

Coupled iron cycling and organic matter transformation across redox interfaces

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Abstract

Soils and sediments are major reservoirs of organic matter (OM), whose dynamic turnover has a major impact on carbon cycling and global climate. OM in soils and sediments is predominantly associated with minerals, which decelerate OM decomposition and could help store carbon. However, iron (Fe) minerals could also degrade OM and release a fraction of OM to the atmosphere as CO₂ and CH₄, but the coupling of these processes is only partly understood. In this Review, we describe the mechanisms and importance of coupled iron–carbon (Fe–C) cycles. Oxygenation of structural Fe(II) in minerals generates reactive oxygen species, which either degrades or synthesizes OM. Reactive oxygen species can also either decrease or increase extracellular enzyme activity and microbial activity, thus indirectly transforming OM. In addition, Fe(III) reduction contributes to OM oxidation through anaerobic respiration. By contrast, OM affects the redox properties of Fe minerals by serving as electron donor, acceptor, shuttle, buffer or conductor and by co-precipitation and complexation with Fe minerals. These feedback mechanisms can result in complex interconnected Fe–C cycling processes; hence, future work must focus on attaining the net impact of combined Fe–C cycles.

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Introduction

Soils and sediments are major reservoirs of organic matter (OM)^{1–3}. However, OM in soils and sediments can be abiotically and microbially degraded, ultimately releasing a fraction of OM to the atmosphere as CO₂ and CH₄. OM stored in soils and sediments is therefore a dynamic repository, and its turnover has a major impact on carbon cycling and global climate. For example, soil OM is responsible for half of the carbon flux from land to atmosphere⁴.

Minerals are the most abundant and reactive constituents in these environments. When minerals and OM come into contact in soils and sediments, they interact physically and chemically to form mineral–OM associations (MOAs)^{2,3,5–9}. These interactions have a vital role in stabilizing OM against microbial degradation¹⁰, and they also control the structure and reactivity of minerals^{2,3,9,11,12}. Turnover times of mineral-associated OM are on average four times longer than those of particulate OM, with specific times depending on the mechanisms of OM association with minerals⁹. However, MOAs are not always stable and the extent of coupling in MOAs and their stability depends on the nature of the mineral and OM, the strength of mineral–OM binding and environmental conditions including soil moisture, redox potential, pH and oxygen availability^{1,9}.

As most minerals contain Fe^{9,13–15}, Fe minerals have a predominant role in the formation of MOAs and transformation of OM^{15–17}. Approximately 21.5% of organic carbon binds to reactive Fe in sediments⁵ and 2–74% binds to reactive Fe in soils¹⁸. Under oscillating environmental redox conditions, mineral-associated Fe undergoes redox cycling, which represents an important mechanism to destabilize MOAs and transform OM¹⁹. Specifically, Fe(II) oxidation and Fe(III) reduction can affect OM transformation via direct and indirect pathways. Conversely, OM affects Fe redox cycling via its roles as electron donor, acceptor, shuttle, buffer and conductor, thus affecting the solubility and reactivity of Fe minerals and their nutrient and contaminant retention capacity²⁰. Therefore, Fe redox cycling and OM transformation are coupled under O₂ fluctuating conditions.

Understanding coupled Fe and C cycles in soils and sediments is therefore of great importance to prediction of ecosystem health and services. For example, OM can promote Fe(III) reduction, thus either inhibiting methanogenesis¹³ or promoting anaerobic methane oxidation²¹. OM-catalysed transformation of Fe minerals changes their solubility and affects the mobility of nutrients and contaminants^{22,23}. Furthermore, minerals and OM can be either beneficial (as sources of energy and other nutrients) or harmful (as sources of toxic materials) to microorganisms²⁰. Coupled iron–carbon (Fe–C) cycles change the bioavailability of minerals and OM, and their associated nutrients and toxic compounds²³, thus affecting microbial activity and functions. However, to date, coupled Fe–C cycles have only been examined in simplified experiments, and previous reviews are focused on mineral–OM interactions¹⁴, Fe redox cycling²⁴ or mineral–microorganism interactions and coevolution²⁰.

In this Review, we explore the role of Fe minerals in stabilizing and degrading OM and the role of OM in enhancing reactivity of Fe minerals under different conditions. We first briefly describe major Fe minerals, types of OM and their interactions. Next, we focus on the mutual interactions between redox cycling of Fe minerals and OM transformation. Finally, we summarize the current understanding and point out future research directions in the field of coupled Fe–C processes, including creating biogeochemical models to improve the predictions of OM turnover, and reactivity and evolution of Fe minerals under varied environmental conditions.

Minerals, OM and their interactions

Fe is the most abundant redox-active metal in soils and sediments with two major oxidation states: Fe(II) and Fe(III). Other than certain environments such as acid mine drainage and organic rich peatlands, most Fe is associated with minerals. Representatives of reduced iron minerals include siderite, vivianite, green rust, magnetite, iron sulfides, phyllosilicates and other silicates. Oxidized iron minerals include iron (oxyhydr)oxides and phyllosilicates^{14,24–26}. The redox potentials of Fe minerals range from –0.5 V to 0.5 V (Fig. 1), depending on the Fe(III):total Fe ratio and particle size²⁴. In this Review, Fe(II) and Fe(III) refer to mineral-bound Fe(II) and Fe(III), respectively, unless stated explicitly.

Depending on either terrestrial or aquatic environments, the composition of OM varies markedly. Marine OM is mostly derived from phototrophic algae, with the composition dominated by lipids, proteinaceous materials and carbohydrates^{27,28}, whereas on land, lignin, cellulose, proteins and humic substances are predominant types^{27,29}. There are also degradation products of OM, as well as synthetic compounds released into the environment by human activities. In this Review, the term OM refers to all of these organics.

Redox reactivity and complexation capacity are two properties of OM that are most relevant to Fe–C cycles^{30,31}. Redox reactivity of OM is characterized by redox potentials^{32–35} and electron-accepting and electron-donating capacities^{36–38}. The overlapping redox potentials between Fe-bearing minerals and OM (Fig. 1) enable the redox reactions to occur between them.

Physical interaction between minerals and OM can protect OM from degradation to CO₂, CH₄ or other OM by nano-aggregates, micro-aggregates and macro-aggregates and even within crystal hillocks³⁹. The physicochemical properties of minerals, the nature of OM and solution chemistry affect the formation of mineral–OM aggregation. When OM is encased within aggregates and hillocks, physical barrier prevents abiotic reactants, microorganisms and extracellular enzymes from accessing OM and thus increases its turnover time.

Chemically, OM can be protected by minerals via adsorption and co-precipitation^{9,14,40}. Adsorption encompasses multiple mechanisms including electrostatic interaction, ligand exchange, hydrophobic interaction, hydrogen bonding and cation bridging^{2,9,14,15,40}. Fe minerals differ greatly in their capacity, affinity and rate of OM adsorption, all of which are controlled by the accessibility of sorbent surfaces in the 3D soil pore structure, but also by the chemical state of the soil solution, especially pH, type and valence of counterions and ionic strength⁴⁰. When adsorption reactions are governed by inner-sphere and outer-sphere complexation, adsorption increases with lowering pH and increasing ionic strength⁴⁰.

Co-precipitation is another major mechanism of chemical protection^{2,9,15,40}, including inclusion and occlusion. The binding strength between OM and Fe mineral and thus the stability of OM within co-precipitates are largely determined by the carboxylate–Fe bond formation⁴¹. The main factors that affect Fe–OM co-precipitation include the C/Fe ratio, the type of OM and pH of the solution⁴⁰. Unlike adsorption, Fe–OM co-precipitation changes both the surface and bulk properties of the mineral to result in disordered mineral structures⁴².

