

Review

Effects of Iron Oxide Phase Transformations in Paddy Soils on Organic Carbon Stabilization: A Review

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Abstract

Iron oxides are crucial for the long-term storage of soil organic carbon (SOC) in paddy soils, making them a key factor in global carbon cycles and important for strategies aimed at combating climate change. This review examines the role of iron oxides in paddy soils, particularly their interaction with SOC, which helps stabilize carbon and contributes to mitigating climate change. These processes of iron oxide phase transformations, wet–dry cycles, and microbial activity help trap carbon in the soil, supporting climate change mitigation efforts. Wet–dry cycles promote mineral dissolution and re-precipitation, forming new reactive surfaces and OC-Fe complexes. Future research should adopt a multi-scale approach to better connect molecular mechanisms with ecosystem-level carbon processes. A deeper understanding of iron oxide behavior in paddy soils will support the development of sustainable soil management practices and improve models for predicting soil carbon sequestration under climate change.

Keywords: iron oxides; soil organic carbon; paddy soils

1. Introduction

Paddy soils, a significant type of anthropogenic wetland ecosystem, are crucial for global food security, providing sustenance for more than half of the world's population. Despite occupying a relatively small area, paddy soils play a critical role in the global carbon cycle, especially in the long-term sequestration of organic carbon [1]. Globally, rice cultivation covers approximately 160 million hectares, accounting for about 11–12% of total cropland area [2]. Continuous anthropogenic management through periodic flooding, ploughing, and drainage profoundly influences pedogenic processes, promoting the distinctive features of these soils, including pronounced iron and manganese mobilization, gleization, and the formation of characteristic plough-pan horizons [3].

Paddy soils, though occupying a small area, are highly effective in storing SOC, which plays a vital role in reducing greenhouse gases and combating climate change. This carbon storage capability makes paddy soils essential for mitigating climate change [4]. The ability of paddy soils to store carbon is largely due to the stabilization of organic carbon through interactions with soil minerals, especially iron oxides [5,6]. Iron-bound organic carbon (OC-Fe) makes up about 21–30% of the total organic carbon in paddy soils, which



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is much higher than in non-flooded soils [7]. OC-Fe refers to organic carbon associated with iron oxides and hydroxides via adsorption, complexation or co-precipitation; the resulting OC-Fe complexes are regarded as a key fraction of mineral-associated organic carbon (MAOC) that plays a disproportionate role in the long-term stabilization of SOC in flooded paddy soil systems. These iron oxides, often referred to as the “rust carbon pool” by forming strong physicochemical bonds with organic molecules, thereby reducing their bioavailability and enhancing their long-term persistence [8,9].

The mechanisms governing the quantity and persistence of SOC are critical to global climate regulation, nutrient cycling, and soil moisture retention [10–12]. Within this broader context, the significant SOC sequestration potential exhibited by paddy soils underlines their global environmental importance and the necessity to understand the mineralogical and biogeochemical factors driving carbon stabilization [13]. Early foundational reviews, such as Kögel-Knabner et al., (2010) provided comprehensive descriptions of the biogeochemical and physicochemical characteristics of paddy soils, with particular emphasis on redox-induced transformations [3]. Although the role of iron in the carbon cycle is well-established, research on how iron oxide transformations affect the long-term stability of SOC in paddy soils is still limited [3]. Given that iron oxides continuously transition between poorly crystalline and highly crystalline states under fluctuating redox conditions (e.g., variations in temperature, inundation frequency, pH, and redox potential(Eh)) [5,14–16], these minerals uniquely govern electron transfer between Fe^{2+} and Fe^{3+} , fundamentally regulating SOC stabilization pathways [6,9].

This review explicitly bridges this knowledge gap by integrating recent mechanistic insights into iron oxide dissolution-precipitation, solid-state conversions, and their intricate coupling with organo-iron complex formation under variable redox conditions. We also examine how these coupled mineral–organic interactions influence aggregate protection, microbial redox reactions, and ultimately SOC stabilization in paddy soils. By synthesizing these interconnected processes, we provide an integrated framework that extends existing understanding and offers targeted strategies for enhancing SOC persistence in flooded agricultural ecosystems.

2. Method

This review synthesizes current knowledge on the role of iron oxide transformations in SOC stabilization in paddy soils. The literature included in this review was selected based on a systematic search and screening process (Figure 1), which is outlined below.

Literature Search Strategy

A comprehensive literature search was conducted using the following databases: Web of Science, Scopus, and Google Scholar. The search was limited to studies published between 2010 and 2025 to ensure the inclusion of the most recent research. Keywords used in the search included “iron oxides,” “iron oxide transformations,” “paddy soils,” “soil organic carbon stabilization,” and related terms. Boolean operators (AND/OR) were used to combine the keywords effectively.

Inclusion and Exclusion Criteria

Inclusion Criteria: Studies were included if they focused on the role of iron oxides in SOC stabilization within paddy soils, provided experimental or field-based data, or discussed the mechanisms of iron cycling (oxidation/reduction processes).

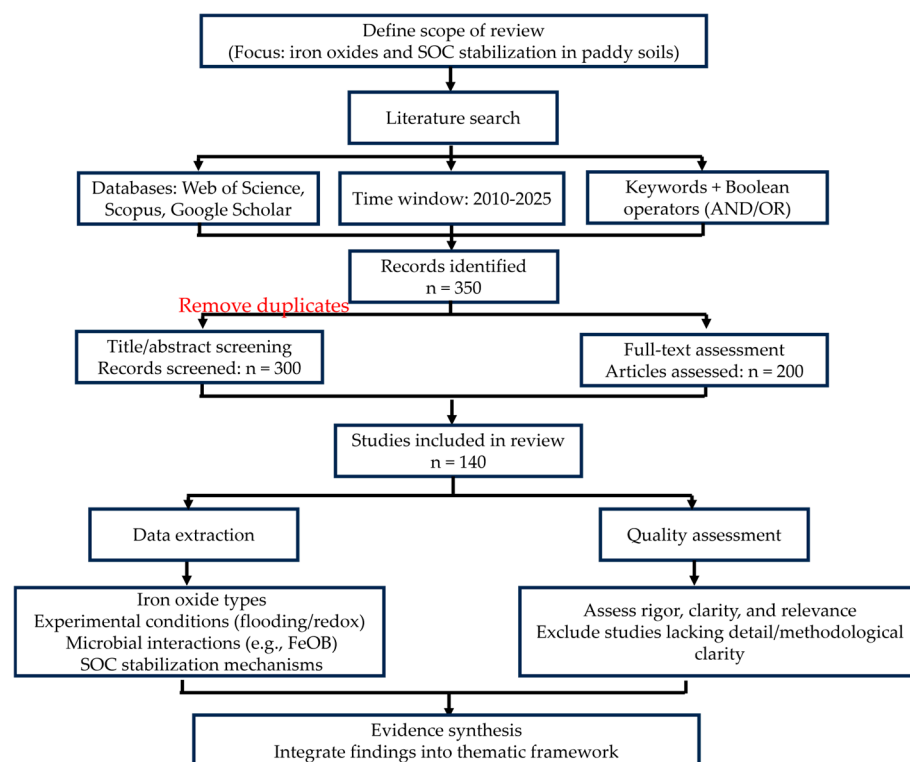


Figure 1. Flowchart of references screening method.

