

REVIEW

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Towards a better understanding of the role of Fe cycling in soil for carbon stabilization and degradation

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Abstract

Iron (Fe) minerals play an important role in stabilizing soil organic carbon (SOC). Fe-mediated SOC protection is mainly achieved through adsorption, co-precipitation, or aggregation. However, newly emerging evidence indicates that the electron transfer role of Fe exerts a crucial influence upon SOC turnover. In this review, we address the pathways of Fe mineral-associated soil organic carbon (Fe-SOC) formation and decomposition, and summarize the Fe-mediated biogeochemical, including redox reactions, and physical processes that control SOC cycling. The reduction of Fe can release SOC from Fe-SOC coprecipitates and Fe(III) cemented micro-aggregates, with the process also releasing CO₂ from the metabolic coupling of SOC oxidation and Fe reduction. The abiotic oxidation of Fe(II) by oxidants can also oxidize SOC to produce CO₂ due to reactive oxygen species production. Therefore, the functional roles of Fe on SOC sequestration may be a double-edged sword, and these processes are rarely explored concurrently. We conclude that the roles of Fe minerals in SOC stability depend on the properties of the Fe mineral, edaphic properties, and anthropogenic influence. We highlight knowledge gaps and promising directions of future research in redox-dynamic environments to optimize carbon storage in soil.

Highlights

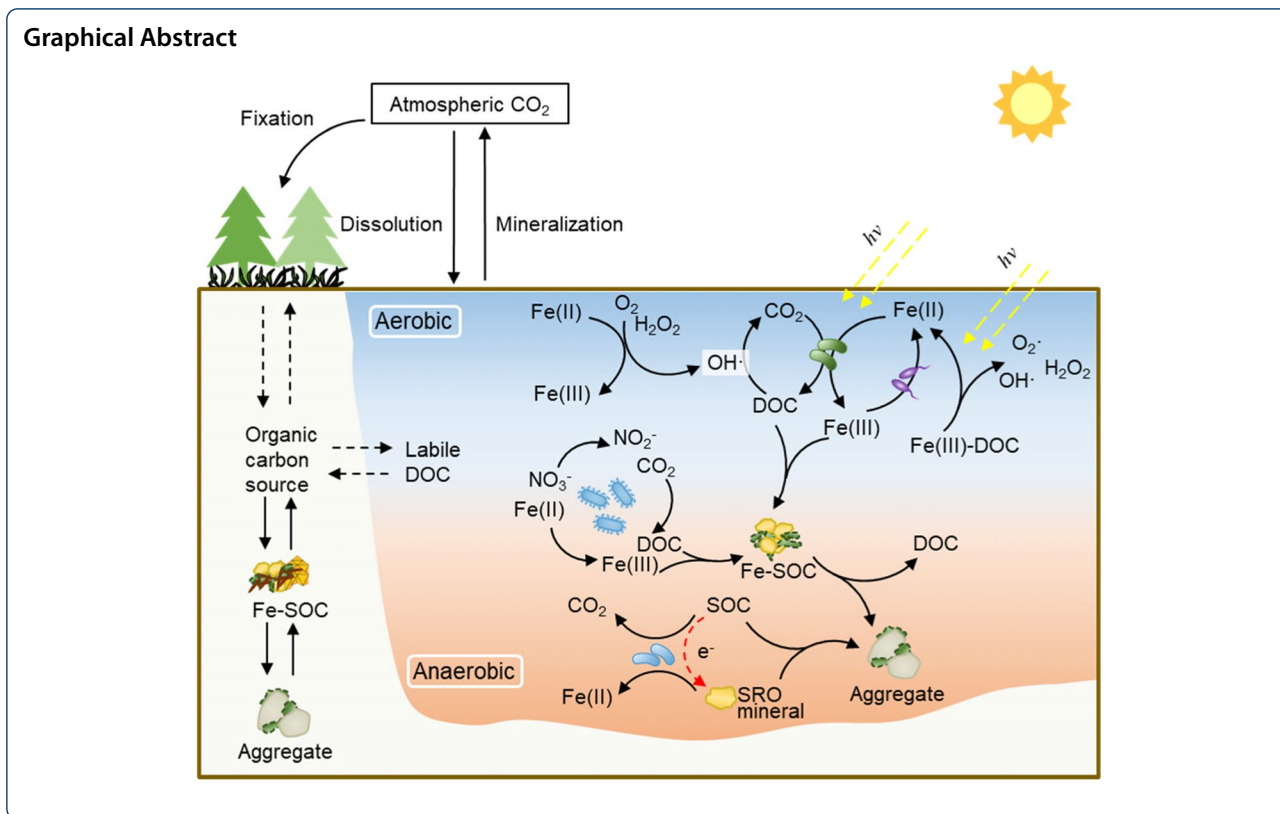
- The redox cycling of Fe plays a two-edged role on SOC stabilization and MAOC turnover.
- Microbial Fe(II) oxidation stabilizes SOC while chemical Fe(II) oxidation decomposes SOC.
- Microbial and photochemical Fe(III) reduction are coupled with SOC degradation.

Keywords: Biogeochemical Fe cycle, Iron oxides, Microorganism, Redox interfaces, Oxidation, Reduction

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1 Introduction

Soil is the largest carbon reservoir in the terrestrial biosphere, in which the soil organic carbon (SOC) pool estimated at 1500 Pg is decreasing due to soil respiration and soil erosion (Lal 2008). Much attention has been paid toward understanding mechanisms for SOC stabilization in soils (Mikutta and Kaiser 2011; Dungait et al. 2012; Crowther et al. 2016; Sanderman et al. 2017; Tamura et al. 2017), on account of that even small changes in the balance between SOC inputs and outputs can substantially affect the concentrations of atmospheric CO₂ (Lal 2004; Smith et al. 2008). The mineral-associated soil organic carbon (MAOC) is considered as one of the main factors for SOC stabilization (Cotrufo et al. 2019). Meanwhile, Lehmann et al. (2020) proposed that the functional complexity can affect the stability of SOC at the lens of decomposers, such as the higher molecular diversity, higher spatial heterogeneity and greater temporal variability can reduce the decomposition of SOC by microorganisms.

Somewhat similar to the concept of functional complexity, Lützow et al. (2006) reviewed the mechanisms of SOC sequestration: (1) selective preservation, which depends on the SOC chemical properties; (2) spatial inaccessibility, which limits microbial access of SOC via occlusion within microaggregates and intercalation within phyllosilicates; and (3) interactions with mineral

surfaces. The third mechanism could control long-term SOC persistence, especially with iron (Fe) mineral surfaces, while the other two mechanisms control short- and medium- term SOC stabilization (Kögel-Knabner et al. 2008). The association between SOC and soil minerals is identified as a non-negligible role (Chenu and Plante 2006; Throckmorton et al. 2015; Singh et al. 2018), and the minerals can be transformed by the prevalent changing climatic conditions, microorganisms, and shifts in the influx of electron donors and acceptors (Rasmussen et al. 2007; Melton et al. 2014; Mejia et al. 2016). However, the effect of mineral phase transformation on MAOC is unclear, especially for the formation and stability of Fe minerals associated SOC (Fe-SOC) during iron redox cycling processes.