Relative to metal (oxyhydr)oxides (including metal oxides, mixed metal oxide-hydroxides and metal hydroxides), knowledge on OM–phyllosilicate interaction is incomplete, despite their importance in protecting OM from degradation^{2,43}. Phyllosilicates, also called clay minerals, have unique structure and chemistry (such as specific surface area and charge density) that are distinct from metal (oxyhydr)

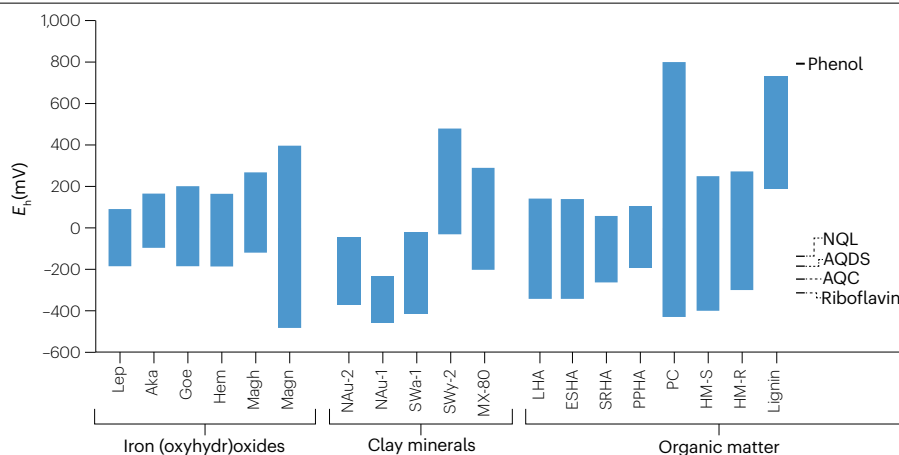


Fig. 1 | Redox potentials of Fe minerals and some representative organic matter. The range of redox potentials (E_h , mV), which is a measure of an environment to either be reducing (negative E_h) or oxidizing (positive E_h), is represented by each bar. E_h values for different materials are compiled from various sources: minerals^{24,209}; standard humic substances^{33,34}; pyrogenic carbon (PC)^{146,210}; humin from soil (HM-S) and river sediment (HM-R)²¹¹; lignin and phenol^{212,213}; organic ligands 2-hydroxy-1,4-naphthoquinone (NQL), 9,10-anthraquinone-2,6-disulfonate (AQDS), 9,10-anthraquinone-2-carboxylic

acid (AQC)²¹⁴; and riboflavin²¹⁵. Aka, akageneite; ESHA, Elliott Soil humic acid; Goe, goethite; Hem, hematite; Lep, lepidocrocite; LHA, leonardite coal humic acid; Magh, maghemite; Magn, magnetite; MX-80, bentonite; NAu-1, nontronite; NAu-2, nontronite; PPHA, Pahokee Peat humic acid; SRHA, Suwannee River humic acid; SWa-1, ferruginous smectite; SWy-2, montmorillonite. The overlapping redox potentials between Fe minerals and organic matter enable coupled redox reactions between the two.

oxides. Adsorption is a major mechanism of OM–phyllosilicate interaction, but co-precipitation is also possible for short-range ordered aluminosilicates such as imogolite and allophane⁴⁴. Surface area and cation exchange capacity are important properties in controlling OM stabilization. In general, un-expandable phyllosilicates (for example, kaolinite and illite) exhibit lower adsorption of OM compared with expandable phyllosilicates (for example, montmorillonite)². The inter-layer space of expandable phyllosilicates has the ability to host organic compounds^{43,45,46}, but the quantitative importance of this intercalated OM for the long-term protection of OM is unclear.

These different types of minerals, OM and their interaction mechanisms determine the specific pathways of the coupled processes of Fe redox cycling and OM transformation under different redox conditions, as described in the following sections.

Fe redox cycling effect on OM alteration

Abiotic oxidation of Fe(II) in air produces reactive oxygen species (ROS), whereas under anoxic conditions biotic Fe(II) oxidation can be either autotrophic or mixotrophic, depending on the Fe(II) oxidation pathways²⁴. Under anoxic conditions, Fe(III) reduction is generally coupled with oxidation of OM²⁴. As a result, mineral-protected OM can be released and degraded, whereas Fe-bearing minerals undergo mineralogical transformations.

Effect of Fe(II) oxidation on OM transformation

Aerobic Fe(II)-oxidizing microorganisms include acidophiles and microaerophiles, whereas anaerobic Fe(II)-oxidizers include phototrophs and nitrate reducers⁴⁷. The microaerophilic and phototrophic Fe(II)-oxidizing microorganisms are mostly autotrophic, producing biomass from CO₂ fixation^{24–26,48}. Acidophilic Fe(II) oxidizers can be autotrophic or heterotrophic⁴⁹. A small number of nitrate-reducing Fe(II) oxidizers are autotrophs, using energy from Fe(II) oxidation to fix CO₂ (refs. 24,26). However, most nitrate-reducing Fe(II)

oxidizers are mixotrophic, capable of assimilating labile OM as a carbon source²⁶.

The Fe(II) oxidation pathways most relevant to OM transformation are abiotic oxidation of structural Fe(II) and generation of ROS. ROS can transform OM through three pathways: direct transformation of OM; indirect transformation of OM through alteration of extracellular enzymes and indirect transformation of OM through regulation of microbial activity.

Direct transformation of OM by ROS. ROS are strong oxidants that transform OM. ROS are generated photochemically in aquatic environments via oxidation of aqueous Fe(II) by O₂. ROS change the molecular size, composition and bioavailability of OM^{50,51}. Fe(II)-bearing minerals are also capable of producing ROS upon oxygenation^{52–54}. One particular type of ROS, hydroxyl radical (•OH), has a vital role in the degradation of OM^{12,19} to produce CO₂ and organic compounds of lower molecular weight⁵⁰.

In soils and sediments, mineral-bound Fe(II) is expected to have a greater role than aqueous Fe(II) in generating ROS and decomposing soil OM, but definitive evidence is lacking. Relative to aqueous Fe(II), mineral-bound Fe(II) is more abundant⁵⁵ and occurs over a wider pH range⁵⁶. In addition, mineral-bound OM (especially Fe-bound OM) is spatially closer to the site of ROS generation so that ROS–OM interaction has a greater probability of encounter. Therefore, despite the short life-time (for example, the half-life of •OH is nanoseconds⁵⁷) and limited diffusion distance of ROS, mineral-generated ROS are hypothesized to have an important role in releasing OM from MOAs and degrading it. However, mechanistic studies are warranted to test this hypothesis further. Preferential association of aromatic and carboxyl functional groups of OM with Fe minerals^{40,58,59} makes these groups particularly susceptible to degradation. Although ROS typically degrade OM to produce more bioavailable compounds^{12,50}, degradation products (for example, unsaturated aliphatic carboxylic acids from

lignin degradation) can undergo polymerization to form condensed aromatic and aliphatic organic compounds^{60,61} and even humic-like OM⁶². Radical polymerization, decarboxylation and cyclization of conjugated unsaturated acids are some of the proposed pathways for polymerization⁶⁰.

ROS can also contribute to the sequestration of OM. Certain OM has a strong chelating capability to solubilize structural Fe(II) in minerals to form Fe(II)–OM complex⁶³. Oxygenation of aqueous Fe(II)–OM complex greatly enhances ROS yield relative to direct air oxidation of structural Fe(II)^{53,64}. ROS produced from Fe(II)–OM complex break the Fe(II)–OM bond and oxidize the released Fe(II) to Fe(III) (oxyhydr)oxides, which sequester OM via co-precipitation or adsorption⁶⁵. These findings can explain OM preservation under the redox fluctuating conditions^{19,66}.

Transformation of OM through ROS-induced alteration of extracellular enzymes. ROS not only directly impact OM transformation but also have an indirect role through their effect on the activity of extracellular enzymes produced by fungi, bacteria and plants. These enzymes include oxidases (such as phenol oxidase), peroxidases (such as lignin peroxidase and manganese peroxidase) and hydrolases^{67,68}. In this section, OM refers to organic compounds that bind specifically to enzymes, typically called substrate. The ‘enzyme latch’ theory⁶⁹ states that oxic environments favour substrate decomposition, because O₂ can serve as electron acceptor of phenol oxidase^{67,70}, thus enhancing its activity towards degradation of phenolic substances. As a result, the enhanced degradation of phenols lowers their toxicity to hydrolase and enhances hydrolase activity to decompose OM.