Exclusion Criteria: Studies were excluded if they focused on non-paddy soil ecosystems, did not address iron oxide interactions with SOC, or lacked sufficient experimental detail or data on iron species involved in the SOC stabilization processes.

Screening Process

The initial search yielded 350 articles. After removing duplicates, 300 articles were screened based on titles and abstracts. Following the abstract screening, 200 articles were selected for full-text evaluation. After thorough review, 140 studies met the inclusion criteria and were retained for this review.

Data Extraction

Relevant data were extracted from the selected studies, focusing on the types of iron oxides studied, experimental conditions (e.g., flooding, redox conditions), the role of microbial interactions (e.g., iron-oxidizing bacteria (FeOB)), and the findings related to SOC stabilization mechanisms.

Quality Assessment

Studies were evaluated based on their experimental rigor, the clarity of their findings, and their relevance to the topic. Studies lacking sufficient detail or methodological clarity were excluded from the final analysis.

3. Sources, Sink Functions and Stabilization Mechanisms of SOC in Paddy Soils

Paddy ecosystems simultaneously function as both carbon sources and sinks [3,17]. labile organic carbon (LOC) contribute to rapid turnover and short-term nutrient cycling, while resistant organic carbon (ROC) play a key role in maintaining soil structure and fertility over longer timescales, ensuring sustainable agricultural productivity [12]. In flooded paddy soils, the main sources of SOC are plant residues and microbial biomass, both

of which contribute significantly to the long-term carbon storage potential of these soils [3]. Agronomic practices, especially the application of organic manures, further promote SOC accumulation by increasing external carbon inputs and stimulating microbial activity [9,18]. Once incorporated into the soil, carbon is retained in various forms, including plant residues, microbial necromass, aromatic structures, and humic macromolecules. Long-term preservation of SOC relies on a synergistic interplay of aggregate occlusion, mineral complexation, and microbial transformation (Figure 2) [19,20]. At the same time, these mechanisms maintain the carbon reservoir in paddy ecosystems.

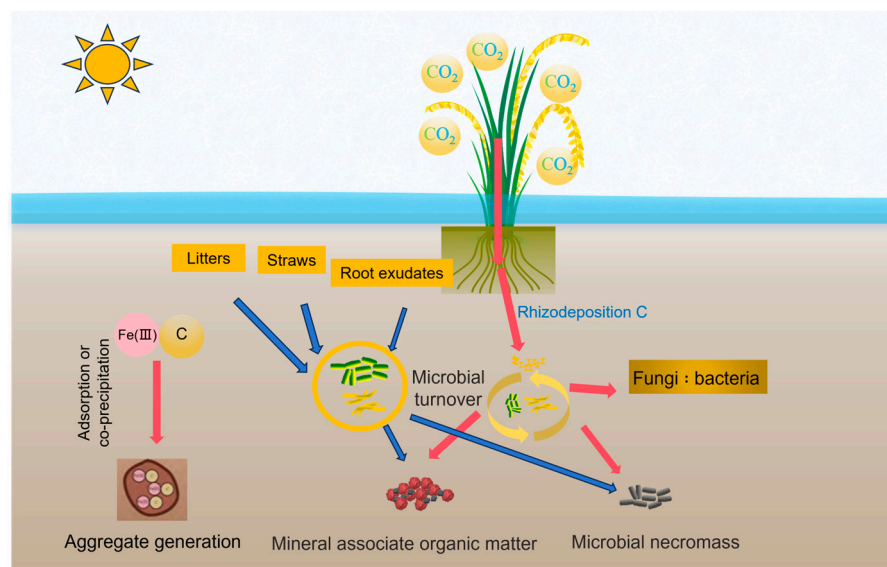


Figure 2. Conceptual model of carbon inputs and Fe–OM–microbe interactions in flooded paddy soils. Plant litter, straw, and root exudates provide organic substrates for microbial growth and rhizodeposition carbon in the rhizosphere. Microbial turnover produces mineral-associated organic matter and microbial necromass (black rod), part of which is stabilized through Fe(III)-C adsorption or co-precipitation and aggregate formation. Blue arrows indicate carbon input fluxes, whereas red arrows represent microbial transformation and stabilization pathways. The Fe(III)-C symbol denotes Fe-bound organic carbon. The red amorphous particles represent minerals, while the small black amorphous particles represent carbon bound to minerals [3,17].

3.1. Carbon Sources and Sink Functions in Paddy Soils

The SOC can be categorized into two main pools: labile organic carbon (LOC), which decomposes rapidly, and resistant organic carbon (ROC), which is more stable and plays a key role in maintaining long-term soil health [20]. LOC consists of dissolved organic carbon (DOC), microbial biomass carbon (MBC), and particulate organic carbon (POC), all of which are highly sensitive to environmental fluctuations and are decomposed at a faster rate [21,22]. In contrast, the relatively stable ROC is primarily composed of MAOC and highly condensed aromatic structures. These compounds are chemically stabilized via inner-sphere complexation or surface adsorption onto clay minerals and Fe/Al oxides, rendering them recalcitrant and pivotal to long-term soil structure and fertility [19,23–25]. Due to its slow turnover, MAOC represents a disproportionately effective leverage point for long-term carbon sequestration and climate change mitigation [26].

Pronounced vertical stratification characterizes SOC fractions within paddy profiles. In a subtropical paddy soil, MAOC represented up to 90% of total SOC at 50–70 cm depth, whereas the relative abundance of LOC fractions fell sharply with depth [27]. Conversely, Jiang et al. (2023) documented a decline in MAOC from 49.5% in the surface horizon to 33.0% at 80–100 cm, accompanied by an increase in POC from 50.6% to 67.0% [28]. Such contrasting depth trends underscore the co-control exerted by mineralogy, physical

stratification, regional climate, cultivation history and water-management regime on the architecture and persistence of carbon stocks in paddy soils [4,17,27].

3.2. Mineralization of SOC in Paddy Soils

The mineralization of organic carbon in paddy soils is a key process in the soil carbon output, where organic carbon compounds in the soil are converted into inorganic carbon compounds [29]. This process plays an extremely important role in the carbon cycle of paddy soil ecosystems. During the planting process of rice from the heading stage to the ripening stage, shallow, wet, and intermittent dry irrigation techniques are used to maintain the rice's high assimilation capacity and vigorous root system. As a result, paddy soils undergo alternating dry and wet conditions followed by continuous flooding.