Fe minerals, mainly including Fe oxides, (hydr)oxides and (oxy)hydroxides, are ubiquitous in soils and highly reactive to SOC (Cornell and Schwertmann 2003; Kappler and Straub 2005; Yang et al. 2017). The influence of Fe minerals on SOC stabilization has been evidenced by the positive correlations between Fe and SOC concentrations (Kaiser and Guggenberger 2007; Lalonde et al. 2012), and the inverse correlations between SOC turnover rates and Fe concentrations (Masiello et al. 2004). Fe mineral could serve as an efficient 'rusty sink' for trapping terrestrially-derived SOC in sediments, and it is a crucial factor in the

SOC long-term storage with contribution to the global C cycling (Lalonde et al. 2012). Using EXAFS spectroscopy, Yang et al. (2017) have indicated that Fe is actively involved in the retention of SOC via Fe mineral adsorption and coprecipitation at high Fe/C ratios, whereas via Fe bridge at low Fe/C ratios. While Fe minerals can act as a SOC sorbent and provide structural roles for SOC protection, they are also involved in electron-transfer as electron donors or acceptors, which can drive SOC oxidation, depolymerization, and CO₂ production (Chen et al. 2020).

This review aims to identify and highlight the pathways of Fe-SOC formation and decomposition, and how the SOC transformation processes are regulated by biogeochemical processes of Fe redox reactions. To better unravel the double-edged sword of the competing processes of carbon stabilization and degradation, our conclusion delivers recommendations for future research and development directions for Fe-SOC in redox-dynamic environments.

2 Pathways of Fe-SOC formation and decomposition

There are multiple pathways of Fe-SOC formation and decomposition (Fig. 1). The first pathway is the source of carbon supplying Fe-SOC pool. Biological carbon fixation converts CO₂ into organic carbon through photosynthesis by plants or autotrophic CO₂ fixation by soil microorganisms. Aboveground and belowground structural residues (e.g., root biomass) primarily supply the faster-cycling, particulate SOC pool (Cotrufo et al.

2015), with mineralization releasing nutrients and CO₂, while a component is also important for macroaggregate development (Rasse et al. 2005). Recently review has concluded that the belowground C allocation by grasses (33%) is greater than crops (21%) (Pausch and Kuzyakov 2018). The low molecular weight plant C substrates (i.e., rhizodeposits) and microbial necromass can act as precursors for Fe-SOC formation (Sokolova 2020; Li et al. 2022). The second pathway is the association of Fe oxides with SOC. Fe minerals (i.e., ferrihydrite, goethite and hematite) can adsorb or co-precipitate SOC due to their large surface area and abundant hydroxyl groups (Kaiser and Guggenberger 2007; Chen et al. 2014; Kleber et al. 2015; Singh et al. 2017b; Churchman et al. 2020). The third pathway is the formation of soil aggregates via physicochemical and chemical processes, which provide physical protection of the Fe-SOC (Eusterhues et al. 2008; Zhang et al. 2015; Totsche et al. 2018; Krause et al. 2020), as shown below (Fig. 1):

2.1 The carbon source for the Fe-SOC pool

2.1.1 Plant

Plant-C inputs to soils include dissolved sugars, organic and amino acids, which can enter the mineral soil from both aboveground and belowground biomass inputs and rhizodeposition (Kuiters and Sarink 1986; Bolan et al. 2011). Aboveground and belowground structural residues primarily supply the faster-cycling, particulate SOC pool (Cotrufo et al. 2015), and can be associated

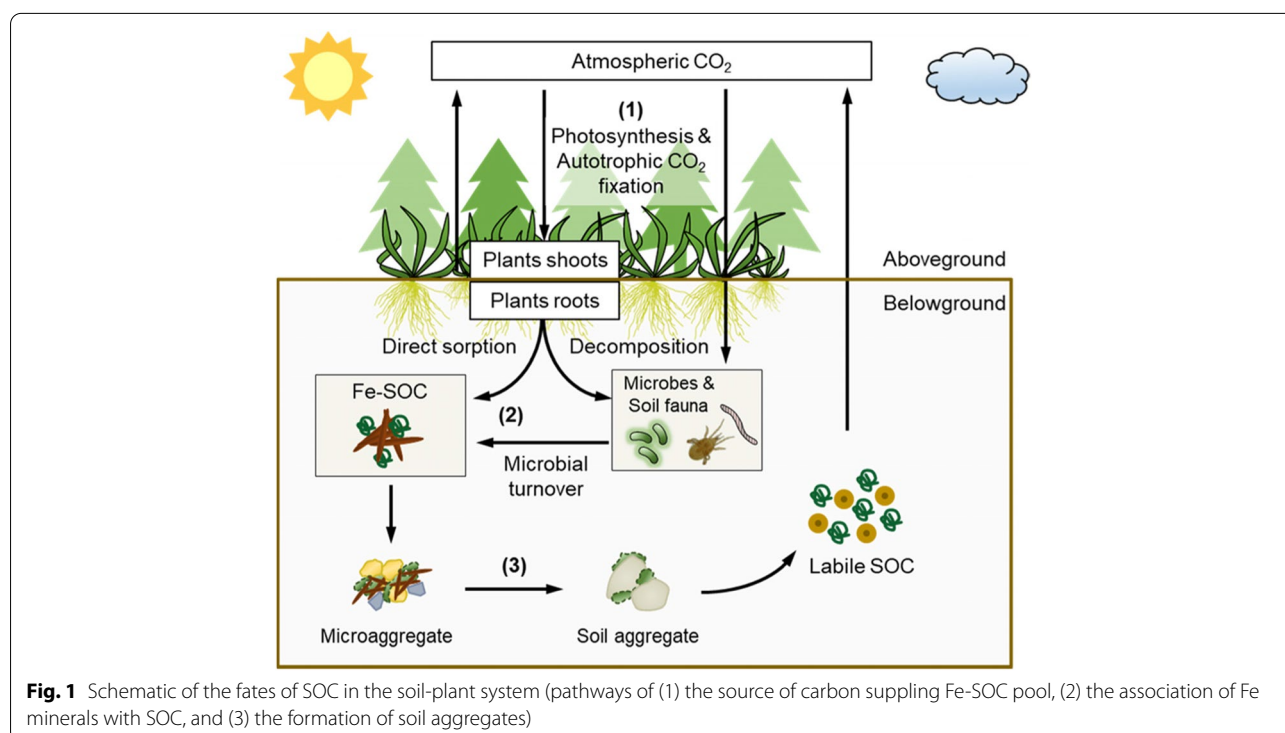


Fig. 1 Schematic of the fates of SOC in the soil-plant system (pathways of (1) the source of carbon supplying Fe-SOC pool, (2) the association of Fe minerals with SOC, and (3) the formation of soil aggregates)

with the formation of macroaggregates (Rasse et al. 2005). In contrast, low molecular weight carbon (LMWC) components of the plant-C source transfer to the slower-cycling Fe-SOC pool (i.e., in vivo microbial turnover vs. direct sorption). Traditional opinions suggested that Fe-SOC could be primarily composed of directly adsorbed plant compounds referred to “the direct sorption pathway” (Kramer et al. 2012). Others, however, showed that the majority of LMWC substrates in Fe-SOC were microbial derived, as the LMWC substrates underwent microbial anabolism, biosynthesis, and turnover. Microbial assimilates were then adsorbed to mineral surfaces - referred to as the “in vivo microbial turnover pathway” (Bradford et al. 2013; Kallenbach et al. 2016). Based on the argument, a recent study reconciled these two divergent ideas around Fe-SOC formation. This study proposes a concept of regional density of microbes, indicating that in areas of high microbial density, such as the rhizosphere, Fe-SOC is primarily formed through the “in vivo microbial turnover” pathway, while in areas of low microbial density, such as bulk soil, Fe-SOC is formed through the “direct sorption” pathway (Vidal et al. 2018; Sokol et al. 2019).