When ROS, extracellular enzymes and OM are co-present, there can be synergistic^{71–74}, antagonistic^{72,75,76} or no interaction (Fig. 2). The mode of these interactions depends on the types of ROS, enzyme and substrate involved and environmental conditions^{77,78}.

Synergistic interaction refers to enhancements of enzyme activity, substrate degradation and ROS yield owing to their mutual interactions. ROS promote the activity of enzyme via their roles as electron acceptor or substrate^{70,74,79}. By giving off electrons to ROS, enzyme exhibits a stronger tendency (relative to without ROS) to oxidize substrates and thus to increase the rate of substrate degradation⁷⁴. ROS can remove toxic substances (such as phenols) from certain enzymes (such as hydrolases) and modify the substrate to facilitate its binding to the enzyme^{12,74}. These two mechanisms increase the enzyme activity. ROS yield can be increased by either Fenton-like reaction induced by H₂O₂-generating oxidases⁷⁰ or reactive intermediate radicals from degradation of the substrate (such as (semi)quinones and phenoxy radicals)^{80,81}. The reactive intermediates can reduce Fe(III) to Fe(II) for sustained ROS generation⁸². Therefore, the joint effect of ROS and enzyme on substrate degradation is greater than the sum of their individual effects.

Antagonistic interaction refers to the case when the interaction between ROS and enzyme lowers their individual capacities of substrate decomposition (Fig. 2). ROS are able to decompose and deform certain extracellular enzymes or change their redox state^{72,75,76}. For instance, ROS can inhibit activities of extracellular lignin peroxidase, α-glucosidase, β-glucosidase and protease^{75,76,83,84}. In soils, the activities of hydrolytic enzymes were markedly lower under oxic than under anoxic conditions, probably owing to an increased concentration of ROS^{84,85}. The decreased enzyme activities are largely attributed to the oxidative alteration of enzyme structures by ROS^{76,84}. In doing so, ROS themselves are consumed. As a result, the joint effect of ROS and enzyme on substrate degradation is lower than the sum of their individual ones.

In addition, it is possible to have no interaction between ROS and enzyme (Fig. 2), because of the spatial distance between ROS and

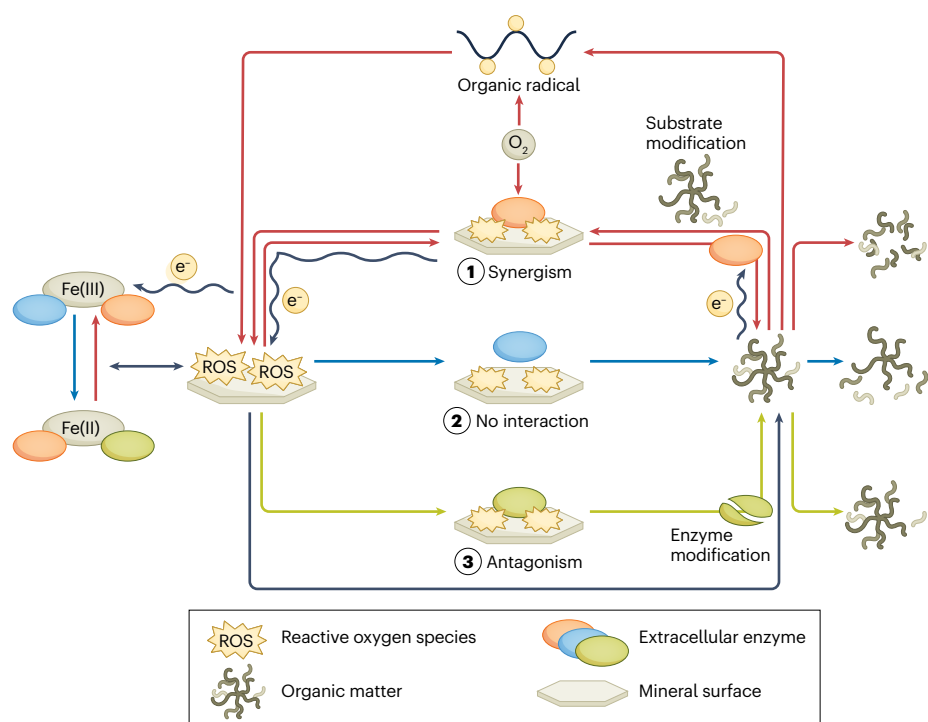


Fig. 2 | Three example interactions among ROS, enzymes and substrate resulting in different effects on organic matter transformation. ① Synergism (orange), where reactive oxygen species (ROS), enzyme and substrate interact to enhance enzyme activity, substrate degradation and ROS yield. Enzyme activity can be enhanced by ROS owing to their roles as electron acceptor and enzyme substrate. Enzyme activity can also be enhanced by the change in substrate owing to ROS-induced modification and removal of toxic substances. Enhanced enzyme activity from the aforementioned two pathways results in increased substrate degradation. ROS yield can be increased by enzyme via Fenton-like reaction and by reactive radical intermediates generated from substrate degradation. ② No interaction between ROS and enzymes (blue), where ROS and enzyme independently exert an effect on substrate degradation. ③ Antagonism (green), where ROS and enzyme interact with each other to consume ROS and to lower enzyme activity, which results in a lower overall substrate degradation than the sum of the individual interactions. The black arrow refers to direct organic matter degradation by ROS. In natural environments, all these three modes of interactions affect OM transformation.

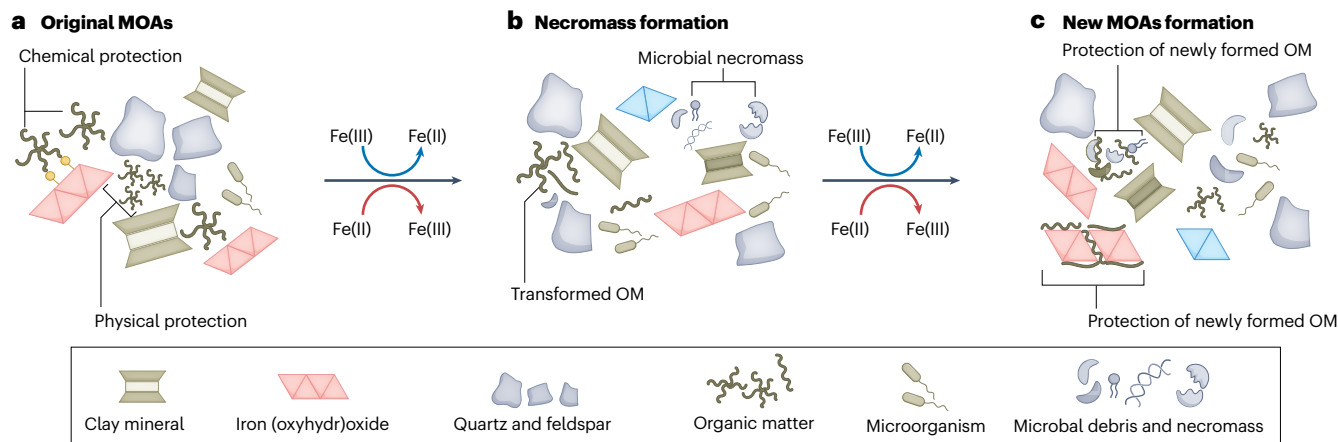


Fig. 3 | Transformation of organic matter driven by Fe redox cycling.

a, Formation of mineral–organic matter associations (MOAs) through strong chemical bonding between organic matter (OM) and minerals (chemical protection) and aggregation and occlusion (physical protection). Some OM can be protected without mineral association by chemical recalcitrance. **b**, Disintegration of original MOAs. OM is released or transformed when Fe(III)

is reduced and attacked by ROS generation upon oxygenation of Fe(II). Released OM serves as substrate to produce microbial biomass and metabolic products (including microbial necromass). **c**, New MOAs formed by recombination of OM and secondary minerals. These formation and disintegration mechanisms of MOAs lead to overall OM preservation in soils and sediments.

enzyme and short lifetimes of ROS, the relatively weak oxidation potential of certain ROS (for example, superoxide or hydrogen peroxide) and/or antioxidant function of enzymes and associated secondary metabolites^{70,76}. In this scenario, the joint effect of ROS and enzyme on substrate degradation is simply the sum of their individual ones.