Long-term flooding may create more stringent anaerobic conditions in the paddy soils. Studies have found that the turnover rate of organic carbon in paddy soils under flooding conditions is higher than under aerobic conditions [30]. Additionally, research has shown that when dry land is converted to flooding management within a certain moisture range, the soil moisture content is positively correlated with organic carbon mineralization rates [31]. The type of organic carbon utilized by microorganisms also differs under varying moisture conditions. A study by Li et al. (2021) indicated that under flooding conditions, soil microorganisms primarily use amino acid-based carbon sources during the early stages of flooding, while in the later stages, they mainly use phenolic acids and amino acid-based carbon sources [32]. Under oxygen-rich conditions, microorganisms predominantly utilize polymeric carbon source [32]. When paddy soils remain flooded for extended periods, the oxygen concentration in the soil decreases, CO₂ concentration increases, soil Eh decreases, and ammonia nitrogen accumulates. This is accompanied by the reduction of NO₃[−], SO₄^{2−}, Fe³⁺, and Mn⁴⁺, which affects the solubility of iron, manganese, and phosphate in paddy fields and alters soil pH [33]. Under long-term flooding, when paddy soils are in an anaerobic state, the Eh decreases, and anaerobic microorganisms dominate the soil, slowing down organic matter decomposition. When the oxygen content in the soil further decreases and reaches strict anaerobic conditions, soil reduction increases. At lower soil Eh, organic matter decomposition becomes incomplete, producing methane and large amounts of harmful intermediate products (such as organic acids, hydrogen sulfide, lactic acid, formic acid, acetic acid, and propionic acid) that are detrimental to crops [34].

3.3. Long-Term Stabilization of SOC in Paddy Systems

The persistence of SOC in flooded soils depends on three interrelated processes. Physical occlusion within aggregates restricts contact between fresh carbon inputs, decomposers, and the atmosphere, slowing the decomposition of SOC [35–37]. Chemical bonding, mediated by ligand exchange, sorption, and co-precipitation, forms organo-mineral complexes that further slow decomposition [38–40]. Additionally, changes in microbial community structure and function regulate substrate turnover, while the gradual accumulation of microbial necromass supplies a durable carbon sink [41–43]. Together, these physical, chemical, and biological processes drive SOC accumulation, contributing to the long-term sustainability of paddy soils and supporting essential ecosystem services such as soil fertility and carbon sequestration [4].

3.3.1. Aggregate-Mediated Protection

Soil aggregates, formed through the binding of mineral particles by organic matter, are fundamental structural units that regulate key ecosystem functions [20,44]. These include the long-term stabilization of SOC and the retention of essential nutrients. Based on size, soil aggregates are commonly classified into macroaggregates (>250 µm), microaggregates (53–250 µm), and the silt and clay fraction (<53 µm) [23,45]. This physical hierarchy parallels

the partitioning of SOC pools into coarse particulate organic carbon (cPOC, $>250\ \mu\text{m}$), fine particulate organic carbon (fPOC, $53\text{--}250\ \mu\text{m}$), and MAOC ($<53\ \mu\text{m}$) [46,47].

In paddy soils, prolonged flooding stabilizes the aggregate framework. Physical occlusion limits microbial attack and atmospheric exchange, markedly lowering SOC mineralization rates [23]. Enhanced aggregation also improves water retention and aeration, reinforcing structural integrity and further protecting SOC [48]. Micropores within aggregates restrict microbial access, reducing the likelihood of carbon decomposition [49]. During growth, rice roots both promote aggregate formation and drive cycles of fragmentation and reassembly, sustaining a dynamic yet steady turnover of organic carbon [20,23]. Encapsulation of SOC is most evident in the cPOC and fPOC fractions [20,24]. Whereas macroaggregates dominate SOC storage in upland soils, paddy soils are typically richer in microaggregates and silt-plus-clay particles [50]. This finer soil matrix accumulates greater amounts of photosynthetically fixed carbon and offers extensive specific surface area that promotes adsorption and long-term SOC stabilization [51].

3.3.2. Organic Matter Mineral Complexation as a Chemical Protection Pathway

Within aggregates, reactive mineral surfaces promote the accumulation of organic carbon through chemical adsorption and complexation [46,52]. Chemical protection is expressed primarily in the MAOC fraction. Within individual aggregates, reactive mineral surfaces adsorb SOC and promote the formation of organic matter mineral complexes that are largely inaccessible to microbial enzymes [53]. This mechanism effectively prolongs the residence time of SOC. In paddy soils, the abundant iron oxides catalyze oxidative and covalent polymerization of low molecular weight organic molecules into larger macromolecules [54,55]. Under reducing conditions, these polymers tend to coagulate or adsorb onto clay particles, processes that collectively enhance SOC stabilization [56]. Recurrent shifts between oxic and anoxic conditions dissolve existing iron oxides and promote their re-precipitation [57]. This cyclical process disrupts and reconstructs soil aggregates, exposes fresh reactive surfaces, and increases the contact between iron oxides and organic substrates [58,59].

Adsorption and co-precipitation with DOC produce OC-Fe complexes that further stabilize carbon [5,52]. These chemical bonds form within aggregates, causing the resulting OC-Fe and other organic matter mineral complexes to become physically integrated into the aggregate structure. Physical occlusion provides an additional barrier to microbial decomposition, further reinforcing the long-term stability of SOC [60].

3.3.3. Microbial Necromass Pathway for SOC Stabilization

Carbon within microbial residues is generally considered the most persistent fraction of SOC, often showing greater stability than plant-derived carbon. Such persistence is largely attributed to the close association of microbial residues with soil minerals within aggregates, physical protection afforded by organo-mineral complexes, and the gradual accumulation of residues through continuous microbial turnover [61–64]. Pulse-labelling with ^{13}C -labelled CO_2 illustrates this contribution. After 110 days of continuous labelling, illuminated paddy soils stored 105.0 to $133.8\ \text{mg kg}^{-1}$ of ^{13}C -SOC, exceeding the storage measured in upland soils. These results indicate a stronger microbial capacity for SOC fixation under flooded conditions [18].

Microbial activity is heavily influenced by soil redox conditions and plays a crucial role in SOC stability. In flooded, anoxic paddy soils, plant residues decompose slowly, which helps retain plant-derived carbon [6,15,65]. In flooded, anoxic paddy soils, plant residues decompose slowly, promoting the retention of plant-derived carbon [4,7]. When

soils are drained and oxygen becomes available, microbial activity increases, decomposition accelerates, and a greater proportion of SOC is transformed into microbial residues [66].

Flooded paddy soils also develop distinctive aggregation and organo-mineral interactions [44,57]. Repeated redox fluctuations fragment large aggregates, highlighting the importance of microaggregate formation and strong mineral–organic associations, especially with iron oxides, in safeguarding carbon [58,67]. At the same time, microbial transformation of plant detritus and biomass into persistent humic substances makes a substantial contribution to SOC stability [63]. The precise pathways and relative importance of these mechanisms remain incompletely understood. For example, it is still unclear how microbially derived humic substances bind to iron minerals, or under what conditions physical occlusion offers more protection than chemical adsorption. Resolving these uncertainties will require integrated approaches that couple detailed molecular characterization of SOM with targeted experiments capable of isolating specific stabilization pathways under field-relevant conditions.