2.1.2 Microorganisms

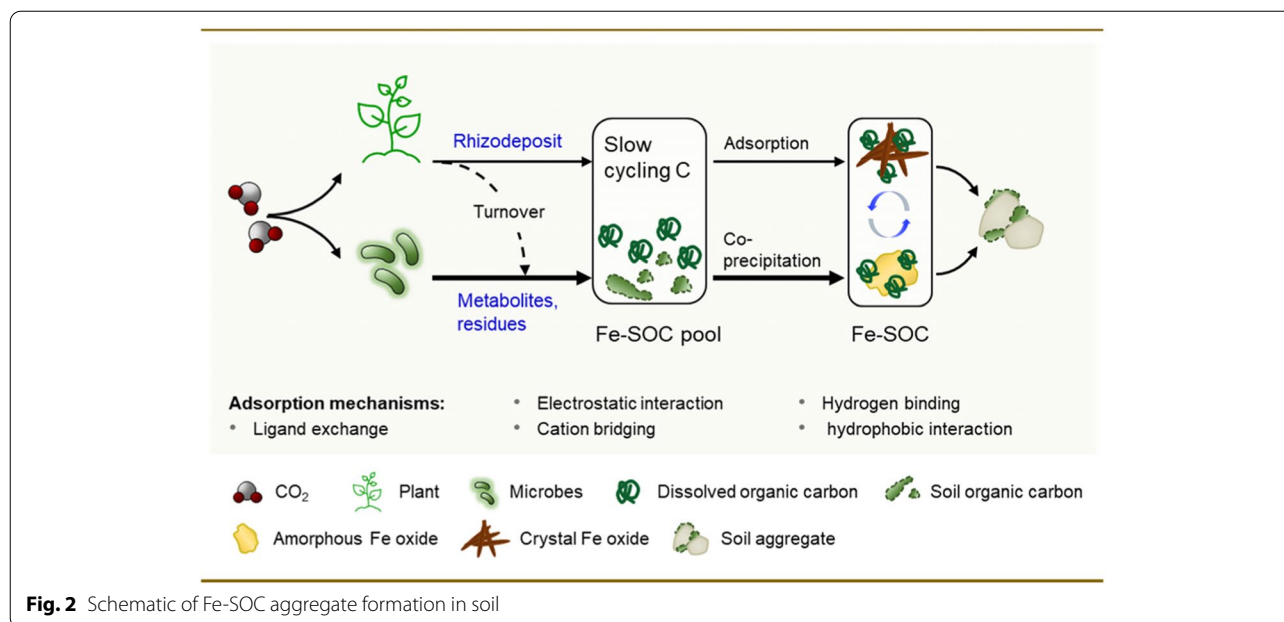
Autotrophic microorganisms are widely present in different ecosystems. The pathways that autotrophic microorganisms assimilate CO₂ include: (i) Calvin-Benson-Bassham (CBB) cycle; (ii) reducing tricarboxylic acid cycle; (iii) anaerobic acetyl-CoA; (iv) 3-hydroxypropionic acid; and (v) succinyl-CoA. The efficiency of CO₂ assimilation by microorganisms affects the inputs and outputs of the SOC pool and other ecological processes. Part of the assimilated C returns to the atmosphere as CO₂ and CH₄ through soil respiration and methanogenesis, while a component is utilized in microbial biomass C with microbial necromass contributing to SOC (Miltner et al. 2012). Microbial-derived compounds are widely considered to be the primary components of stable SOC (Lundberg et al. 2001; Grandy and Neff 2008; Xu et al. 2018). Liang et al. (2017) further showed that the coupling of the soil microbial carbon pump and the entombing effect resulted in the persistence of majority of carbon in soils. The greater production of microbial residues should be transformed to more C compounds that are subsequently available for mineral-sorption (Cotrufo et al. 2013). With the decay of plant materials, soil microbes convert available C into microbial biomass, necromass or microbially processed compounds. The microbial residues accumulate on mineral-associated soil fractions (Kögel-Knabner et al. 2008; Cotrufo et al. 2013), and are considered to be relatively stable (Glaser et al. 2004) and accrue in the soil with

iterative community turnover. Using ¹³C and ¹⁵N labeling, Kopittke et al. (2020) found that N-rich microbial metabolites of plant residues bind with mineral particle surfaces and stabilize SOC. The stabilization of rhizodeposits in soil has been shown to be a balance between microbial mineralization and Fe mineral associations, and branched filaments of organisms can promote aggregate formation and protect SOC from microbial access (Jeewani et al. 2020). A recent opinion proposed that the energy of SOC controls which fractions could be mineralized or stabilized, which was related to the net energy consumption during microbial decomposition of SOC (Gunina and Kuzyakov 2022). Microbial activities are controlled by the soil redox condition and subsequently affect the SOC composition. Generally, microbial decomposition of plant residues and SOC is slow under anoxic conditions, which is conducive to the enrich of plant-derived C in paddy soil, while oxic condition (e.g., in upland soil) favors the replenishment of microbial-derived C (Chen et al. 2021; Wei et al. 2021).

2.2 The associative mechanism of Fe mineral and SOC

The association of SOC with Fe minerals is an important mechanism to stabilize SOC against biodegradation (Singh et al. 2018). Fe minerals and SOC may form intricate associations via myriad interactions, and provide most of the reactive surface sites onto which SOC can be adsorbed (Yang et al. 2017). The adsorption of dissolved organic carbon (DOC) on Fe (hydr)oxides represents an important and well-documented process for SOC and contributes to SOC accumulation (Bolan et al. 2011). For example, the addition of Fe oxides such as goethite can decrease the decomposition rate of composts through increasing immobilization of SOC (Bolan et al. 2012). Similarly, increasing Fe contents of biosolids can slow down the rate of decomposition of biosolids, which is attributed to the adsorption or complexation of SOC by Fe cations (Bolan et al. 2013). Recently, Bao et al. (2021) systematically summarized the mechanisms showing the adsorption and co-precipitation of SOC on Fe oxides (Fig. 2).

