatty acid and polysaccharides C. Moreover, analyses using μ -FTIR confirmed the spatial distribution of polysaccharides overlapped with Fe-O minerals within macro-aggregates (Jeewani et al., 2021b). In addition, similar findings have also been reported by Li et al. (2022c) who found that the correlation between Fe-O and polysaccharides-C was better than that between Fe-O and aliphatic-C/

Table 2

Selected spectroscopy and imaging techniques for exploring the distribution of Fe oxides and OC in soils.

Methods	Probe type	Depth of analysis	Spatial resolution	Sample room and requirements	Target compounds	Reference
Fourier transform infrared spectroscopy (FTIR)	Infrared light	Micrometer	Micrometer	Flexible, air, micrometer thin layer	Chemical forms of organic matter, minerals	Hall et al., 2018
X-ray photoelectron spectroscopy (XPS)	Photoelectron	Surface (~2–10 nm)	Micrometer (10 nm minimum)	Ultra-high vacuum	Elemental composition, C, N, O existing forms	Arnarson and Keil, 2001; Huang et al., 2020b; Wen et al., 2019
Scanning electron microscope energy dispersive spectroscopy (SEM-EDS)	Electronic	Surface	Nanometer	Tens of Torr, element content > 1 %	Soil structure and morphology observations, chemical element information	Schlüter et al., 2018; Allegretta et al., 2022
Electron probe micro analysis (EPMA)	Electronic	Surface (micrometer)	Nanometer	High vacuum	Elemental composition and distribution	Sun et al., 2017; Xiao et al., 2019
Synchrotron-based Fourier transform infrared (SR-FTIR) spectromicroscopy	X-ray absorption	Variable	Micrometer	Flexible, air, micrometer thin layer	Composition and chemical form	Xiao et al., 2018; Wan et al., 2019
Scanning transmission X-ray microscopy (STXM)	X-ray	Pierce through	Nanometer	Low vacuum, helium, thin layer	Elemental composition and chemical forms	Sowers et al., 2018; Huang et al., 2021a, 2021b
Nano-secondary ion mass spectroscopy (NanoSIMS)	Ion source	Surface	Nanometer	High vacuum 10–10 bar, smooth sample, ppb/ppm element contents	Light elements (C, N) and heavy elements (Fe, Cu) and their isotopes	Li et al., 2018; Li et al., 2020; Pohl et al., 2021

aromatic-C under inorganic and organic fertilizer treatments in tea garden soil. Collectively, based on the SR-FTIR results, Fe oxides were predominantly associated with polysaccharide compounds.

The analytical approach outlined above allows us to increase our knowledge of the micro-scale spatial distribution of OC and Fe oxides at molecular level, thereby improving our understanding of organo-mineral interactions and OC storage in soils that would be impossible without synchrotron radiation techniques. However, investigating the spatial distribution characteristics of organic and mineral components in soil aggregates using SR-FTIR and the subsequent qualitative and quantitative interpretation of spectra to observe changes in OM chemistry is sometimes relatively difficult. This is particularly problematic due to the effects of O—H stretching and the bending of sorbed water, clay minerals, and metal oxides, as well as Si—O—Si stretching, carbonates, and other inorganic soil constituents resulting in overlap between individual absorption bands of organic and inorganic soil components (Lehmann and Solomon, 2010; Calderón et al., 2013).

4.2. STXM-NEXAFS

Compared to electron microscopy, STXM is an effective spectroscopy and imaging technique that generates element-specific component maps at high spatial resolution (<25 nm) for important elements (e.g., C, N, P, S, and Fe), with a minimally prepared sample and little radiation damage (Arachchige et al., 2018; Sowers et al., 2020; Huang et al., 2021b). In addition to describing spatially defining C speciation, NEXAFS is also capable of analyzing the K-edges or L-edges of several elements associated with organo-mineral composites like Al, Si, Ca, and Fe (Solomon et al., 2012; Chen and Sparks, 2015; Prietzel et al., 2018; Sowers et al., 2018). Hence, a key feature of STXM is that it can provide spatial element-specific chemical information at the nano-scale that exhibit the greatest relevance for soil environments. Using STXM, Kinyangi et al. (2006) examined unaltered soil microaggregates, observing that a large amount of the OM was either bound to mineral surfaces or comprised aromatic C or aliphatic C in particulate forms. Combined STXM-NEXAFS was used by Keiluweit et al. (2012) to identify that soil microstructures are enriched in aliphatic C and amino N, indicating that microbial lipids and proteins can quickly combine with Fe oxides. Further, Chen et al. (2014b) and Henneberry et al. (2012) employed a combination of ATR-FTIR and STXM-NEXAFS to identify that carboxylic acid moieties were the primary OC species associated with ferrihydrite through adsorption complexes and coprecipitates via inner-sphere ligand exchange reactions. Moreover, Wan et al. (2007) and Chen et al. (2014a) used STXM-NEXAFS mapping, observing that soils with high concentrations of Fe oxides exhibited strong spatial elemental associations between C and Fe. Subsequently, Dynes et al. (2015) used STXM alongside a simple sample preparation technique and three common approaches to resolve nano- and micro-scale information for soils. Sowers et al. (2018) also applied STXM-NEXAFS analysis to spatially analyze Fe, Ca, and OC correlations in soils, while also investigating the influence of Ca on sorbed OC speciation. Ca exhibits significant co-associations with OC in soils containing high Fe concentrations and increases OC sorption to poorly crystalline Fe oxides, consistent with long-standing hypotheses that Ca forms bridging complexes with Fe and OC.