4. Mineralogical Characteristics and Dynamics of Iron Oxides in Paddy Soils

4.1. Redox Dynamics Influence on Iron Cycling in Paddy Soils

Iron in paddy soils is primarily found in two forms: Fe^{2+} and Fe^{3+} . These forms are influenced by environmental factors such as soil pH, oxygen levels, and Eh, which govern iron's role in soil processes [37]. In soils with little oxygen (anaerobic conditions), Fe^{2+} remains stable [37]. In oxygen-rich environments (aerobic conditions), Fe^{2+} reacts with oxygen and changes into Fe^{3+} , which is less soluble and tends to form insoluble iron oxides and hydroxides with different chemical properties, such as a higher capacity to adsorb organic carbon [5]. The oxidation rate of Fe^{2+} is influenced by factors such as temperature, pH, dissolved oxygen, and the concentration of Fe^{2+} [68]. At pH values below 4, the oxidation rate of Fe^{2+} is slow, even in the presence of oxygen [5,69]. And this rate increases significantly under alkaline conditions. In anaerobic, neutral conditions, microbial activity primarily drives Fe^{2+} oxidation, often coupled with electron acceptors such as NO_3^- , ClO_3^- , and ClO_4^- . These microorganisms are capable of oxidizing not only dissolved Fe^{2+} but also ferrous iron in solid and mineral forms, such as FeCO_3 [69]. In illuminated environments, photoautotrophic ferrous oxidizing bacteria can also oxidize Fe^{2+} while using CO_2 as a carbon source [70]. Under microaerophilic, neutral conditions, microaerophilic Fe^{2+} -oxidizing bacteria compete with non-biological oxidation of O_2 and Fe^{2+} , thereby mediating ferrous oxidation, which is crucial for iron cycling in aerobic environments [71]. In flooded soils, with an Eh of around 120 mV, Fe^{3+} is reduced to Fe^{2+} [14].

4.2. Chemical Extraction Procedures for Iron Oxide Fractional in Paddy Soils

In paddy soils, iron appears in several forms: as free iron oxides (Fed), as amorphous (poorly crystallized) iron oxides (Feo), and as iron bound to organic molecules or minerals (Fep) [5]. Fed is commonly extracted using the dithionite-citrate-bicarbonate (DCB) method, which targets the reducible pool of “free” iron oxides, including highly reactive colloidal amorphous phases and crystalline minerals such as goethite and hematite [72,73]. This method also serves as an integrative indicator of the total abundance of iron oxides and their eluviation-illuviation dynamics [74]. Feo refers to the fraction extracted by acid ammonium oxalate, representing poorly crystalline or amorphous iron oxides that lack distinct XRD diffraction peaks [75]. This pool broadly reflects re-precipitated and newly formed iron minerals, together with part of the short-range ordered phases that readily undergo dissolution and reconfiguration in response to pH-Eh fluctuations [76,77]. Fep refers to the fraction of organically complexed or coated iron extracted by sodium pyrophosphate [78].

While not fully soluble in oxalate, it plays a key role in iron translocation, colloidal transport, and the formation of organo-mineral complexes [78,79].

Within this framework, the difference between Fed and Feo is often approximated as crystalline iron (Fec), providing an operational index of more crystalline iron oxide forms that is conceptually linked to the sequential extraction scheme of Poulton and Canfield and widely applied in contemporary geochemical modelling [80]. Spectroscopic analyses indicate that pyrophosphate may lead to the excessive extraction of humus-bound Fe and Al [81]. However, sequential extraction and isotopic evidence suggest that the mobile organic matter iron complexes identified in the Fep fraction contribute significantly to organic matter mineral associations and play a key role in long term carbon sequestration [82]. Taken together, the Fed-Feo-Fep (and derived Fec) indices constitute a complementary suite of metrics constraining the balance between crystalline and amorphous phases, the degree of organic complexation, and gradients in Fe reactivity, thereby providing a foundational framework for elucidating iron cycling in paddy soils [83,84].

4.3. Iron Oxides Commonly Found in Paddy Soils

At the mineralogical scale, the dominant iron oxide phases in paddy soils comprise ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), lepidocrocite ($\gamma\text{-FeOOH}$), goethite ($\alpha\text{-FeOOH}$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), and magnetite (Fe_3O_4) with their composition and spatial distribution highly sensitive to redox conditions [85,86]. Their crystal structures and principal physicochemical properties are summarized in Figure 3 and Table 1.

Table 1. Naturally occurring iron oxides [85–90].

Iron Oxide Mineral	Specific Surface Area ($\text{m}^2 \text{g}^{-1}$)	Common Morphology	Thermodynamic Stability
Ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$)	200–300	Irregular spheres	Unstable
Lepidocrocite ($\gamma\text{-FeOOH}$)	100–200	Platy or lath-like	Metastable
Goethite ($\alpha\text{-FeOOH}$)	20–80	Needle-like	Stable
Hematite ($\alpha\text{-Fe}_2\text{O}_3$)	10–50	Rhombohedral or platy	Stable
Magnetite (Fe_3O_4)	5–50	Octahedral or rhombic dodecahedral	Moderately stable

Ferrihydrite, characterized by its high specific surface area and poor crystallinity, commonly acts as a transient precursor to more stable crystalline phases and is repeatedly generated and transformed under periodic flooding [89]. Under drained or oxic conditions, ferrihydrite and dissolved Fe^{2+} rapidly transform to goethite and lepidocrocite; among these, goethite is thermodynamically more stable and thus tends to dominate in long-term paddy cultivation systems [90], whereas lepidocrocite is preferentially enriched in microenvironments such as the rhizosphere and structural surfaces where redox conditions oscillate intensely [91]. Hematite formation generally requires stronger and more persistent oxidizing conditions, resulting in limited abundance in continuously flooded or poorly drained paddies but a more frequent occurrence under upland-rice rotations or well-drained regimes [86]. Magnetite and maghemite typically occur in trace amounts and are often linked to specific parent materials, localized intense reduction, or microbially mediated transformations [85]. Collectively, the rates and pathways of interconversion

among these phases exert first order control on the reactivity of the iron oxide pool and its capacity to stabilize associated organic carbon.

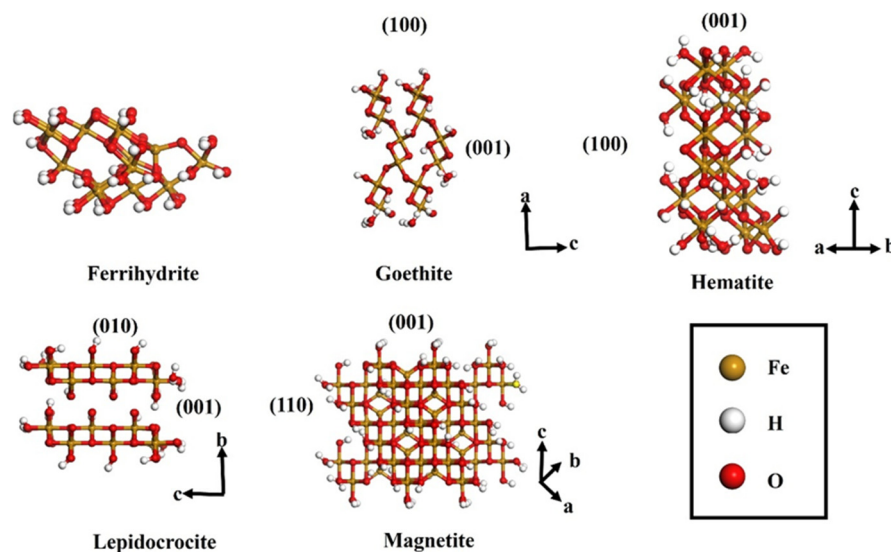


Figure 3. Schematic diagram of the crystal structures of common iron oxides in soils, including ferrihydrite, goethite, hematite, lepidocrocite, and magnetite [14,85,86,88,89]. a, b, c are the coordinate axes of the unit cell spatial coordinate system representing the crystal structure.