Co-precipitation of SOC with Fe is ubiquitous in water and soils due to changes in pH or redox potential, which could explain the critical role of Fe oxides in C storage (Wagai and Mayer 2007). Natural environments tend to have periodically fluctuating redox conditions, and as such the interaction between SOC and Fe (hydr)oxides may not only involve organic coatings on mineral surfaces, but also form Fe-SOC co-precipitates in soil solutions containing large amounts of DOC and Fe(II) during the oxidation stage. For example, in temporarily waterlogged soils (e.g., paddy soils),



where the molar C/Fe ratios of soil pore water are 0.2–6 (Kato et al. 2004; Cheng et al. 2010), upon aeration Fe(II) is quickly oxidized to relatively insoluble Fe(III), which concurrently adsorbs SOC and ions. In contrast, after aeration a large amount of SOC was co-precipitated with Fe in the soil pore water with a high molar C/Fe ratio (10–30) (Riedel et al. 2013). Unlike the adsorption complexes, the co-precipitation of SOC with Fe can also alter the particle size and structural order of newly-formed Fe (oxy)hydroxides (Eusterhues et al. 2008; Mikutta and Kretzschmar 2011) and affect its reactivity (Eusterhues et al. 2014; Mikutta et al. 2014). Han et al. (2019) found that ferrihydrite-SOC associations in co-precipitates are more resistant to chemical reduction than the adsorption complexes. In addition, SOC composition was also found to be a crucial role controlling the SOC loadings and fractionation during adsorption and co-precipitation. Eusterhues et al. (2011) observed that SOC polysaccharide components were more enrichment in adsorption than in co-precipitation. However, for either straw-derived DOC that is rich in aromatic constituents, or SOC that is rich in carboxyl functional groups, less in aromatic and phenolic compounds, the co-precipitation could result in much higher SOC retention (Chen et al. 2014; Sodano et al. 2017).

2.3 The formation and stability of soil aggregates

Physical protection of SOC via micro-aggregation induced by Fe (hydr)oxides is another mechanism of SOC stabilization (Huang et al. 2016; Xue et al. 2019).

Cationic bridges in soil are formed between ferric ion and microorganisms, and the bridge represents an organic mineral complex. The Fe (hydr)oxides are generally considered as one of the most important mineral phases involved in microaggregate formation (Totsche et al. 2018), and Fe-SOC serve as the nuclei for aggregate formation (Silva et al. 2015), and their oxides act as flocculants, binding fine particles to inorganic and/or organic molecules by physicochemical and chemical interactions involving cementing and gluing agents to form aggregates (Borggaard 1982), and promoting the stability of microaggregate occlusion in macroaggregates (Krause et al. 2020). The filamentous bacteria contributed to the development of aggregation via mycelium structures that promote the binding of soil particles to form microaggregates (Jeewani et al. 2020). Therefore, SOC adsorbed by minerals would be further protected by aggregation, which is the result of synergistic effects of biological, chemical, and physical mechanisms in SOC stabilization (Amézqueta 1999; Filimonova et al. 2016; Jeewani et al. 2020).

3 Mechanisms of Fe cycling coupled with C stabilization and degradation

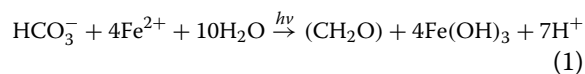
The biogeochemical process of Fe(II)/(III) is closely related to the fixation and mineralization of SOC in soil, and SOC protected by soil aggregates may also be released and decomposed by Fe cycling, especially for Fe-SOC, which is considered as a type of MAOC sensitive to environmental conditions.

3.1 Biogeochemical reactions of Fe(II) and Fe(III)

Generally, Fe(II) oxidation favors CO₂ sequestration (Widdel et al. 1993), and dissimilatory Fe(III) reduction favors SOC mineralization (Weiss et al. 2005), except the Fenton reaction, which promotes SOC mineralization during oxidizing Fe(II). According to the order from top to bottom in flooded soil, we summarize these reactions under light, aerobic, microaerobic and anaerobic conditions in Figs. 3 and 4.

3.1.1 Phototrophic Fe(II) oxidation coupled with CO₂ fixation

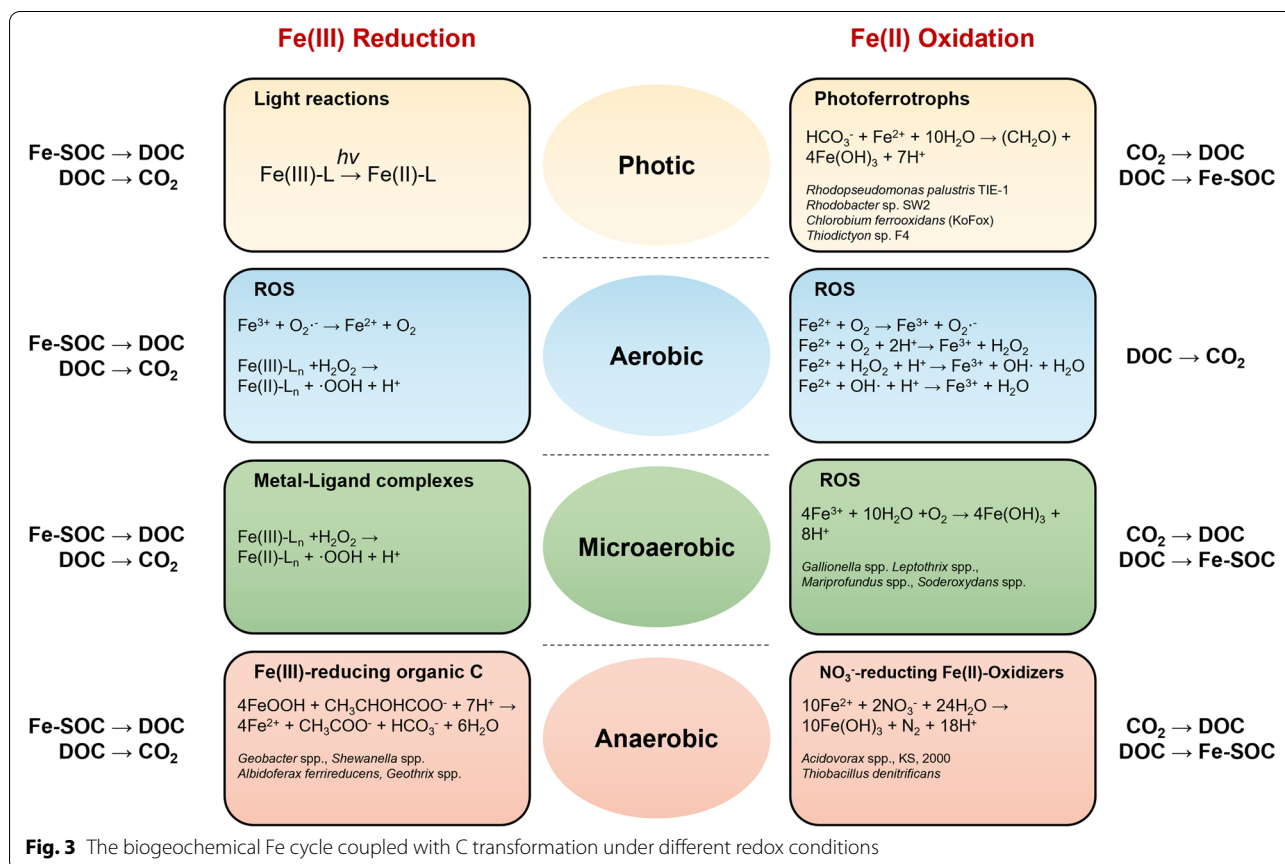
Oxidation of Fe(II) to Fe(III) by bacteria or by chemical oxidation has been previously thought to involve oxygen as the electron acceptor. However, in a hypoxic experiment, Fe(II) oxidation is probably driven by phototrophic microorganisms, which include *Rhodospseudomonas palustris* TIE-1, *Rhodobacter* sp. SW2, *Chlorobium ferrooxidans* (KoFox) and *Thiodictyon* sp. F4 (Melton et al. 2014). Photoferrotrophs can oxidize Fe(II) to poorly crystalline ferric (oxy)hydroxides using light energy, bicarbonate as the electron acceptors and carbon sources, and Fe(II) as the electron donor (Figs. 3 and 4). Widdel et al. (1993) described the first isolate of anoxygenic phototrophic Fe(II)-oxidizing bacteria that oxidized Fe(II) to brown Fe(III) and reduced CO₂:

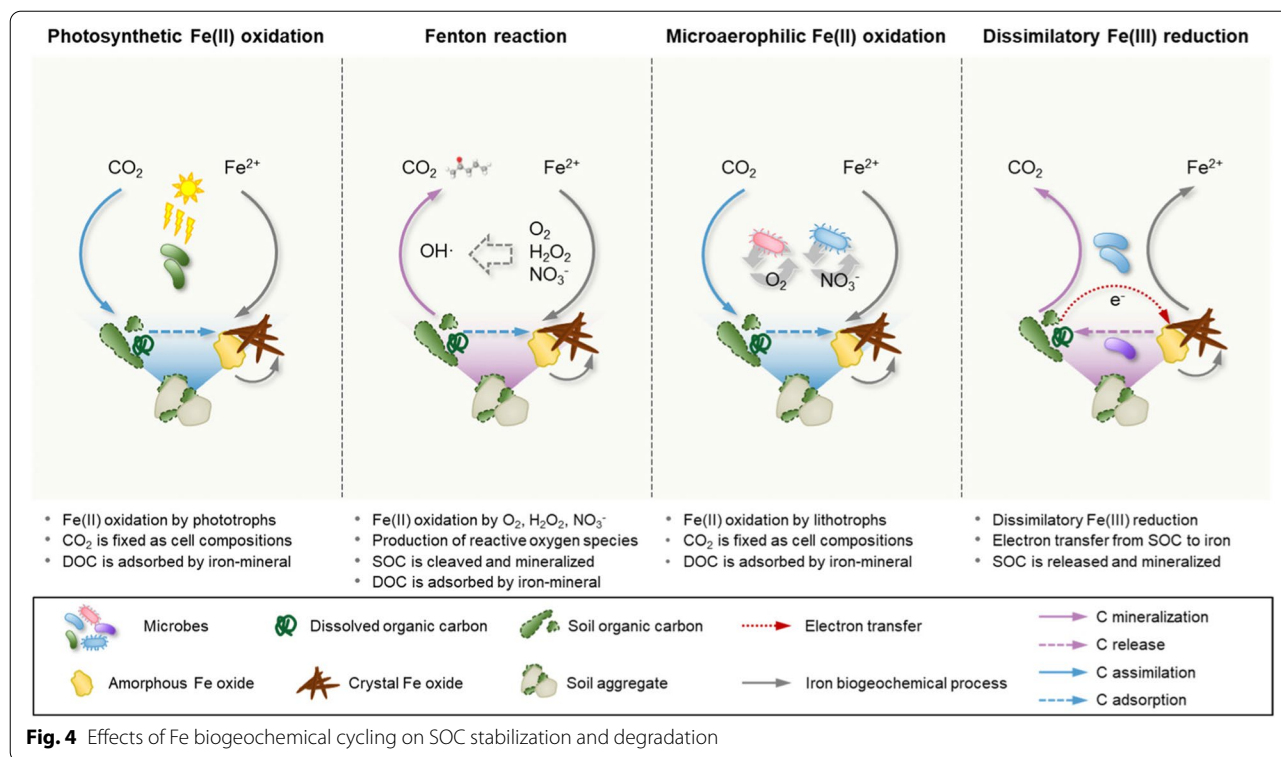


It is estimated that photoautotrophic Fe(II)-oxidizing bacteria can synthesize 48 billion tons of organic carbon per year in the ocean (Raiswell and Canfield 2012). The phototrophic Fe(II)-oxidizing bacteria are widely distributed on the land surface and the ocean (Kappler et al. 2005; Kappler and Straub 2005; Hedrich et al. 2011). Jiao et al. (2005) showed that 5.36 mg of biomass produced per mmol of Fe(II) which was oxidized by purple nonsulphur Fe(II)-oxidizing phototrophs - *R. palustris* TIE-1. This represents ~72% of the theoretical cell yield of 7.5 mg/mmol of Fe(II). Thus, within the photic zone, the Fe(II) oxidation coupled with CO₂ assimilation process is an important pathway of SOC production.

3.1.2 Fenton reaction-induced SOC mineralization

Few microbial communities can produce oxidase that degrades lignin, and therefore soil abiotic Fe(II) oxidation is one of the important mechanisms that can facilitate the degradation of lignin and other phenolic compounds (Thevenot et al. 2010; Hall and Silver 2013, 2015; Wang et al. 2017b). The dissolved Fe(II)

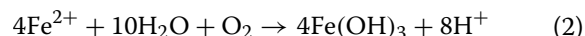




could be generated via biotic or abiotic reduction of Fe(III) under light or oxic conditions (Fig. 3), such as the direct bio-reduction of Fe(III) by cyanobacterial enzymes and the photochemical reduction of organic ligand bounded Fe(III) (Kranzler et al. 2011; Swanner et al. 2018). During the photochemical process, light drives electron transfer from ligand to Fe(III) and generates reactive oxygen species (ROS), including ¹O₂, O₂⁻, OH· and H₂O₂ (Pang et al. 2019; Lueder et al. 2020b). In oxic environments, Fe(III) could be reduced to Fe(II) by ROS, which is ubiquitous in surface waters and formed by atmospheric precipitation, photochemical reaction or biological production (Lueder et al. 2020a; Yu and Kuzyakov 2021). Thus, there is a Fe(II) pool under oxic conditions, and the Fe(II) can donate electrons to oxidants, such as O₂, NO₃⁻, or H₂O₂ (Melton et al. 2014). The Fenton reaction leads to the production of ROS, especially OH·, which can directly oxidize SOC to small molecule compounds, increase the bioavailability of SOC, and even mineralize SOC into CO₂ (Figs. 3 and 4) (Hall and Silver 2013; Patel et al. 2021). Chen et al. (2020) conducted experiments in soil slurries, and found an 8% increase in C mineralization, when MAOC was generated via Fe(II) oxidation without added SOC.