Biogeochemical processes can be further illuminated by STXM spectromicroscopy. However, STXM typically can only analyze a few samples and replication is typically limited, and thus, its reproducibility and scalability have been questioned (Wan et al., 2007; Dynes et al., 2015; Stuckey et al., 2017). Integrating spectroscopic information from STXM with SEM and probing large-scale ecological systems provides the most optimal means of analyzing ecological data at large scales. With the development of bulk spectroscopic XAS analysis, geochemical modelling has been revolutionized by enabling direct observations of the Fe—OC bonding mechanisms and the ability to determine poor crystalline phase structures.

4.3. NanoSIMS

In addition to its widespread application in geosciences, mineralogy, and other related fields, NanoSIMS exhibits significant promise in the field of soil

science. NanoSIMS is the most modern technique for analyzing surfaces and interfaces, leading to a wide range of its applications (Vogel et al., 2014; Schweizer et al., 2018; Du et al., 2022; Ouyang et al., 2022). Unlike conventional techniques, NanoSIMS uniquely performs high lateral resolution (50–150 nm) and elemental sensitivity (mg kg^{-1}), allowing the examination of both light elements and most heavy elements simultaneously. Hence, NanoSIMS can potentially be applied to explore complex metal-soil aggregate systems (Mueller et al., 2013; Dorau et al., 2019; Schlüter et al., 2022). Mueller et al. (2012) used resin-embedding of soil aggregates and NanoSIMS to demonstrate that microorganisms exhibit different use efficiencies of ^{13}C - and ^{15}N -labeled proteins on the surfaces of aggregates based on soil culture experiments. Most studies incorporating NanoSIMS analyses have tracked labeled compounds or focused on changes in light elements. For example, Keiluweit et al. (2012) found that N from fungal cell walls can be quickly and preferentially coated on Fe oxide surfaces with an organic film using NanoSIMS mapping of ^{15}N and Fe. Further, by conducting a 42-day experiment with ^{13}C - and ^{15}N -labeled litter, Vogel et al. (2014) subsequently applied NanoSIMS to observe that newly added OM more easily bound the mineral surfaces of existing OM. Rumpel et al. (2015) demonstrated that ^{13}C - and ^{15}N -labeled plant-derived OM along with Fe and Al oxides shape stable and inordinance complexes in the 30 cm layers, while microbially-derived OM along with Fe and Al oxides formed oval organic particles in 90 cm layers. Applying isotope labeling and NanoSIMS, Yu et al. (2017) recently showed that SRO minerals play an important role in OC sequestration across long-term field experiments (e.g., 23, 154, and 170 years). These results are consistent with those reported by Kopittke et al. (2018) who applied NanoSIMS to analyze differences in mineral associations between newly attached OM and the existing SOM in Vertisols and Alfisols. According to their analyses, nitrogen-rich microbial products adhere more strongly to mineral surfaces after 365 days, offering evidence that the surfaces of carbon-free minerals can react with these products to form new organic mineral assemblages, thereby potentially resulting in additional OC sequestration. Montmorillonite and kaolinite constitute the primary clay minerals of the two soil types, and thus, the differences between them are most likely due to their different mineral compositions.