5. Impact of Iron Oxide Structural Transformations on Persistent SOC Stabilization in Paddy Soils

The following subsections synthesize how iron oxide phase and structural transformations contribute to long-term SOC stabilization through three interlinked pathways: (i) aggregate-scale physical protection mediated by iron oxides [92,93]; (ii) chemical stabilization via the formation, restructuring and persistence of OC-Fe associations [52,94]; and (iii) feedbacks between iron redox cycling, microbial metabolism and SOC turnover [93,95].

5.1. Aggregate-Scale Influence of Iron Oxides on SOC Stabilization

Iron oxides act as binding agents or form organo-mineral complexes, promoting aggregate formation and restricting microbial and enzymatic access to SOC, thereby favoring long-term carbon storage [44]. Their large specific surface area (SSA), abundant surface hydroxyl groups, and high sorption capacity enable iron oxides to readily interact with SOC through mechanisms such as adsorption and co-precipitation [52]. These processes promote the formation of OC-Fe complexes.

5.1.1. Physical Pathway: Promotion of Aggregate Formation

Alternating wetting and drying cycles drive iron redox transformations and the repeated formation and breakdown of soil aggregates. These processes play a central role in regulating SOC sequestration within aggregate interiors. During flooding, declining oxygen creates reducing conditions that promote the reduction of Fe^{3+} oxides to soluble Fe^{2+} . The resulting Fe^{2+} readily interacts with SOC in the pore water, facilitating its adsorption and potential stabilization [96]. After drainage, oxygen re-enters the soil, oxidizing Fe^{2+} to Fe^{3+} oxides and generating amorphous or organic complexed forms [57,97]. When aggregates disintegrate, fresh mineral surfaces are exposed, promoting the binding of aromatic carbon to iron minerals. These newly formed complexes are subsequently embedded and protected during soil re-aggregation [57]. The structure of iron oxides produced during redox oscillations directly influences soil aggregation [98,99].

5.1.2. Chemical Pathway: Formation of OC-Fe Complexes

Globally, OC-Fe complexes account for roughly one quarter of total SOC, equivalent to about 58.7 Pg [8]. The high abundance of iron oxides in paddy soils plays a crucial role in carbon retention [55]. Iron oxides react with DOC through adsorption or co-precipitation to form OC-Fe complexes that stabilize SOC [5,52]. Adsorption of organic matter onto iron oxides is predominantly mediated by inner-sphere ligand exchange, whereby deprotonated carboxylate and phenolic hydroxyl groups replace surface hydroxyls ($\equiv\text{Fe-OH}$) to form strong Fe-O-C bonds, while additional outer-sphere electrostatic interactions, hydrogen bonding and cation bridging also contribute to weaker associations [52]. Owing to the saturation of available sorption sites, the maximum amount of OC that iron oxides can retain is constrained, with a molar C/Fe ratio typically approaching 1 [100,101]. Co-precipitation arises from changes in pH or Eh, leading to the formation of insoluble Fe^{3+} -organic complexes. In flooded paddy soils, intensive Fe redox cycling promotes the co-precipitation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ with DOM, where organic ligands modulate Fe polyhedral linkage, generate defective or short-range ordered structures (e.g., ferrihydrite-like phases), and partially inhibit the transformation to more crystalline goethite or hematite [102]. During subsequent oxidation-reduction cycles, these OC-laden precursors may recrystallize into finely grained, strain-rich iron oxides or composite phases, in which OC is intercalated, occluded within nanopores, or trapped along crystal boundaries, thereby reorganizing the internal structure and crystallographic domains of iron oxides and enhancing the persistence of OC-Fe in paddy soils [103]. In this case, OC is not only adsorbed onto the mineral surface but may also be incorporated into the mineral matrix or occlude reactive sites, thereby altering the internal structure and crystallographic properties of the iron oxides [94,104,105]. Successive cycles of iron reduction, secondary mineral formation and periodic carbon diffusion create onion-like layers in which the C/Fe ratio can reach 6 to 10 [106–108].

5.2. Structural and Morphological Evolution of Iron Oxides and Its Influence on SOC Stabilization

The formation pathways of OC-Fe complexes are largely governed by the surface chemistry of specific iron oxide minerals (Figure 4). In ferrihydrite, DOC sorption generally increases with temperature due to enhanced diffusion and reaction rates [109]. Goethite and hematite preferentially bind aromatic and carboxyl rich organic compounds via inner-sphere complexation, while lepidocrocite and magnetite interactions are strongly influenced by carboxyl group density, molecular conformation and pH [110]. Overall, short-range ordered iron oxides exhibit higher sorption capacities and greater sensitivity to redox- and pH-driven transformation, whereas well-crystallized phases such as hematite display more stable sorption behavior across moderate environmental fluctuations [111].

Mineral phase transformation inherently entails coupled changes in both crystal structure and particle morphology. During Fe^{2+} -induced transformation of ferrihydrite, only minor carbon loss is observed. However, the increase in H_2PO_4 -extractable organic carbon suggests a decline in MAOC stability [106]. Ageing of ferrihydrite-humic acid co-precipitates result in a modest yet continuous release of carbon into solution under both oxic and anoxic conditions [112,113]. Comparable carbon loss is observed when ferrihydrite transforms into goethite or hematite [113]. Along the transformation pathway from ferrihydrite to lepidocrocite, SOC forms inner-sphere complexes where carboxyl and related functional groups coordinate with surface Fe^{3+} . This strengthens the mineral-organic bond and reduces the likelihood of desorption or degradation [114]. The formation of magnetite usually produces aggregated particles that trap fulvic acids within surface pores and lattice defects, thereby enhancing their retention [114]. These studies demonstrate that crystal structure transitions and morphological changes jointly regulate SOC stability.