3.1.3 Microaerophilic Fe(II) oxidation coupled with CO₂ assimilation

Microaerophilic Fe(II) oxidizers are lithotrophic bacteria that oxidize Fe(II) with O₂ (Figs. 3 and 4) according to the following stoichiometric equation:



These microaerophilic Fe(II) oxidizing bacteria belong to the phylum Proteobacteria, including the marine genus *Mariprofundus* and the freshwater genera *Leptothrix*, *Gallionella* and *Sideroxydans* (Kucera and Wolfe 1957; Weiss et al. 2007; Fleming et al. 2011; Emerson et al. 2013). Growth of the microaerophilic Fe(II) oxidizers widely distributed in freshwater and marine environments exposed to O₂ (Emerson and Moyer 1997; Edwards et al. 2003; Hegler et al. 2012) is severely inhibited under anoxic conditions, except for culture KS, which is chemolithoautotrophic nitrate-dependent Fe(II) oxidation enrichment culture and contains *Sideroxydans* spp. (Blöthe and Roden 2009). These chemolithoautotrophic microorganisms are widely distributed in marine and terrestrial wetland ecosystems (Weiss et al. 2007). Microaerophilic Fe(II)-oxidizing bacteria belong to the *Gallionella* and *Leptothrix* of *β*-proteobacteria, which can significantly increase cell production or ferrous Fe oxidation, thereby fixing CO₂ (Bryan et al. 2012).

NO₃-dependent Fe(II) oxidizing bacteria can oxidize Fe(II) and obtain energy from it to fix CO₂ (Kappler and Straub 2005).

3.1.4 Dissimilatory Fe(III) reduction coupled with SOC mineralization

The main Fe(III) reduction processes include: photochemical Fe(III) reduction, O₂^{•-}-mediated Fe(III) reduction, and microbial Fe(III) reduction (Melton et al. 2014). Dissimilatory Fe(III) reduction is a form of microbial respiration, which can use Fe(III) as the terminal electron acceptor and produce CO₂ by oxidating electron donor (i.e., SOC) under anoxic conditions (Figs. 3 and 4) (Lipson et al. 2010). The electron donor and terminal electron acceptor availability influences anaerobic mineralization of SOC. Sutton-Grier et al. (2011) showed that soils amended with electron acceptors resulted in greater SOC mineralization in long term experiments, which increased with the free energy yield of electron acceptor pathway (Fe(III) respiration > SO₄²⁻ reduction > methanogenesis). In soils from higher rainfall locations, microbial Fe reduction can account for up to 44% of anaerobic SOC oxidation (Dubinsky et al. 2010). This is consistent with the findings of Chen et al. (2020) that the Fe(III) was preferentially reduced, increasing the anaerobic mineralization of SOC by 32–71% under oxygen limited conditions in humid soil. Therefore, the coupling process of dissimilatory Fe(III) reduction and SOC mineralization plays a crucial role in C stabilization and degradation.

3.2 Biogeochemical reactions of Fe minerals

The SOC distributed in soil aggregates is stable slow-cycle carbon, but the Fe-SOC part in it is sensitive to environmental conditions. The reaction of Fe minerals under redox fluctuation conditions affects not only the stability of Fe-SOC but also the stability of soil aggregates, resulting in the SOC stabilization or degradation.

3.2.1 Effects on the formation and decomposition of Fe-SOC

Water saturated conditions in soil influence the concentration and distribution of high surface area minerals that are sorbents for C in soils (Wagai and Mayer 2007; Chen et al. 2017). Under aerobic condition, the change in morphology of Fe minerals can affect the stability of SOC, which may be partly due to Fe minerals transformed by Fe(II) oxidation forming Fe-SOC which is resistant to microbial mineralization (Mikutta et al. 2005; Rasmussen et al. 2006; Saidy et al. 2012). During the oxidation of Fe(II), the catalyzed production of hydroxyl radicals can enhance the oxidative activity of phenol (Sinsabaugh 2010; Hall and Silver 2013), resulting in simultaneous stabilization and decomposition of SOC.

Recent studies have focused on the process of dissimilatory Fe(III) reduction under anaerobic conditions, which leads to the dissolution of Fe minerals. Here, SOC is usually incompletely decomposed, resulting in the accumulation of SOC, especially short-chain fatty acids (Wu et al. 2015), and the dissimilatory Fe(III) reduction process can be coupled with the oxidation of short-chain fatty acids (Hori et al. 2010; Ding et al. 2015), thereby decreasing SOC content. Recent studies on the fate of Fe-SOC have demonstrated that Fe reduction can undermine the role of Fe minerals in stabilizing SOC (Pan et al. 2016; Adhikari et al. 2017; Zhao et al. 2017). During wetting and drying cycles, even in anoxic environments, Fe(II) can be oxidated through coupled biotic-abioc reactions with oxidants such as NO₂ and MnO₂ (Hedrich et al. 2011; Picardal 2012; Roden 2012). Moreover, Liu et al. (2019) found that the contribution of nitrite to Fe(II) oxidation was higher than that of biological processes. The composition and diversity of microbial communities changed during the anaerobic nitrate reduction and Fe(II) oxidation at circumneutral pH (Li et al. 2016).

3.2.2 Effects on the formation and dissociation of soil aggregates

When the environmental conditions changed from aerobic to anaerobic during flooding, Fe oxides can be reduced to Fe(II), weakening the binding within the microaggregates in the process (De Campos et al. 2012). Soil aggregates are dissociated and exposed to fresh surfaces to form Fe mineral-aromatic C complexes, which are then protected by re-aggregation during the transition from anaerobic to aerobic conditions (Huang et al. 2018). Different forms of Fe minerals produced during redox fluctuations can influence aggregation. For example, short-range-ordered (SRO) Fe oxides have stronger cementing ability and may play an important role in the formation and stabilization of soil aggregates (Hou et al. 2007; Wang et al. 2016). However, Xue et al. (2019) found that in the > 0.25 mm aggregates, amorphous Fe oxides are the most important binder, while in 0.25–0.053 mm aggregates, amorphous and complex Fe oxides play a more prominent role in binding aggregates.

4 Key factors of Fe cycling coupled with C stabilization

The effects of Fe biogeochemical cycling on SOC sequestration are controlled by the characteristics of the Fe mineral, and environmental and soil conditions, which are relevant to the processes of Fe redox and formation of Fe-SOC (Table 1).

Table 1 Key factors for Fe cycling coupled with C sequestration

	Factors	Effects	Processes
Fe mineral	SSA	positive	Large SSA minerals adsorb more SOC (SSA: Fh > Geo > Mag > Lep)
	Crystallinity	negative	Poorly crystalline Fe minerals have high SSA, but are associated with faster-cycling SOC
	Fe oxidation states	/	Fe mineral-mediated electron transfer processes enhance SOC decomposition, and Fe(II)-catalyzed mineral transformations influence SOC binding capacity
Natural factors	Soil pH	Positive & negative	At acidic pH, Fe(II) has a slower oxidation rate and SRO mineral production rate. Acidic pH is beneficial to enhance the electro-affinity of DOC and Fe minerals
	Soil texture	/	Fine soil fraction rich in Fe/Al oxide and clays can stabilize SOC
	OM composition	/	The short-chain fatty acids mineralization is coupled with Fe(III) reduction
	Climate	/	Wet and warm conditions may favor (bio)chemical weathering and enrich poorly crystalline minerals with higher activity, but may also promote mineral reduction and release SOC. Dry and cold conditions may slow down the transformation of ferrihydrite to crystalline Fe oxide and favor SOC protection
Anthropogenic factors	Fertilization & cultivation	/	N and P inputs decrease the SOC due to decrease pH, destabilization of aggregates and change the microbial community. Crop introduced microbes and root exudates may stabilize and/or release MAOC