Although NanoSIMS allows the direct imaging of multi-element mappings, its scanning area is limited to $50 \times 50 \mu\text{m}^2$ compared to the 1 mm^2 area for STXM. Thus, NanoSIMS analyses enable the systematic investigation of multi-component interactions in highly heterogeneous soils. Compared to traditional methods, molecular and nano-scale technologies can, however, provide useful and in-depth information about environmental processes and mechanisms underlying OC associations. Consequently, these methods can provide insight into OC forms, distributions, sequestration, and turnover in soils. Indeed, microscale techniques like those mentioned above are powerful tools for probing mechanisms, transformations, and OC fates in soils. Nevertheless, limitations of individual techniques necessitate the combination of several technologies to comprehensively explore the chemical mechanisms of OC associations among diverse micro-domains and at the micro-scale within heterogeneous soils. Furthermore, innovative advancements in this field have not yet resulted in identification of biogenic OM producers.

Tracking biologically active elements in mineral assemblages using isotopic tracing and STXM-NEXAFS in conjunction with NanoSIMS is possible via isotopic labeling, thereby potentially defining and spatially resolving the microbially-driven biogeochemical processes (Keiluweit et al., 2012; Remusat et al., 2012). In addition to the experimental design and sample-handling challenges associated with combining STXM-NEXAFS and NanoSIMS analyses of the same sample (Remusat et al., 2012; Kopittke et al., 2020; Li et al., 2022a), the most fundamental challenge remains to connect nano-scale observations of soil biogeochemical process with ecosystem-scale processes (Standing et al., 2007; Dynes et al., 2015).

5. Future challenges and prospects

As summarized in this review, it is apparent that a better understanding of Fe biogeochemical processes in soils and their associations with organic C turnover is needed (Fig. 4), in addition to feedback effects on climate