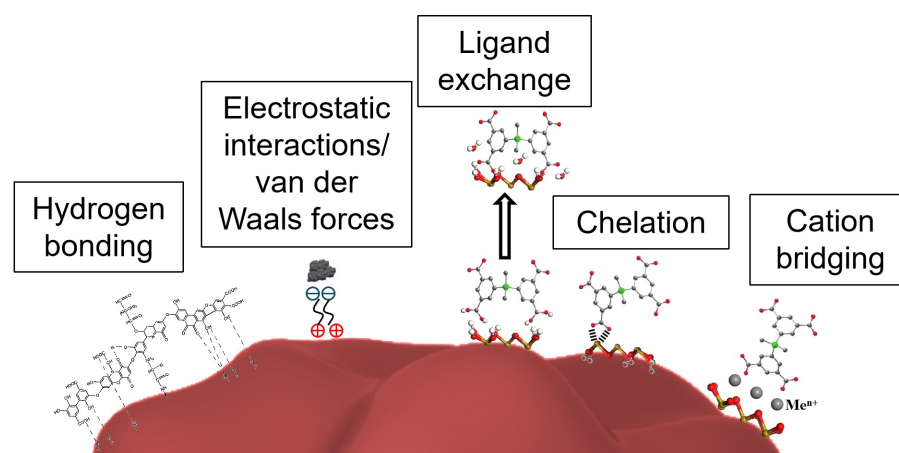


Figure 4. Conceptual mechanisms of organic matter association with ferrihydrite surfaces. The red amorphous surface represents reactive ferrihydrite surfaces. Stick models illustrate representative organic ligands. The main interaction mechanisms include hydrogen bonding, electrostatic interactions/van der Waals forces, ligand exchange, chelation, and cation bridging. Grey spheres (Me^{n+}) denote polyvalent metal cations that act as bridges between negatively charged functional groups on minerals and organic matter [14].

Morphological evolution influences SOC not only by altering SSA but also through the underlying crystal growth mechanism. Classical dissolve-reprecipitate pathways erode mineral surfaces and release bound carbon [115]. Fluctuating hydrological regimes impose alternating redox conditions that drive repeated cycles of dissolution, organic matter adsorption and surface recrystallisation [67]. These processes generate an onion-like architecture that promotes carbon preservation (Figure 5) [30]. Non-classical routes such as particle to particle oriented attachment also occur. Which pathway dominates depends on factors such as temperature, Fe^{2+} concentration and the presence of organic ligands. These routes yield products rich in lattice defects, pores and fractures [116–118], features that enhance the adsorptive and co-precipitative capacity of iron oxides for SOC [114]. Dynamic coupling between crystal growth and structural transformation therefore exerts a primary control on the long-term stabilization of organic carbon in paddy soils.

5.3. Influence of the Iron Redox Cycle on SOC Stabilization

Iron oxides immobilize organic carbon by fostering aggregate formation and generating OC-Fe complexes, both of which restrict microbial access to SOC [44,120]. In flooded paddy soils, however, the bulk soil is anoxic. Rice roots adapt to submergence by transporting stored O_2 through aerenchyma to the rhizosphere, where the gas oxidizes Fe^{2+} to Fe^{3+} . The precipitated Fe^{3+} accumulates on root surfaces as an “iron plaque”, which provides a continuous supply of electron acceptors for microbial Fe^{3+} reduction [121]. This root-driven Fe^{2+} - Fe^{3+} cycle links microbial energy generation to SOC turnover [121]. Microorganisms harvest energy from electron transfer that accompanies the Fe^{2+} - Fe^{3+} redox couple, and they use soil organic carbon as an additional substrate to fuel their metabolism; together, these processes indirectly shape the stability of SOC [122–125].

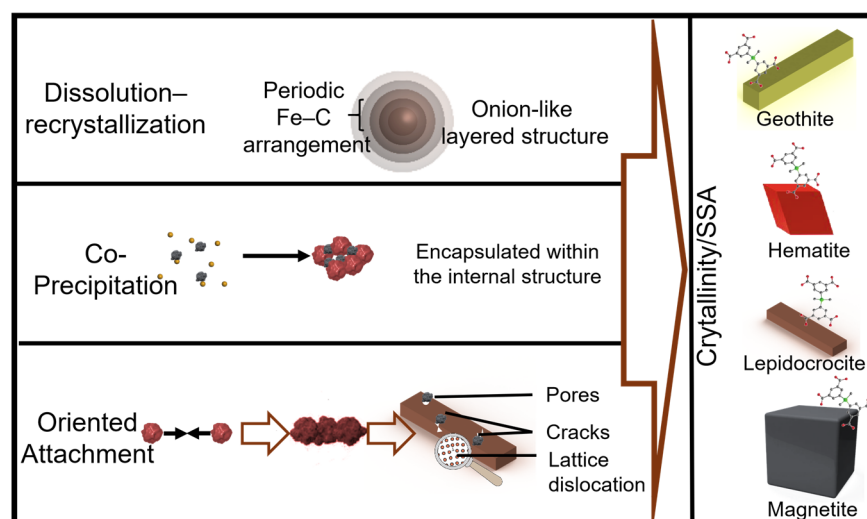


Figure 5. Schematic representation of Fe oxide formation and OC-Fe oxide associations. Primary Fe(III) polymers aggregate into short-range-ordered Fe oxides, which progressively transform into more crystalline phases during pedogenesis. The panels on the right show representative organic ligands bound to different Fe oxides, including goethite, hematite, lepidocrocite, and magnetite. The brown bracket qualitatively indicates the trend of increasing crystallinity and decreasing SSA along this transformation sequence [114,118,119].

5.3.1. Fe²⁺ Oxidation and Its Influence on SOC Stabilization

Microorganisms form the core biological engine of iron redox cycling in paddy soils and exert decisive control over the stabilization or mineralization of SOC. Among them, iron-oxidizing bacteria (FeOB) (Table 2) and iron-reducing bacteria (FeRB) constitute two functional guilds with contrasting metabolisms that directly shape Fe–C coupling under fluctuating redox regimes [6,15].

Table 2. Metabolic traits of Fe²⁺-oxidizing microorganisms [6,126–130].

Microbial Group	Oxygen Requirement	Predominant Metabolic Mode	Main Carbon Source	Energy Source
Microaerophiles	Aerobic	Mostly autotrophic	CO ₂ fixation	Fe ²⁺ oxidation coupled to O ₂ reduction
Acidophiles	Aerobic	Autotrophic or heterotrophic	CO ₂ or organic substrates	Fe ²⁺ oxidation coupled to O ₂ reduction
Photoferrotrophs	Anaerobic	Mostly autotrophic	CO ₂ fixation	Fe ²⁺ oxidation driven by light energy
Nitrate-reducing Fe ²⁺ oxidizers	Anaerobic	Few autotrophic, mainly mixotrophic	CO ₂ or organic substrates	Fe ²⁺ oxidation coupled to NO ₃ [−] reduction

FeOB-including microaerophilic Gallionellaceae, *Acidithiobacillus ferrooxidans*, *Pseudomonas* spp., and photoferrotrophs-use Fe²⁺ as an electron donor and precipitate highly reactive Fe³⁺ oxides that strongly associate with organic matter via inner-sphere complexation, co-precipitation, and aggregation [52,131–133]. In the rhizosphere, oxygen leakage further stimulates FeOB activity and promotes the formation of Fe plaques that serve as persistent reservoirs of sorptive Fe(III) phases.

FeOB-mediated Fe²⁺ oxidation also produces reactive oxygen species (ROS), creating strong selective pressure on microbial communities. Most FeRB (e.g., *Geobacter*, *Shewanella*) are obligate anaerobes with low oxidative-stress tolerance, whereas many FeOB thrive

under microaerophilic or oxic conditions [134]. Thus, redox oscillations impose a “biological filter” that shifts the balance between FeOB and FeRB, determining whether the Fe cycle favors SOC stabilization through Fe(III) regeneration or SOC mineralization through Fe(III) reduction [56,124,125].