4.1 Fe mineral

There is a strong positive relationship between pedogenic Fe (Fe oxyhydroxide) content and C stocks when comparing disparate soils at regional and global scales (Kramer et al. 2012; Kleber et al. 2015). The significance of Fe/Al oxides in the persistence of SOC has partly been attributed to their physicochemical properties. The major features include:

4.1.1 Specific surface area

The association of SOC with soil minerals is generally attributed to the large specific surface area (SSA) of soil minerals (Kiem and Kögel-Knabner 2002; Singh et al. 2016), based on the positive relationship between soil mineral SSA and SOC storage (Singh et al. 2018, 2019; Churchman et al. 2020). Kennedy et al. (2002) found that 85% of variation in total SOC could be explained by mineral SSA in a black shale soil. Comparing ferrihydrite, iron sulfide, hematite and pyrite, the ferrihydrite has the highest carbon adsorption per mass, although its carbon adsorption per SSA is not the highest (Wang et al. 2019). The results may be due to the highest SSA of ferrihydrite among the four minerals, leading to its highest sorption capacity, which is consistent with the previous conclusion. However, other studies have found that the correlation between SSA and SOC in some soils is not very significant (Mayer and Xing 2001; Wiseman and Püttmann 2005), and it is still difficult to predict the potential of soil for SOC storage through SSA. This may be because SOC is distributed in heterogeneous patches within the soil microstructure (Vogel et al. 2014; Steffens et al. 2017), limiting the direct relationship between SSA

and SOC concentration. The general lack of agreement between SSA of Fe minerals and SOC storage requires further work, which can be resolved in future work using micro-spectroscopic techniques (Weng et al. 2021).

4.1.2 Fe mineral crystallinity

Compared to the ordered minerals (e.g., lepidocrocite, goethite and hematite), the SRO iron minerals such as ferrihydrite are considered particularly important for SOC stabilization due to the higher SSA and more surface hydroxyl groups (Chorover et al. 2004; Zhang et al. 2013; Wen et al. 2014; Xiao et al. 2015; Huang et al. 2018). Poorly crystalline Fe/Al oxides have been shown to be better predictors of stable SOC content in acid soils, compared to crystalline Fe/Al oxides (Kleber et al. 2005). The SRO iron can facilitate the rapid accumulation of plant-derived SOM, whereas crystalline iron tends to associate with microbial-derived SOM, the slower-cycling SOC (Hall et al. 2018). In addition, SOC association can slow down the transformation of poorly crystalline iron minerals by inhibiting the nucleation and the electron transfer, so that more SRO minerals can be retained to stabilize SOC (Hu et al. 2018; Lu et al. 2019).

4.1.3 Fe oxidation states

Fe minerals can directly transfer the electrons as a (semi) conductor, or indirectly mediate electron transfer process via the redox cycling between Fe(II) and Fe(III), resulting in the enhancement of SOC decomposition (Hu et al. 2021). Fe minerals can also promote the interspecies electron transfer between microbes and sequentially enhance the biodegradation of SOC and methane emission (Baek

et al. 2018; Yin et al. 2018; Ren et al. 2020). The Fe oxidation states may affect their electron transport ability of Fe minerals (Li et al. 2019), and specifically, the conductivity of magnetite with Fe(II) and Fe(III) was much higher than most Fe minerals with Fe(III), such as ferrihydrite and goethite. Due to the coexistence of Fe(II) and Fe(III), magnetite can act as both an electron acceptor and donor and consequently promote energy metabolism for microbes under various conditions (Byrne et al. 2015). In addition, Fe(II) adsorbed on Fe mineral surface or defects could also promote the formation of secondary minerals, such as hematite and magnetite (Han et al. 2018; Notini et al. 2018), which could influence the SOC binding capacity via changing the electron transfer ability, surface charges, SSA and crystallinity of Fe minerals.

4.2 Impacts of natural and anthropogenic factors

4.2.1 Climate

Many studies have shown that climate change, including temperature and precipitation, is closely related to the SOC chemical diversity, and could induce variation of Fe-SOC in soils. For example, Doetterl et al. (2015) found that in humid regions with mild to warm temperatures, where (bio)chemical weathering rates are high, SOC is predominantly found in association with the mineral fraction. This may be due to the fact that in environments with humid climates and abundant primary minerals, poorly crystalline minerals (i.e., Fe/Al (oxy)hydroxides) increase with weathering process (Slessarev et al. 2021), and reduced Fe-bearing clays act as antibacterial agents (Wang et al. 2017a) to inhibit microbial activity, thus protecting SOC through physicochemical barriers. The humid environment is favorable to the formation of poorly crystalline iron minerals and binding to SOC, while higher precipitation might result in the microbial reduction of Fe and release of SOC in reducing environments (e.g., poor soil aeration) (Adhikari et al. 2016; Inagaki et al. 2019). The cold and dry conditions are also favorable for Fe-SOC (Mu et al. 2016), a possible explanation is that the colder and drier environments slow down the transformation of ferrihydrite and provide stronger protection for Fe-SOC, especially the aromatic SOC components (Gnanaprakash et al. 2007; Zhao et al. 2016).

It is worth noting that climate is not the dominant factor in the coupling of Fe cycling and carbon stabilization, and the common effects of geochemical factors cannot be ignored (Doetterl et al. 2015, 2018). For instance, temperature may not affect the formation or the stability of Fe-SOC associations (Nguyen et al. 2019), but depends on the properties of mineral and SOC. Overall, climate change alters Fe-SOC stability by affecting the weathering of Fe-bearing minerals, the formation and transformation of iron minerals, and microbial activity, which

can also explain the fact that the decomposition of stable SOC is more sensitive to changes in temperature (Conant et al. 2008; Singh et al. 2017a).

4.2.2 Soil pH and Eh

Soil pH is always inversely correlated with redox potential (Eh), which is the result of coupling multi biogeochemical processes in soil (Yang et al. 2021). Soil pH affects Fe-OC bonding possibly through changes to the Fe speciation state and charge characteristics, and plays a key role in Fe cycling (Kappler and Straub 2005). In theory, under more acidic conditions Fe(II) has a slower oxidation rate, while under alkaline conditions Fe(II) has a faster oxidation rate. At acidic pH, Fe(II) can persist, even under oxic conditions (Cornell and Schwertmann 2003; Stumm and Morgan 2012). At neutral or alkaline pH, Fe(II) is only stable in anoxic environments and oxidized to Fe(III) minerals by molecular oxygen.