In the presence of Fe minerals, adsorption of enzymes onto redox-inert minerals typically lowers their activity but prolongs their lifespan^{86,87}, largely owing to the conformational changes of adsorbed enzymes and protection of their active sites from encounter with the substrate^{88,89}. When the mineral surface is the source of ROS, only the activity of β -glucosidase was inhibited because of adsorption but subsequently both the activity and lifespan decreased owing to ROS attack⁷⁶. However, the effect of ROS on the activity of surface-adsorbed enzymes is highly dependent on the specific enzyme, the mineral surface property and the microenvironments in which they interact with each other. The interaction becomes more complex when both enzyme and substrate adsorb to the Fe mineral and jointly interact with mineral surface-generated ROS. These complex interactions are poorly understood and represent a major area of future research.

OM transformation through regulation of microbial decomposers by ROS. Because OM is a possible substrate for heterotrophic microorganisms, ROS can indirectly affect OM transformation through their impact on microbial communities⁹⁰. ROS are effective in selectively killing or inhibiting a wide range of microorganisms through cascade reactions such as oxidative damage of lipids, proteins and DNA molecules^{56,90–92}. Fe(III)-reducing bacteria are more susceptible to ROS-induced mortality compared with Fe(II)-oxidizing bacteria⁹³, because many Fe(II)-oxidizing bacteria are aerobes or microaerophiles. However, exposure of Fe(III)-reducing bacteria to low doses of ROS have been found to actually improve their Fe(III)-reduction ability⁹⁴, through either genetic mutation or enhanced nutrient availability⁶⁵. Furthermore, ROS can alter the ability of a microbial community to produce enzymes⁹⁵, which further affects OM transformation.

Effect of Fe(III) reduction on OM transformation

Under anoxic conditions, abiotic and biotic reduction of structural Fe(III) in minerals coupled with oxidation of OM represents an important pathway of OM transformation^{19,96,97}. Current understanding is mostly based on laboratory studies, in which iron (oxyhydr)oxides are the predominant Fe(III)-containing minerals, and OM serves as electron donor. In some cases, H₂ is added as an additional electron donor.

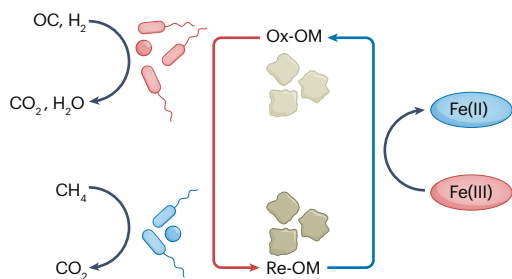
Both respiratory and fermentative microorganisms can catalyse coupled reaction of Fe(III) reduction and OM transformation, but respiration is by far the predominant mode of energy-yielding metabolism to support microbial growth²⁵. In comparison, fermentative microorganisms only transfer a small fraction of the available reducing equivalents (<5%) to Fe(III), and microbial growth does not require Fe(III) reduction²⁵. Fe(III) reduction has been observed as a complementary pathway to discard excess reducing equivalents and to buffer pH by fermentative microorganisms^{98–100}.

OM transformation induced by Fe(III) reduction has also been observed in field studies, in which Fe(III)-reducing bacteria promoted Fe mineral dissolution, organic carbon mobilization and greenhouse gas emission in peatland soils⁹⁷. However, the extent of OM oxidation by Fe(III) reduction is rarely determined except for a few cases. In coastal wetlands, dissimilatory microbial Fe(III) reduction can contribute anywhere between 5% and 109% of anaerobic OM oxidation¹⁰¹. This proportion is logarithmically correlated with the content of Fe (oxyhydr)oxides¹⁰¹; therefore, any environmental changes (such as frequent redox oscillations) that generate Fe (oxyhydr)oxides likely have an important role in anaerobic OM respiration¹⁰².

OM transformation driven by Fe redox cycling

After a review of the individual roles of Fe redox cycling in OM transformation, it is important to put them into a perspective (Fig. 3). OM is initially associated with Fe minerals in MOAs and is protected from microbial degradation via a combination of chemical binding to Fe minerals and physical aggregation (Fig. 3a). Some OM can be chemically

a Electron shuttle or buffer



b Electron conductor

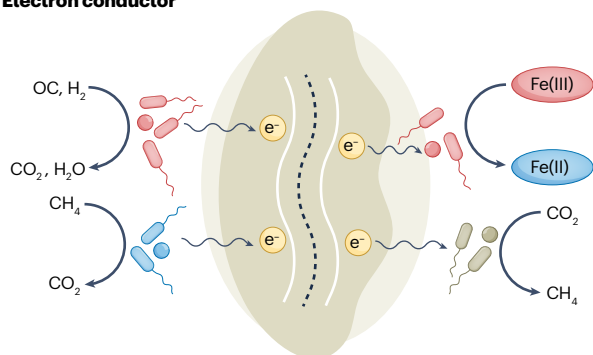


Fig. 4 | Organic matter as an electron shuttle or electron conductor to enhance Fe(III) bioreduction. **a**, Organic matter (OM) can serve as either an electron shuttle or buffer to enhance coupled reduction of Fe(III) minerals and oxidation of organic carbon, H₂ or methane. OM functions as an electron shuttle when it accepts electrons from microbial cells and subsequently donates them to Fe(III). OM serves as an electron buffer when it accepts electrons, stores them for a while and then donates them when Fe(III) becomes available. **b**, Solid OM can act as an electron transport pathway, transferring electrons from microorganisms to Fe(III) and other electron acceptors. Electrons can be derived from multiple sources (such as organic carbon, H₂ and methane) and shared by multiple acceptors (Fe(III) and CO₂). As a result of electron sharing, multiple biogeochemical processes can occur simultaneously. The combination of electron-shuttling, electron-buffering and electron-conducting functions of OM accelerates and connects multiple biogeochemical processes over space and time.

protected without forming mineral associations, possibly owing to intrinsic chemical recalcitrance.

However, ROS and Fe(III) reduction can disintegrate such MOAs and release the protected OM (Fig. 3b). Once released, OM undergoes transformation by abiotic and biotic processes. Abiotic transformation is mediated by ROS, whereas biotic transformation is driven by Fe(III)-reducing microorganisms. As a result, new biomass and microbial products are produced^{103–106}. Minerals disassociated from MOAs undergo secondary mineralization.

In the redox cycle, dead biomass (called microbial necromass¹⁰⁷) and microbial products, along with transformed OM, are re-associated with minerals to form new MOAs for OM preservation (Fig. 3c). Indeed, microbially derived products represent sizeable fractions of OM in soils (up to ~50%)^{104,105}, marine sediments¹⁰⁸ and black shales¹⁰⁹. The importance of these products has been either proposed in frameworks¹¹⁰, observed visually¹⁰³ or measured with bulk methods^{104,105}. Mechanistic

understanding of necromass–mineral interactions is limited and its quantitative contribution to the OM stabilization is poorly known^{104,105}. It is imperative to quantitatively assess the preservation potential of microbial necromass in MOAs in the presence of active microbial decomposers.

Through repeated Fe redox cycles at redox boundaries, OM undergoes continued transformation (including degradation and synthesis). The ultimately buried OM in soils and sediments is microbially transformed OM that is more stably associated with Fe minerals.