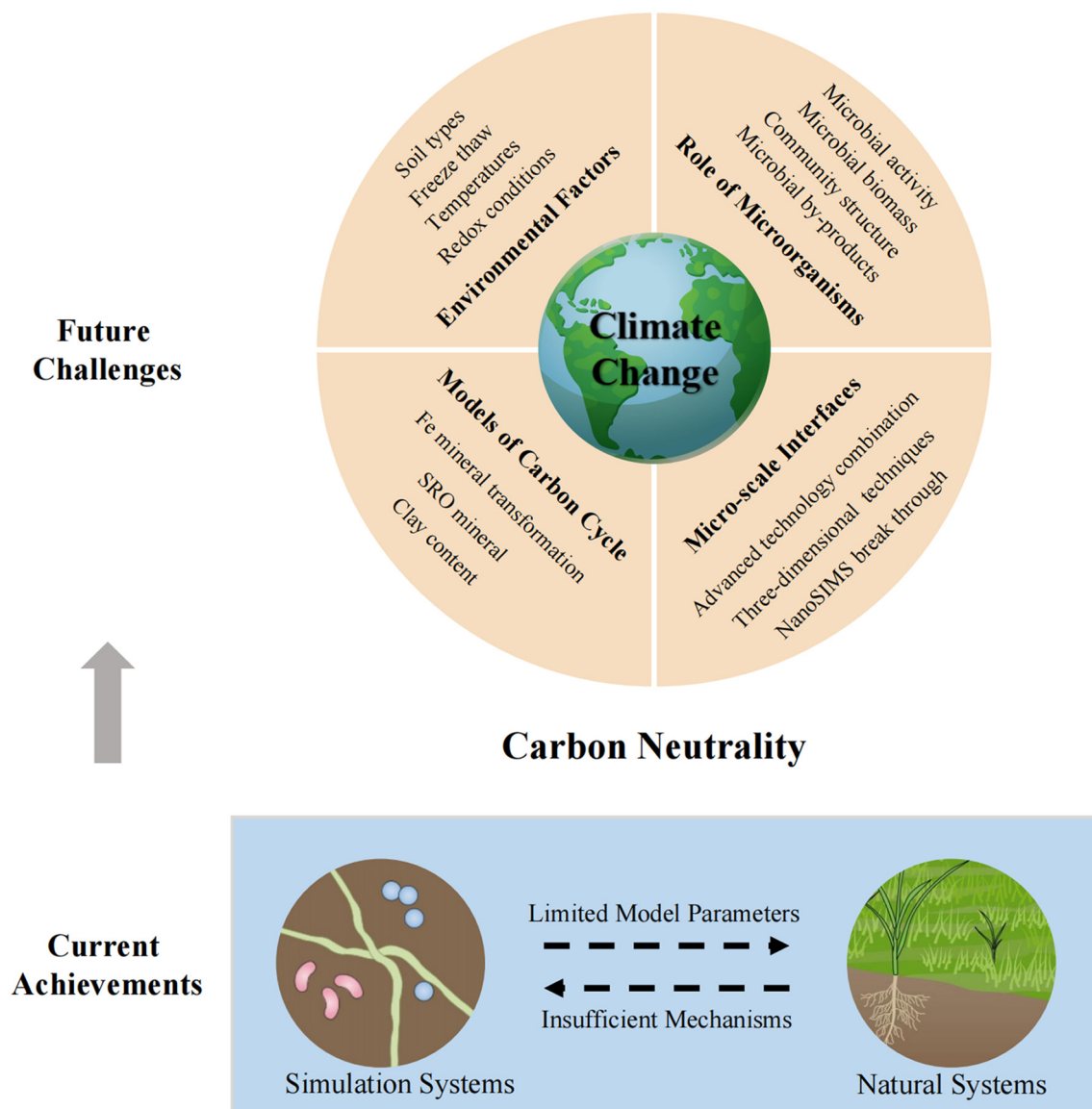


Fig. 4. Overview on the future challenges regarding Fe-OC at soil interfaces.

change, have significantly advanced in recent years, although gaps and poorly-understood processes remain. Below, research areas or questions that merit special attention in future studies are highlighted.

5.1. Responses of coupled biogeochemical Fe and OC cycles to environmental changes

A comprehensive understanding of the intricate interplay and complex feedback loops therein are needed to provide ecosystem services like SOC fixation by maintaining and restoring soil fertility and to accomplish sustainable development goals. In the context of global climate warming, the consolidation of the potential of Fe oxides for OC sequestration beyond chemical stability is important. In particular, an interpretation of Fe-OC changes in response to extensive shifts in environmental conditions (e.g., redox conditions, temperature, soil type, and vegetation) is useful as a starting point for formulating hypotheses and predictions of future ecosystem changes (Barré et al., 2014; Aftabtalab et al., 2022). However, identifying processes of Fe-OC cycling in soils may be aided by considering spatial information such as that shown here, including for informing stability, storage, and responses to a changing climate.

Ferric minerals may undergo redox reactions in some soil environments that can destabilize Fe-OC and destroy Fe(III) oxide-SOC complexes

(Adhikari et al., 2016; Pan et al., 2016; Wagai et al., 2020). Limited studies have observed that Fe-OC is easily destabilized at a release rate constant of $0.011\text{--}1.49\text{ min}^{-1}$ during the initial stage, which is significantly higher than that of Fe, with a release rate constant of $6.67\text{--}13.0 \times 10^{-3}\text{ min}^{-1}$ (Adhikari et al., 2016). Biogeochemical Fe cycling is likely to either directly or indirectly affect SOC stability and thus, management practices that govern biogeochemical Fe cycling in arable soil profiles like soil amendments (i.e., Fe-based biochar) can be applied to enhance soil C storage. Indeed, evidence is growing that plants possess the adaptive ability to destabilize Fe-OC, such as through the exudation of organic macromolecules to liberate existing OM from mineral surfaces (Keiluweit et al., 2015; Yao et al., 2022) and the alteration of microbial community compositions to achieve optimal functionality (Zhalnina et al., 2018). Taking these developments into account, we propose that Fe-OC protection should be re-evaluated to more accurately estimate the cycling and stability of Fe-OC as an explanation for OM persistence, and particularly in dynamic environmental systems.

5.2. Establishing a more comprehensive global carbon cycle model

Global C cycle models should integrate SOC stabilization mechanisms and biogeochemical Fe cycles in terrestrial ecosystems to enhance our understanding of global C balances and climate change. Once the traditional

parameters like clay content and type are combined in a carbon model along with consideration of the key role of iron minerals, the prospects for promoting soil carbon stability and saturation may be revolutionized. Nevertheless, additional research is needed to assess how much and how fast exogenous OM application will enrich SRO minerals, including field rates and potentials. In addition, further research is necessary to examine how Fe minerals and exogenous organic matter can simultaneously absorb cations and organic carbon. Given the vast differences between laboratory and field conditions, it is necessary to consider the diversity of natural soil samples and field conditions in future studies of organo-mineral mechanisms. By considering the above factors, new models should be able to answer the following two questions: (i) To what extent can soil C sequestration be enhanced by quantifying and balancing the benefits and costs of various actions? (ii) What are the best ways to combine different measures to maximize soil C storage? Solving these questions may guide the manipulation of soil C sequestration approaches to respond to global carbon neutral strategies.