In addition to their direct redox metabolism, iron-cycling microorganisms influence SOC turnover by regulating extracellular enzyme systems. Under aerated conditions, phenol oxidase uses O₂ as a terminal electron acceptor, decomposing phenolic inhibitors and enhancing hydrolase activity—an “enzyme-latch” effect that accelerates SOC decomposition [127,128]. In contrast, during re-oxygenation after anoxic periods, rapid Fe²⁺ oxidation reduces Fe²⁺ availability and suppresses phenol oxidase activity, leading to the accumulation of aromatic compounds that inhibit hydrolases. This “iron-gate” mechanism slows SOC breakdown and demonstrates how FeOB modulate both mineralogical and biochemical pathways of SOC stabilization [99,129].

Collectively, the interactions among FeOB, FeRB, extracellular enzymes, ROS dynamics, and mineral transformations form an integrated microbial–mineral feedback system that regulates SOC persistence in paddy soils. Future work combining metagenomics, isotopic tracing, and synchrotron spectroscopy is needed to resolve the co-evolving microbial and mineral processes that underpin long-term SOC stabilization.

5.3.2. Fe³⁺ Reduction and Its Influence on SOC Stabilization

In anoxic environments, coupled abiotic and biotic reduction of structural Fe³⁺ in minerals provides an important route for SOC oxidation [119,135,136]. Laboratory studies typically use iron hydroxides as electron acceptors with organic matter and sometimes H₂ as electron donors [6]. Both respiratory and fermentative microbes catalyse Fe³⁺ reduction, though respiration provides the majority of cellular energy (Table 3) [101]. Fermenters transfer fewer reducing equivalents; Fe³⁺ reduction in these organisms helps dispose of excess electrons and buffers pH [137–139]. Field observations confirm that Fe³⁺ reduction can drive SOC turnover, for example, through the dissolution of iron minerals in peat soils (Table 3) [119]. However, quantitative data on the extent of SOC oxidation remain limited. In coastal wetlands with hydrological regimes similar to those of paddy soils, the contribution of dissimilatory Fe³⁺ reduction to anaerobic SOC oxidation correlates with the abundance of iron hydroxides, suggesting that frequent redox cycling and mineral regeneration play an important role in carbon respiration [13,140].

Table 3. Overview of recent studies on iron oxide transformations and SOC stabilization in paddy soils and related redox-dynamic environments, including research gaps and future directions [6,13,15,30,37,44,46,52,56,58,73,77,82,92–94,103,104,106,111,115,119,121].

No.	System/Soil Type	Key Insights on Iron Oxides and SOC (Faithful to Paper)	Research Gaps/Future Direction	Reference
1	Temperate and tropical mineral soils	Batch sorption experiments and literature synthesis showed that hydrous iron oxides strongly sorb organic matter and thereby stabilize a distinct pool of soil organic carbon, with sorption capacity controlled by mineral type and surface area.	Need for field studies linking sorption to long-term SOC sequestration; understanding of seasonal cycles of Fe mineral transformation and SOC stability.	Wagai & Mayer (2007) [92]

Table 3. Cont.

No.	System/Soil Type	Key Insights on Iron Oxides and SOC (Faithful to Paper)	Research Gaps/Future Direction	Reference
2	Marine and estuarine sediments	Selective extractions demonstrated that a substantial fraction of sedimentary organic carbon is associated with reactive iron phases, indicating that Fe-bound organic matter forms an important and persistent carbon pool in marine sediments.	Exploration of how Fe-bound SOC varies with hydrodynamic conditions in coastal ecosystems and the role of microbial activity in breaking down these bonds.	Lalonde et al., (2012) [94]
3	Synthetic Fe–organic matter associations	Compared Fe–organic associations formed by coprecipitation versus adsorption and showed that coprecipitated Fe–OM complexes have higher C loadings and different bonding environments, with implications for long-term organic carbon retention.	Investigation into the impact of environmental conditions on the transformation of coprecipitated Fe–OM complexes and their role in SOC stabilization.	Chen et al., (2014) [104]
4	Ferrihydrite with Fe ²⁺ and organic matter	Demonstrated that coprecipitated organic matter retards and modifies Fe ²⁺ -induced transformation of ferrihydrite into more crystalline iron oxides, thereby altering mineral products and the fate of associated elements and organic carbon.	More research is needed on the role of pH and temperature in modulating Fe–OM interactions and their effects on SOC stability.	Chen et al., (2015) [106]
5	Forest and grassland mineral soils	Developed a sequential selective dissolution method that partitions organic carbon among Al- and Fe-hydroxide-associated pools and showed that these Al/Fe-bound fractions contain a significant and relatively stable portion of soil organic carbon across sites.	Expansion of this methodology to different soil types, especially in tropical and subtropical regions, where Fe–SOC dynamics may vary.	Heckman et al., (2018) [82]
6	Tropical forest soils with imposed redox regimes	Incubations under static oxic, static anoxic, and fluctuating redox conditions showed that redox oscillations mobilize Fe and dissolved organic carbon and alter CO ₂ production, highlighting tight coupling between iron cycling and carbon turnover in redox-dynamic soils.	Further research on how microbial communities mediate redox cycling of Fe and the impact on SOC mineralization in tropical soils.	Bhattacharyya et al., (2018) [77]
7	Rice–rape rotation, subtropical paddy soils	A long-term field experiment showed that conservation tillage and straw return increase macroaggregate stability; statistical analyses identified soil organic carbon and amorphous Fe oxides as main drivers, with Fe indirectly enhancing aggregation via organo-Fe complexes.	Need to investigate the long-term effects of tillage practices on Fe–SOC stabilization and microbial activity in aggregates.	Xue et al., (2019) [93]

Table 3. Cont.