Effect of OM on Fe redox cycling

OM consists of aliphatic, carbohydrate and aromatic carbon species, as well as carboxyl, phenolic, quinone, carbonyl and aromatic functional groups^{31,111}. The redox reactivity of OM is often described in terms of electron-accepting and electron-donating capacities, with the sum of the two being the electron exchange capacity¹¹². The redox activity of Fe(III) minerals can be similarly characterized¹¹³. Because of these redox and chelating properties, OM can have multifaceted roles in mediating Fe redox processes as electron acceptor, donor, shuttle, buffer and conductor. OM can also adsorb onto mineral surfaces, co-precipitate with Fe minerals and form complexes with Fe, all of which change the physicochemical properties of the Fe mineral host and affect Fe redox cycling.

OM as electron acceptor and donor

Since the initial discovery of humic substances as respiratory electron acceptor¹¹⁴, it is well known that both dissolved and particulate OM can accept electrons from Fe(III) reducers^{34,115} and other microorganisms, because of the presence of electron-accepting moieties in OM^{31,34,116}. Electron donor is typically H₂ or small organics (such as acetate and lactate). Because of the overlapping redox potentials between Fe(III) minerals and OM (Fig. 1), the presence of OM could possibly inhibit Fe(III) reduction because of their competition for electron donor.

A number of OM types, including both solid (such as lignin, biochar and particulate OM) and dissolved forms (such as humic substances), can serve as electron donor to abiotically reduce structural Fe(III) in (oxyhydr)oxides^{117,118} and clay minerals^{119–121}. The rate and capacity of abiotic Fe(III) reduction is highly dependent on pH and OM composition, with polyphenolic-rich OM¹²² and hydroquinone-like moieties exhibiting a higher reduction capacity¹²³. In the presence of Fe(III)-reducing microorganisms, the capacity of OM as respiratory electron donor to reduce Fe(III)^{24,124} is higher than that of abiotic Fe(III) reduction^{119,120,125,126}, because of additional enzymatic oxidation of OM. As a result, OM can decrease the contents of electron-donating phenolic and aromatic moieties^{36,122,126}. Interestingly, when certain humic substances served as respiratory electron donor for microbial reduction of structural Fe(III) in clay minerals, they underwent decomposition to produce amino acids¹²⁷. When the electron-donating capacity of OM is higher than that of Fe(II) minerals, the presence of OM inhibits oxidation of Fe(II) by microaerophilic Fe(II)-oxidizing microorganism, because of their competition for electron acceptor¹²⁸. Because of common co-presence of OM, Fe(II) and microaerophilic microorganisms in nature, these effects deserve further study.

OM as electron shuttle, buffer and conductor

On receipt of electrons, oxidized OM is reduced. By subsequently donating electrons to Fe(III), reduced OM becomes re-oxidized, ready for the next redox cycle (Fig. 4a). This cyclic process is typically termed electron shuttle. The residence time of electrons in reduced OM is often

short. When OM serves as electron shuttle between microorganisms and Fe(III), the first electron transfer step is microbial and the second one is abiotic. The overall electron-shuttling process is often limited by the second step¹²⁹.

The ability of OM to serve as electron shuttle has several requirements. First, redox-active moieties, such as quinones and phenols, should be present in OM molecules^{32–34,111,130}. Second, oxidized OM should have a higher redox potential than that of the Fe(III) mineral such that it preferentially receives electrons from cells. Third, reduced OM should have a lower reduction potential than the Fe(III) mineral such that abiotic electron transfer from reduced OM to Fe(III) is thermodynamically favourable^{129,131}. Fourth, for dissolved humic substances, the concentration should be greater than ~2–10 mg C l⁻¹ for effective electron shuttling^{129,132}. If the concentration of OM is too low, the efficiency of electron transfer is not enough to enhance Fe(III) reduction. Finally, redox cycling should not result in any compositional and structural changes of OM.

Various OM have been used as electron shuttle to enhance microbial reduction of Fe(III) minerals when coupled with oxidation of H₂ or labile organic compounds^{24,133,134} and methane¹³⁵ (Fig. 4a). In some cases, OM can serve as both a respiratory electron donor and a shuttle to enhance Fe(III) bioreduction^{30,121,125,127}. For dissolved OM electron shuttles, diffusion is required to transfer electrons from microorganisms to Fe(III) minerals¹³⁶. Solid humic substances and pyrogenic carbon are also capable of facilitating electron transfer from microorganisms to Fe(III) minerals^{115,137–139}. In this case, physical contact among microorganisms, OM and Fe(III) minerals is required.

In general, the presence of electron shuttles enhances the rate of Fe(III) reduction. The amount of enhancement is related to the redox activity of the OM. A compilation of published literatures reveals positive correlations between the rate of Fe(III) bioreduction and the electron-donating and exchange capacities of OM (Supplementary Fig. 1). The scatter of data reflects differences in experimental conditions, including the Fe(III) minerals, bacteria, solution chemistry and OM concentration. In particular, the electron-donating, electron-accepting and exchange capacities of Fe(III) minerals can be important, especially when the Fe(II)/Fe ratio and the mineralogy change as Fe(III) reduction continues¹¹³. Because electron-accepting and electron-donating capacities of OM depend on aromatic and phenolic moieties¹¹¹, such correlations reinforce the important role of these functional groups in shuttling electrons. The presence of electron shuttles enhances the extent of Fe(III) reduction^{140,141}, although no enhancement has been observed in other experiments^{142,143}. Such discrepancy can be caused by difference in incubation time¹⁴³.

The electron-shuttling function of OM opens the possibility for other microorganisms to reduce Fe(III) that are not capable of direct enzymatic reduction. Therefore, the diversity of microorganisms able to reduce Fe(III) increases because of the presence of electron shuttles. Possible microorganisms include typical anaerobic Fe(III) reducers, sulfate reducers and methanogens, as well as anaerobic methane oxidizers (Fig. 4a).

If OM retains electrons and releases them later when Fe(III) becomes available, this function is defined as electron buffer. Therefore, although fast electron transfer constitutes an electron shuttle which is important to sustain anaerobic respiration, relatively slow electron transfer results in an electron buffer, which is important to buffer redox reactions. Electron transfer from humic substances to electron acceptors is initially fast but then slows down¹⁴⁴. Therefore, humic substances act as electron shuttle initially but change to buffer

later. The electron-buffering capacity of OM explains the persistence of aqueous Fe(II)¹⁴⁵ and other reductants in oxic environments, because OM might preferentially donate electrons to oxidants, thus protecting Fe(II) and other reductants from oxidation. The electron-buffering capacity of OM allows electron transfer from reductants to oxidants over a long distance. OM can be charged by electrons from reductants when they are replete and discharged when electron acceptors become available, similar to a geobattery^{37,102,146,147}. In doing so, OM geobattery can minimize the demands of organic carbon as electron sources, with a wide range of environmental applications.

Solid OM, such as granular activated carbon, biochar and pyrogenic carbon, can serve as an electron conductor to facilitate direct interspecies electron transfer between microbial cells of the same and different species¹³⁴ (Fig. 4b). Although electron transfer between metal reducers and methanogens has been well studied¹⁴⁸, anaerobic methane oxidizers and sulfate reducers can also form partners via this process¹⁴⁹. Therefore, electrically conductive solid OM accepts electrons from various microorganisms and donates them to Fe(III) minerals via solid OM as an effective electron transport pathway, thus connecting multiple functional groups of microorganisms across micrometre-to-millimetre scales^{148,150}. Because of these multiple roles of solid OM, ecologically separated processes such as Fe(III) reduction and methanogenesis can take place simultaneously¹⁴⁸.