5.3. Coupled Fe-OC biogeochemical processes in soil environments at micro- and molecular-scales

Soil characteristics are the consequence of numerous microenvironments, in addition to physicochemical conditions (e.g., redox potential), and the constituents may considerably differ among micro-environments and from average soil characteristics. Importantly, the biogeochemical processes associated with such micro-environments are intense, rapid, and interdependent. Exploring these processes in detail is a challenging research endeavor because micro-environments (i) comprise intricate heterogeneous assemblages of biogenic minerals, microorganisms, and abundant biomacromolecules produced by organisms and plant roots (Fimmen et al., 2008; Kuppe et al., 2022); (ii) exhibit exceedingly sharp and dynamic (nano-/micro-scale) gradients in biogeochemical parameters like pH and Eh; and (iii) represent uneven distributions of soil solid-phase active components and binding associations (e.g., organic-mineral microbial complexes). Considering the significant spatial complexity that microorganisms, minerals, and pore spaces likely exhibit that differentially affect Fe-OC forms, spatially explicit information can serve as a critical foundation to improve our comprehension of soil Fe-OC association processes.

Two categories of methods attempt to explore the heterogeneity of soil structures, even at the nano-scale: the extraction methods that attempt to separate Fe-OC into meaningful subsets, and visualization methods that aim to investigate Fe-OC in natural environments. First, it remains controversial whether the citrate-bicarbonate-dithionite (CBD) extraction method can truly reflect the association of Fe oxides, wherein various extractants replace soil complex components, thereby simplifying complexity problems (Lalonde et al., 2012; Fisher et al., 2021). Consequently, this method has been extensively applied to quantify Fe-OC contents in soils (Zhao et al., 2018; Wan et al., 2019; Patzner et al., 2020; Joss et al., 2022). Nevertheless, the extraction efficiency of this method remains unknown. More effective and accurate extraction methods should be explored. Future work to quantify the global importance of the Fe-OC sink requires a uniform methodological approach to be deployed with modification among diverse environments. These extractions should be conducted with the knowledge that this represents the operationally defined, not absolute, Fe-OC content of soils. In addition, an integrated understanding of Fe-OC functions within a specific pedological context is best attained using a combination of extraction methods alongside detailed molecular characterization of Fe-OC compositions and analysis of their dynamics. Second, newly developed spatially- and temporally-resolved techniques have opened up a broad range of new possibilities for gaining in-depth knowledge of localized Fe-OC biogeochemical processes. Combining STXM-NEXAFS with NanoSIMS yields more comprehensive insights than NanoSIMS imaging alone. The implementation of a combination of methods has enabled the possibility to test hypotheses that arise from bulk scale studies by visualizing the given process. The unique insights resultant from such combinations, consequently, provide new perspectives for understanding geochemical and ecological processes at the sub-micrometer scale. Fe-OC distributions

in soils are not redundant with OM characterization when examining nano-scale distributions. Nevertheless, these small-scale observations clearly show the limitation of combined observations of spatially intricate mixtures like soils that exhibit highly distinct characteristics on very fine scales.

Notably, differences in Fe-OC forms at the scale of hundreds of nanometers determined by modern instrumental techniques revealed greater differences than those for OC characteristics of soils from different climates and ecoregions at the global scale. Owing to this spatially detailed mapping of Fe-OC, it is also challenging to scale observations from a single location to processes occurring at the landscape scale. Thus, obtaining representative samples and measuring sufficient sample material are both methodological and statistical issues that require further development. To obtain precise spatial information at such a fine scale, sample preparation and spectral quantification need to be carefully considered (Lehmann et al., 2009; Höschel et al., 2015).

This review discusses combining spectroscopic and microspectroscopic techniques that provide two-dimensional chemical information on the surface of a sample. Soils exist, of course, in three dimensions, and thus the development of three-dimensional analytical techniques (e.g., μ CT, STXM and NanoSIMS) holds significant promise to explore biogeochemical processes in physically representative environments without loss of spatial information (Behrens et al., 2012; Kravchenko and Guber, 2017; Wiesmeier et al., 2019; Pohl et al., 2021; Li et al., 2022a). As discussed above, modern spectromicroscopic techniques provide the possibility to define biogeochemical process mechanisms at the nano-scale. Overall, geostatistical approaches should be utilized via process-based understandings to understand their effects at larger scales.

CRediT authorship contribution statement

Qi Li: Conceptualization and writing the manuscript.

Weifang Hu: Drawing figure and made suggestions of the manuscript.

Linfeng Li: Editing and made suggestions of the manuscript.

Yichun Li: Supervision, Writing - Reviewing and Editing.

Data availability

No data was used for the research described in the article.

Declaration of competing interest

The authors declare that they have no competing interests.

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