No.	System/Soil Type	Key Insights on Iron Oxides and SOC (Faithful to Paper)	Research Gaps/Future Direction	Reference
8	Two paddy soils with contrasting properties	Aggregate fractionation and chemical analyses showed that higher contents of soil organic carbon and free/amorphous Fe oxides are associated with larger proportions of water-stable macroaggregates, indicating that Fe oxides and SOC jointly contribute to aggregate formation and stability in paddy soils.	Potential research into the role of other metal oxides (e.g., Al oxides) in aggregate stability and SOC sequestration.	Xue et al., (2019) [37]
9	Temperate mineral soils, Fe-bound SOM	Sorption and incubation experiments indicated that organic matter bound to iron oxides is relatively resistant to microbial decomposition and that sorption temperature has little effect on the stability of Fe-bound SOM compared with organic matter composition.	Further exploration of temperature and moisture effects on the stability of Fe-bound organic carbon in long-term incubations.	Nguyen et al., (2019) [111]
10	Global mineral soils (data synthesis)	By separating particulate versus mineral-associated organic matter, the study showed that mineral-associated organic carbon dominates long-term SOC storage and is constrained by mineral surface properties, including Fe and Al (hydr)oxides, providing a framework for MAOC-based C saturation in soils.	Need for more mechanistic studies on how mineral–organic interactions vary by mineral type and SOC characteristics across different ecosystems.	Cotrufo et al., (2019) [46]
11	Arable Luvisols	Field and laboratory data showed that colloidal iron and organic carbon strongly promote the formation and stability of soil aggregates; Fe–OC-rich colloids act as effective binding agents that help stabilize soil structure.	Further investigations into how different types of organic matter (plant-derived vs. microbial-derived) interact with Fe-rich colloids in different soils.	Krause et al., (2020) [115]
12	Soils along a saturation-frequency gradient	Comparisons across sites with different water table fluctuation frequencies showed that more frequent saturation enhances Fe reduction and increases potential C losses, but the role of organic matter in these processes needs further exploration.	Exploration of microbial controls on Fe reduction during cyclic saturation processes and its implications for SOC turnover.	Possinger et al., (2020) [58]
13	Thawing permafrost mineral soils	Incubations and spectroscopy revealed that dissolution of Fe minerals during permafrost thaw releases both iron and previously Fe-associated organic carbon into solution, indicating that the Fe-bound carbon sink can be reversed under reducing conditions.	More studies on the impact of thawing cycles on Fe-bound organic carbon in permafrost and its long-term effects on carbon release.	Patzner et al., (2020) [119]

Table 3. Cont.

No.	System/Soil Type	Key Insights on Iron Oxides and SOC (Faithful to Paper)	Research Gaps/Future Direction	Reference
14	Freshwater wetland rhizosphere and bulk soils	Sequential extraction showed that Fe-bound organic carbon comprises a major fraction of total SOC and remains relatively conserved across hydrological gradients, supporting the view that Fe-bound SOC is a stable carbon reservoir in wetland soils.	Need for studies on how land use and water management practices influence Fe-bound SOC pools in wetland systems.	Duan et al., (2020) [121]
15	Coastal wetland soils and sediments (global synthesis)	Review of global data demonstrated that cycling of iron (hydr)oxides in coastal wetlands regulates the balance between organic carbon burial and release, with Fe reduction and re-oxidation repeatedly binding and liberating organic carbon at redox interfaces.	Exploration of how different types of iron minerals contribute to SOC stabilization and release under varying environmental conditions.	Yu et al., (2021) [13]
16	Soils, sediments, aquatic systems (review)	Synthesized advances in microbial iron cycling, emphasizing how Fe-oxidizing and Fe-reducing microorganisms form, transform, and dissolve iron minerals, thereby strongly influencing the stabilization and mobilization of associated organic carbon.	Need for more field-based studies on microbial-mediated Fe cycling and its implications for SOC stability under real-world conditions.	Kappler et al., (2021) [15]
17	Broad range of mineral soils (conceptual review)	Proposed a dynamic view of mineral–organic matter interfaces in which sorption, desorption, dissolution, and precipitation continuously reshape organo-mineral associations; highlighted that Fe oxides can both protect organic matter from decomposition and catalyze its transformation.	Further studies on the environmental controls of Fe–SOC interactions across different land use types and climates.	Kleber et al., (2021) [52]
18	Goethite suspensions with natural DOM under light	Laboratory experiments showed that light-induced Fe redox cycling at goethite surfaces generates reactive oxygen species that oxidize dissolved organic matter, directly linking Fe mineral photochemistry to organic carbon transformation at mineral surfaces.	Exploration of the impact of different light wavelengths and intensities on Fe redox cycling and SOC transformation at the mineral–organic interface.	Yang et al., (2022) [73]
19	Flooded paddy soil microcosms	μ -scale spectroscopy and incubation experiments demonstrated that ferrihydrite rapidly transforms into more crystalline Fe phases (e.g., goethite, lepidocrocite, magnetite) in flooded paddy soils, with distinct spatial patterns that influence the distribution of potential binding sites for organic carbon.	Further studies on how microbial activity and environmental fluctuations influence ferrihydrite transformation and its role in SOC stabilization.	Grigg et al., (2022) [103]

Table 3. Cont.

No.	System/Soil Type	Key Insights on Iron Oxides and SOC (Faithful to Paper)	Research Gaps/Future Direction	Reference
20	Soils and sediments at redox interfaces (review)	Comprehensive review that formalized the “coupled iron–carbon cycling” and “rusty carbon sink” concepts, detailing how iron mineral transformations under fluctuating redox conditions govern organic matter sorption, release, and microbial accessibility in a wide range of ecosystems, including paddies and wetlands.	More specific experimental data on the coupling of Fe and carbon cycles in different redox environments is needed.	Dong et al., (2023) [6]
21	Subtropical paddy soils under six-year rice straw recycling	A six-year field trial showed that rice-straw recycling strategies that build both SOC and Fe/Al oxide contents enhance macroaggregate formation and stability; Fe/Al oxides and organic carbon act synergistically to stabilize paddy soil aggregates and, by implication, associated SOC.	Long-term studies needed to assess the sustainability of rice-straw recycling and its impact on soil health and carbon dynamics in paddy soils.	Gu et al., (2024) [44]
22	Scirpus-dominated coastal wetland soils (rhizosphere vs. bulk)	Along salinity and tidal-elevation gradients, iron-bound organic carbon in rhizosphere and bulk soils varied systematically with Fe oxide forms and plant root activity, showing that Fe-bound SOC responds sensitively to redox regime and vegetation in wetland environments that are biogeochemically analogous to paddy soils.	Need to explore the role of vegetation type and environmental change in regulating Fe-bound SOC in wetlands and paddy soils.	Bi et al., (2024) [30]

6. Conclusions

Paddy soils are dynamic redox systems in which iron oxides act as active regulators, influenced by management practices such as alternating flooding and drainage, fertilization, and organic inputs. These processes lead to continuous restructuring of iron oxide phases, governing the availability of reactive surfaces for organic carbon stabilization. Within this framework, paddy soils can accumulate substantial OC-Fe, but this capacity is intrinsically sensitive to imposed hydrological and nutrient regimes. Recent studies suggest that moderate, recurrent redox oscillations promote the renewal of short-range ordered OC-Fe complexes and enhance MAOC formation by facilitating aggregation and occlusion of organic matter and microbial residues. Excessive reduction or shifts toward more crystalline iron oxides weaken organo-mineral associations, increasing SOC vulnerability to microbial and oxidative loss. Balanced mineral fertilizers and organic inputs stabilize reactive OC-Fe complexes, while unbalanced or low-input regimes reduce sorption site diversity and erode the protective matrix. Therefore, SOC sequestration in paddy soils should be seen as the result of management-driven iron oxide phase transformations, rather than simply a function of bulk carbon inputs.

Future research should focus on: resolving the dynamics of OC-Fe interactions using advanced techniques, incorporating OC-Fe interactions into soil carbon models as

management-sensitive pools, and translating these findings into climate-smart paddy management strategies to optimize MAOC retention and improve agricultural sustainability. Recognizing and deliberately harnessing iron oxide transformations in flooded paddy systems offers a concrete pathway to align agricultural production with long-term carbon sustainability.

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