Effect of OM adsorption on Fe redox cycling

Adsorption of OM to Fe(III) mineral surfaces changes the redox activity of OM and surface properties of Fe mineral, thus exerting a strong effect on Fe redox cycling through several mechanisms. First, preferential adsorption of carboxyl compounds^{58,151} to Fe minerals results in compositional fractionation of OM. The adsorbed and aqueous pools of OM have different electrochemical properties than those of original OM¹⁵², which affects Fe redox cycling¹⁵³. Second, OM adsorption-induced decrease in particle size of Fe minerals should enhance Fe(III) bioreduction¹³². Third, OM adsorption to Fe(III) mineral blocks Fe(III) sites through particle aggregation and therefore decelerates microbial reduction of Fe(III)^{153,154}. In addition, adsorption of redox-inactive OM to Fe minerals creates a physical barrier between Fe minerals and microorganisms and thus inhibits Fe(III) bioreduction, when a physical contact is essential. However, if adsorbed OM serves as electron acceptor, donor, shuttle, buffer or conductor, spatial proximity to Fe centres likely facilitates Fe redox cycling.

For structurally anisotropic clay minerals, OM adsorption and its effect on Fe redox cycling are orientation-dependent. Most OM adsorbs to edge sites^{2,14} via inner-sphere complexation. Edge-adsorbed OM should be able to readily transfer electrons to the Fe(III) exposed at the edge sites. For Fe-rich clay minerals, the resulting edge-Fe(II) propagates electrons to the interior Fe(III) (Fig. 5) via an electron hopping mechanism, because Fe atoms in the octahedral sheet are adjacent to each other. Likewise, edge-adsorbed Fe(II) can transfer its electrons to the octahedral Fe(III) in nontronite via the same mechanism¹⁵⁵.

For Fe-poor clay mineral montmorillonite, the octahedral Fe(III) is also highly reducible by aqueous Fe(II)^{156,157}, despite the difficulty of electron hopping across spatially isolated Fe atoms in the octahedral sheet¹⁵⁸. This difficulty can be circumvented if redox-active OM can enter the interlayer to help electron transfer. Many different types of OM can be intercalated into the interlayer of expandable clay minerals, including cysteine¹⁵⁹, soil OM⁴⁶ and humic materials¹⁶⁰. Certain intercalated OM, such as phenolic compound 1-naphthol¹⁶¹ and cysteine^{159,162}, can reduce octahedral Fe(III) in montmorillonite. These findings are

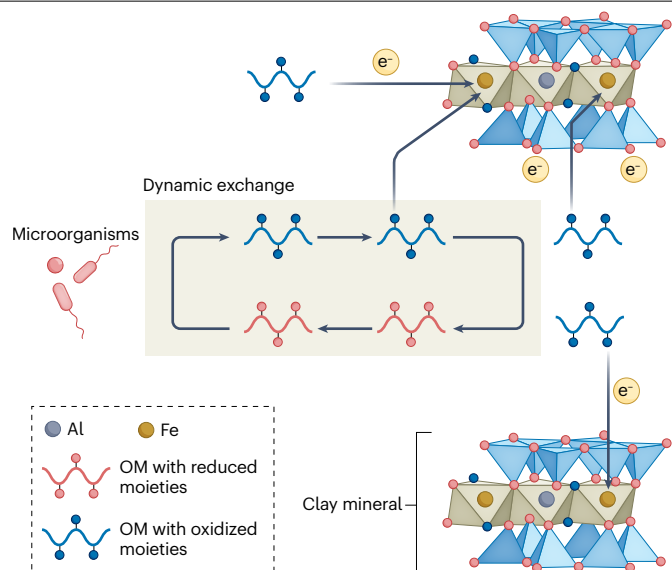


Fig. 5 | Site-specific roles of organic matter as electron donor and shuttle in expandable clay minerals. Reduced organic matter (OM) adsorbed at clay mineral edge sites transfers electrons to Fe(III) along the octahedral layer, whereas OM in the interlayer transfers electrons to octahedral Fe(III) through the cavity of the tetrahedral sheet. The resulting oxidized OM diffuses out of the interlayer into aqueous solution and is reduced again by microorganisms, ready to enter the interlayer to start the next cycle. A dynamic exchange of OM between the interlayer and aqueous solution allows extensive reduction of Fe(III) in Fe-poor montmorillonite.

brought together in a dynamic exchange mechanism (Fig. 5). Reduced OM enters the interlayer region and donates electrons to the octahedral Fe(III) across the tetrahedral layer¹⁶². The resulting oxidized OM diffuses out of the interlayer and is reduced by microorganisms. The reduced OM diffuses back into the interlayer to start the next cycle. This mechanism combines adsorption (intercalation) and electron-shuttling functions of OM to answer one of the most difficult electron transfer questions in clay minerals.

Effect of Fe-OM co-precipitation

Co-precipitation of OM with Fe(III) minerals has both positive and negative effects on Fe(III) bioreduction. On the one hand, co-precipitation of Fe(III) minerals with OM results in smaller crystal size and greater structural disorder^{154,163,164}, which favour microbial reduction of Fe(III). On the other hand, OM can promote particle aggregation of Fe(III) minerals and decrease their surface area^{15,165}, thus lowering Fe(III) bioreduction. Furthermore, OM can block active Fe sites and decrease the surface charge of Fe(III) minerals, which is unfavourable for Fe(III) bioreduction. The relative importance of these processes primarily depends on the C/Fe ratio¹⁶⁶.

OM-Fe co-precipitation retards transformation of the host Fe mineral (such as ferrihydrite) in both oxic and anoxic environments^{41,167}. In either aqueous Fe(II)-catalysed¹⁶⁷ or microbially catalysed transformation of ferrihydrite under anoxic environments^{126,168}, marked retardation results when OM and ferrihydrite form a strong carboxylate-Fe bond via ligand exchange¹⁶⁹. Because the amount of OM in OM-ferrihydrite co-precipitates is much higher than that in OM-crystalline Fe oxide co-precipitates, retarded transformation of

ferrihydrite favours OM preservation. However, in the case of microbial reduction, ferrihydrite provides a more bioreducible substrate for Fe(III)-reducing bacteria and a higher probability of OM release upon bioreduction.

Although OM retards ferrihydrite transformation, partial transformation still occurs over time. The mineral transformation products and their physicochemical properties are determined by the C/Fe ratio and the nature of OM. In the absence of OM, goethite and magnetite are common products of ferrihydrite transformation¹⁷⁰. In the presence of OM, lepidocrocite forms from Fe(II)-catalysed ferrihydrite transformation^{170,171}, but siderite, magnetite, green rust and vivianite are the common products from microbially catalysed ferrihydrite transformation^{126,166,168}. The presence of OM in ferrihydrite results in Fe(III) mineral products with more defects and greater porosity than those formed from pure ferrihydrite¹⁷², which is beneficial to OM sequestration.

Fe-OM complexation impacts on Fe redox cycling

Although Fe-OM complexation can be the first step of Fe hydrolysis towards adsorption and co-precipitation⁴⁰, aqueous Fe-OM complexes also form from dissolution of Fe minerals by OM. Here Fe-OM complexation refers to the latter case. Carboxylic, aromatic, phenolic, hydroxylic, quinone and ketonic carbonyls are the main functional groups of OM able to form complexes with Fe^{15,31}. The formation of Fe-OM complexes changes the solubility, speciation, reactivity and distribution of Fe^{173,174} and therefore affects Fe redox cycling in several positive ways.

There are two positive effects of OM complexation on reduction of Fe(III). First, if OM dissolves Fe(III) minerals and forms Fe(III)-OM complex, the rate of Fe(III) reduction is often enhanced^{126,133,175,176}, owing to easier microbial access to aqueous Fe(III)-OM complex. Second, OM complexation with biogenic Fe(II) prevents its sorption onto residual Fe(III) mineral and microbial cell surfaces, thus removing the passivating effect¹⁷⁶. The ultimate impact of OM on microbial Fe(III) reduction is a result of these processes, which depends on the nature of the OM-Fe interaction, for example, the relative complexation capacity of Fe(II) versus Fe(III).