The structure and electro-affinity of DOC and Fe-containing minerals during the coprecipitation processes of Fe and DOC are directly affected by pH (Nierop et al. 2002; Jansen et al. 2003). The density of negative charge on the Fe hydroxides surfaces increases with the increase of the solution pH, and can enhance the affinity for DOC (Jansen et al. 2003; Bolan et al. 2011). The decrease in pH enhanced the co-precipitation of DOC and Fe, which is consistent with the adsorption of DOC on Fe oxides (Du et al. 2018; Wang et al. 2021). DOC components with high molecular weight and abundant O-containing functional groups, including carboxyl and phenolic groups, have a stronger affinity for Fe (Kaiser et al. 2007; Wang et al. 2021). Newcomb et al. (2017) demonstrated that pH significantly changes the free energy of bonding. The interaction of the organic-mineral pairs with changes in pH, when the pH was tested below the pKa (pH=4), the binding force between carboxylic acid and mica increased by an order of magnitude. This pH dependency has been reported for several organic-mineral systems, as stronger inner-sphere coordination generally occurs at low pH, while weaker outer-sphere complexation is observed at higher pH (Kleber et al. 2005; Persson and Axe 2005; Newcomb et al. 2017).

4.2.3 Soil texture

Giannetta et al. (2018) found that more thermally labile compounds were protected in the heavy fraction of soils in various ecosystems. Some studies showed that fine-sized residues often decompose faster than the coarse-sized ones, particularly in sandy and sandy loam soils (von Haden et al. 2019), suggesting that soil texture could control the residues decomposition and that clay minerals may favor the residue-derived C stabilization (Ye et al. 2017). The fine fractions of soils have higher SSA

and be expected as active fraction for SOC adsorption, which contain many clay minerals and Fe/Al oxides. SOC could be stabilized by clays through weak electrostatic interactions and hydrogen bonds, precipitated by cations bridges, and associated with Al/Fe oxides (Stevenson 1994). Although the coarse fractions of soils, including sand and coarse silt, generally exhibit low SOC affinity, they can be coated by Fe oxides through electrostatic forces, Van der Waals interactions, and Fe-O-Si bonds (Scheidegger et al. 1993), thus increasing SOC adsorption and cation exchange capacity.

4.2.4 Anthropogenic activity

The application of N and P fertilizers can change a wide range of soil properties, with detrimental effects including acidification, aggregate destabilization, microbial community shift towards bacteria, and loss of oxidative enzyme activities, which could contribute to the change of SOC. Fertilizer N inputs have been shown to lower Fe-SOC through decreasing microbial growth and C-bound C, which is sensitive to soil pH, but at the same time increase total SOC and light fraction C content (Ye et al. 2018). Shen et al. (2018) also found that nutrient amendment did not affect total SOC content, but increased MAOC with decreasing soil aggregate stability, based on an experiment combining nitrogen and phosphorus inputs continuously for 15 years. The reduced aggregation and increased MAOC was attributed to the decrease of fungal biomass and increase of bacterial biomass (Shen et al. 2018).

Specific plant functional traits, such as biological nitrogen-fixation, are recognized as important drivers of C accumulation in grassland (Fornara and Tilman 2008; De Deyn et al. 2009, 2011) and cropland soils (Kallenbach et al. 2015; Frasier et al. 2016). Legumes enhanced the formation of organo-mineral complexes through increasing particulate organic matter nitrogen and microbial biomass nitrogen (Canarini et al. 2018). Organic acids (e.g., oxalic acid), components of root exudates, can release SOC from the protective mineral phases, and further stimulate the microbial reductive release of Fe-SOC under anoxic conditions (Ding et al. 2021). Hence, the crop type is an important anthropogenic activity affecting the stability of Fe-SOC.

5 Conclusions

The interaction between soil minerals, in particular the cycling of Fe minerals, and SOC has been widely recognized as a key driver for the stabilization of C in soil. Microbial Fe(II) oxidation is shown to favor the formation of amorphous Fe minerals thus promoting SOC adsorption and CO₂ assimilation. Whereas chemical Fe(II) and microbial Fe(III) reduction oxidation facilitate

the SOC mineralization via ROS or electron transfer, respectively. Photochemical Fe(III) reduction provides Fe(II) and ROS for the Fenton reaction, which indirectly promotes SOC mineralization. During Fe(II) oxidation, poorly crystalline Fe minerals with high reactivity are generated, which can facilitate SOC stabilization through the formation of Fe-SOC. On the contrary, the reductive dissolution of Fe minerals dissociates Fe-SOC and favors microbe access to degrade SOC. The coupled processes are largely controlled by redox conditions, the nature and properties of Fe minerals and edaphic properties. Thus, the cycling of Fe controls the two-edged of SOC stabilization and Fe-SOC turnover (Fig. 4).

6 Research needs and perspectives

The fate of Fe-SOC has been reviewed in light of the mechanisms which control these processes in soil. However, many knowledge gaps have been highlighted, not least being the ability to accurately quantify and visualize these organo-mineral assemblages (Weng et al. 2021). To gain a better understanding of the factors that control both the formation and composition of these organo-mineral associations, we have suggested some priority areas for future research:

- (1) The effects of Fe on SOC sequestration under oxic conditions have been of great interests, however, these have been rarely studied under anoxic conditions (i.e., paddy soils) or in the systems with fluctuating redox conditions. Some studies only focus on dissimilatory Fe reduction, and there is a lack of research on the extent and direction of other reaction processes under anaerobic conditions, such as ferrous oxidation on SOC stabilization processes. Therefore, understanding the Fe cycle, including biological aspects, under a range of conditions is required.
- (2) Based on the diversity and complexity of SOC components, different SOC components may have different binding mechanisms with Fe minerals and result in different stability of Fe-SOC. Therefore, it is essential to investigate the molecular mechanisms of Fe-SOC interactions under redox conditions using advanced characterization techniques (e.g., EXAFS, FT-ICR-MS, and NMR).
- (3) Most studies on the effect of Fe redox process on the accumulation of SOC are mainly qualitative, while Fe oxidation and reduction processes often occur simultaneously, and the intermediate processes governing these two major processes remain a “black box”. As much of the data to date is qualitative, we recommend greater quantification to clarify the contribution of each reaction process of the Fe

cycle in relation to SOC sequestration. A kinetic modelling approach could provide additional valuable insights towards quantification.

- (4) Current studies on the effects of Fe minerals on SOC sequestration are mostly based on non-disturbed ecosystems. However, soils are commonly subjected to anthropogenic and natural disturbances. It will be crucial to gain a mechanistic understanding of which processes may result in greater stabilization via Fe-SOC, or indeed result in the dissociation of soil aggregates. This can then guide management practices to optimize soil C sequestration opportunities.

Authors' contributions

XXS and PW: Conceptualization, Literature collection and analysis, Visualization, Writing. LVZ, NB, HLW and XML: Review and Editing. KC, YY and MLW: Literature collection and analysis. TXL: Supervision, Conceptualization, Review and Editing. FBL: Supervision, Conceptualization. The author(s) read and approved the final manuscript.

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Availability of data and materials

Data sharing not applicable to this article as no datasets were generated or analysed during the current study.

Declarations

Consent for publication

All authors declare that they are consent for publication in the journal of *Carbon Research*.

Competing interests

Lukas Van Zwieten, Nanthi Bolan, Hailong Wang, Tongxu Liu and Fangbai Li are editorial board members for *Carbon Research* and were not involved in the editorial review, or the decision to publish this article. All authors declare that there are no competing interests.

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