Likewise, there are two positive effects of OM complexation on oxidation of Fe(II). First, organic ligands alleviate encrustation of Fe(II) minerals and cells by newly produced Fe(III) minerals through complexation with Fe(III)¹⁷⁷. Second, organic ligands can solubilize a fraction of structural Fe(II) to form aqueous Fe(II)-OM complex. Upon oxidation, the resulting Fe(III)-ligand complex enhances the oxidation rate of Fe(II) in pyrite¹⁷⁸, FeS and Fe⁰ (ref. 179). In this oxidation reaction, ligand-complexed Fe(III) and Fe(II) redox pair serves as electron shuttle¹⁸⁰. Indeed, humic acids enhanced abiotic^{53,64} and biotic¹⁸¹ oxidation of Fe(II) in reduced nontronite through solubilization of structural Fe(II) and formation of the aqueous Fe(II)-ligand complex. The oxidation process is sustained via reduction of the reaction product, Fe(III)-ligand complex, back to Fe(II)-ligand complex by structural Fe(II) via interfacial electron transfer¹⁵⁵. Thus, the Fe(III)-ligand and Fe(II)-ligand redox couple effectively serves as electron shuttle to accelerate electron transfer from structural Fe(II) in reduced minerals to oxidants O₂ (ref. 53) and microorganisms¹⁸¹. Furthermore, the presence of OM greatly increases the yield of ROS¹⁸², which would enhance Fe(II) oxidation. However, high concentrations of OM can also scavenge ROS.

Through cycling between Fe(II)-ligand and Fe(III)-ligand complexes, this ligand-facilitated electron transfer pathway expands the

bioavailable pools of Fe. For example, structural Fe(III) in illite and magnetite is not readily bio-reducible^{183,184}, but in the presence of organic ligands, structural Fe(III) can become more bio-reducible. Likewise, Fe(II) in siderite, biotite, magnetite, pyrite, arsenopyrite, nontronite and illite is subject to microbial oxidation^{25,26,185}. The presence of ligands can enhance the oxidation of structural Fe(II) in these minerals. When the ligand-enhanced Fe redox cycling is rapid, it might be cryptic¹⁸⁶, because concentrations of Fe(II)–ligand and Fe(III)–ligand complexes can be too low to be detectable owing to rapid cycling between them.

Effect of redox-transformed OM

Because Fe-redox-transformed OM has different compositions, structures and electrochemical properties, its role in the subsequent Fe redox cycle will undoubtedly change. However, definite evidence is lacking. Current understanding is limited to change of OM bioavailability after photochemical degradation of OM. There are two general observations. If OM is of terrestrial origin, solar irradiation preferentially degrades aromatic substances to produce hydroxylated aromatic compounds and small organic acids, which generally increases OM bioavailability^{30,51}. If OM is labile (such as amino acids and polypeptides), solar irradiation in the presence of dissolved Fe(II)–OM and Fe(III)–OM complexes can decrease its bioavailability owing to polymerization⁶¹. However, all these experiments focused on aerobic microbial respiration of OM, and no similar experiments have been performed on anaerobic respiration.

Because the electron-donating, electron-accepting and exchange capacities of OM depend on the redox-active functional moieties^{32,130,187}, any processes that change such moieties will likely change the role of OM in Fe redox cycling. For instance, air oxidation of reduced OM can form phenolic or quinone moieties³⁵. Because these moieties serve as electron donor, acceptor and shuttle^{32,34,187}, their formation can enhance the ability of OM to mediate Fe redox cycling. Likewise, oxidation of lignin-derived OM compounds can increase the carboxyl content¹⁸⁸, thus enhancing the complexation capacity of OM with Fe(II). In addition, because the redox state of OM affects

its adsorption to Fe(III) (oxyhydr)oxides¹⁸⁹, redox transformation of OM likely alters its adsorption capacity. Furthermore, increased bioavailability of transformed OM likely stimulates the activity of Fe(III)-reducing and Fe(II)-oxidizing microorganisms to enhance Fe redox cycling.

Interlinked OM and Fe redox cycling

For the purpose of clarity, all effects of OM on Fe redox cycling are presented individually. However, in nature, these effects can be intertwined across multiple interfaces and spatiotemporal scales. To provide a clearer perspective, all roles of OM can be classified into those initiating mineral redox reactivity, those enhancing mineral redox reactivity and those important to mineralogical transformation (Fig. 6).

Certain Fe (oxyhydr)oxides and some Fe-bearing clay minerals are redox-active, but others, including some sulfides (such as pyrite) and Fe-bearing silicates (illite and biotite), are marginally active or inactive. However, in the presence of OM as a chelator to complex with Fe, part of structural Fe becomes redox-active through dissolution of minerals and formation of aqueous Fe–OM complexes (Fig. 6). Electron and atom exchange reactions occur at the interface between Fe–OM complexes and structural Fe in minerals^{155,190}. These reactions increase bioavailability of Fe minerals and initiate redox reactivity (both the rate and extent of Fe redox cycling).

Once activated, the redox activity of Fe minerals further increases by the electron-shuttling, electron-buffering and electron-conducting functions of OM. Electron-shuttling capacity and frequency of OM accelerate the rate of Fe redox cycling. Electron-buffering capacity increases the extent of Fe redox cycling. Electron-conducting capacity of OM increases the flux of electron flow from reductants to oxidants, which has a positive effect on both the rate and extent of Fe redox cycling. As a result of these functions of OM, the redox activity of Fe minerals is greatly elevated.

Finally, all possible functions of OM contribute to Fe mineral transformation, because OM changes the physicochemical properties of Fe minerals, including solubility, Fe oxidation state, surface chemical

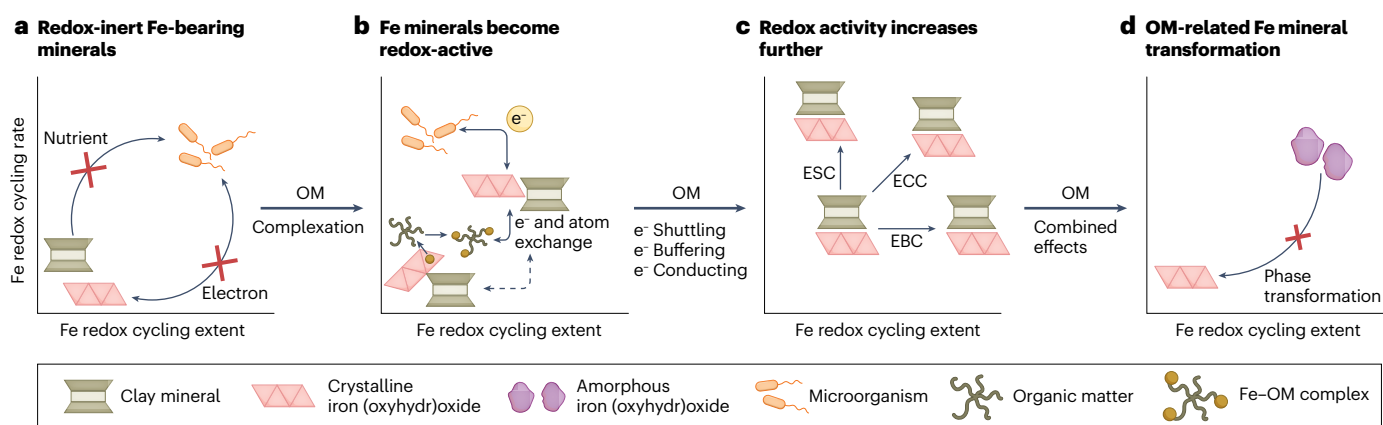


Fig. 6 | Functions of organic matter in moderating redox cycling of Fe minerals arranged into a sequence.

a, Many Fe-bearing minerals are redox-inert. There is no exchange of electrons between minerals and microorganisms.

b, When organic matter (OM) dissolves a fraction of Fe minerals and releases some Fe to form aqueous Fe–OM complexes, Fe minerals become redox-active owing to atom and electron exchange between Fe–OM complexes and structural Fe in minerals. **c**, When electron-shuttling, electron-conducting and

electron-buffering OM interacts with Fe minerals, their redox activity further increases. Specifically, electron-shuttling capacity (ESC) of OM increases the rate of Fe redox cycling, electron-buffering capacity (EBC) increases the extent and electron-conducting capacity (ECC) increases both the rate and extent.

d, All functions of OM have a role in Fe mineral transformation. In the presence of OM, transformation of Fe minerals is inhibited or retarded, particularly in poorly crystalline ferrihydrite.

Glossary

α -Glucosidase

A carbohydrate-hydrolase that releases α -glucose.

β -Glucosidase

An enzyme that catalyses the hydrolysis reaction of cellobiose.

Autotrophic

Ability of microorganisms to produce biomass from inorganic carbon (CO_2) using energy from sunlight or inorganic chemical reactions.

Fenton-like reaction

Reduction of O_2 to H_2O_2 and subsequent reaction with Fe(II) .

Heterotrophic

Ability of microorganisms to produce biomass from organic carbon.

Hydrolases

Enzymes that break down a chemical compound by reaction with water.

Microbial decomposers

A microbial community that decomposes organic matter.

Microbial necromass

Dead biomass, including all microbial products and constituting an important fraction of soil organic matter.

Mineral–OM associations

(MOAs). Mineral–organic matter association via physical and chemical interactions.

bonding and reduction potential. In general, the presence of OM, especially via adsorption and co-precipitation, retards mineralogical transformation and maintains a poorly crystalline or amorphous nature (for example, ferrihydrite). The extent of mineral transformation and secondary mineral formation depends on the specific roles of OM.

In summary, the multiple interlinked effects of OM not only elevate the reactivity of Fe minerals but also alter mineralogical transformation. The net result of these effects depends on the nature of Fe minerals and OM as well as environmental conditions.

Summary and future perspectives

Although the coupled Fe–C processes are separately described for clarity, it is important to emphasize that these processes are entangled and occur simultaneously in nature. In soils and sediments, multiple

Mixotrophic

Ability of microorganisms to be either autotrophic or heterotrophic depending on the availability of carbon substrate and environmental conditions.

Oxidases

Enzymes that catalyse chemical reactions involving donation of a hydrogen atom and reduction of oxygen to form water or hydrogen peroxide.

Peroxidases

Enzymes that catalyse the oxidation of a substrate by peroxide.

Phototrophic

A special type of autotrophic lifestyle, using sunlight as a source of energy to synthesize organic compounds out of inorganic carbon (CO_2).

Reactive oxygen species

(ROS). Highly reactive chemical species, owing to the presence of unpaired electrons, formed from reaction with molecular O_2 .

Redox potential

The thermodynamic driving force of a chemical species to be either reduced by accepting electrons or oxidized by donating electrons.

Substrate

Organic compounds that specifically bind to enzymes to support microbial growth.

minerals, microbial communities, complex mixtures of OM compounds and extracellular enzymes are co-present. There are positive and negative feedback mechanisms to result in synergistic, antagonistic or no interactions among them (Fig. 2). In particular, ROS–enzyme interactions are greatly understudied and their joint role in OM transformation is poorly known, especially in the presence of Fe minerals⁷⁶. Investigations of such complex interactions are sparse, and much of the current knowledge is based on greatly simplified experiments under well-controlled conditions. Speculations and inferences are often made about more complex systems. Therefore, it is imperative to determine the net effect of all these concurrent processes by taking a holistic approach. In this section, we describe most relevant implications of coupled Fe–C cycles for carbon sequestration and redox reactivity of Fe minerals.

A mechanistic understanding of coupled Fe–C redox processes under varying environmental conditions is essential for developing strategies for sequestering carbon and mitigating greenhouse gas emissions. Fe minerals have important roles in stabilizing organic compounds through organo-mineral associations, but they also act as a transformer to degrade OM¹⁹. The ability of Fe minerals to protect or degrade OM highly depends on environmental conditions and the reactivity of Fe minerals. It is essential to establish such conditions and identify redox-active Fe minerals that either protect or degrade OM. Although Fe minerals have been shown to preserve OM for decades to millennia^{6,191}, both laboratory experiments and models have also shown that organic compounds associated with Fe minerals can experience redox transformation or be released to solution^{96,192,193}. To quantitatively determine the contribution of Fe minerals to soil carbon storage, more research, especially experiments combined with simulations, is needed to quantify the amount, composition and age of organic compounds associated with specific Fe minerals under diverse environmental conditions.

Changes in C storage and Fe mineral stability should be assessed over time and across multiple environmental gradients such as temperature, precipitation and vegetation type. There are different approaches that could be carried out, including use of artificial soils to test the specific effect of a particular variable¹⁹⁴, or a better approach is to use natural soils in controlled laboratory incubations^{101,195}. For example, dissimilatory Fe(III) reduction rates of wetland soils are correlated with incubation temperature, the stock of poorly crystalline Fe(III) (oxyhydr)oxides and C/N ratio¹⁰¹. Similar correlations can be made between the rates or extents of various Fe–C processes and controlling variables (mineralogy, ROS yield, OM composition and OM–mineral binding strength). Spectroscopy, microscopy and mass spectrometry can be used to quantitatively characterize the mineralogy and OM composition^{196,197}. Various indices can be calculated to indicate the composition and oxidation state of OM¹⁹⁸, which can be correlated with the Fe and C process rates. However, it is a challenge to scale laboratory-based rates of biogeochemical process to field scales.

A more meaningful approach is to conduct experiments in the field. A benefit of this approach is the capture of spatial heterogeneities of Fe–C redox reactions across different interfaces. The drawback is the difficulty of isolating specific controlling factors. Because multiple feedbacks could be operating simultaneously, some processes might be magnified, but others might be cancelled. Furthermore, current experiments are limited to surface soils and sediments, and there are few efforts to examine Fe mineral–OM–microorganism interactions at depth. For example, when MOAs are buried in sedimentary basin or

subseafloor, with increasing temperature and pressure, clay minerals undergo transformation¹⁹⁹, and OM undergoes cracking, isomerization and alkylation to generate hydrocarbons and kerogen²⁰⁰. However, their mutual interactions are not well understood.

These efforts provide a context for achieving a greater goal of quantifying the impact of Fe-mediated processes on C storage and persistence across diverse ecosystems. Achieving this goal will require development of biogeochemical models that link multiple spatial and temporal scales. The carbon cycle models typically use a rate modifier to account for the effect of minerals on OM turnover in soils and sediments²⁰¹ but do not sufficiently consider the mechanistic pathways of coupled Fe–C cycles under fluctuating redox conditions. An improved ecosystem-level carbon cycle model can be achieved through a mechanistic understanding via quantification of redox-active Fe minerals, mineral-specific OM transformation and production of CH₄ and CO₂ linked to Fe-cycling pathways. Such biogeochemical models will fill an important knowledge gap by improving predictions of OM decomposition or preservation as a result of Fe redox cycling under a climate change scenario.

By far, most studies on Fe mineral redox cycling have focused on (oxyhydr)oxides because these minerals are highly reactive¹⁵. In comparison, aluminosilicates are less studied²⁰², apparently because of their lower redox reactivity^{184,203}. However, the presence of OM can enhance the redox reactivity of these apparently inert minerals^{119,181}. When Fe minerals transform to new phases as a result of their interaction with OM, their physicochemical properties change, including adsorption and co-precipitation capacities, redox reactivity and catalysis, and thus their retention capacities of nutrients and contaminants will be different^{22,24,204,205}. For instance, when Fe minerals are dissolved by OM, mineral-associated nutrients, toxic elements and OM will be released. The mobility and bioavailability of these nutrients and toxins are essential to the survival and functions of microorganisms.

OM can be both desirable (as sources of energy, carbon, nitrogen and other nutrients) and undesirable (as a source of toxic materials) to microorganisms. Therefore, understanding OM bioavailability is of great importance to prediction of ecosystem functions. Likewise, OM has a high adsorption capacity for trace metals such as Mo²⁰⁶, Cu and Zn²⁰⁷, among others. OM transformation will change the mobility and bioavailability of these trace metals, thus affecting soil fertility and crop productivity. Therefore, coupled Fe–C cycles strongly regulate a range of biogeochemical and environmental processes in terrestrial and aquatic environments. Systematic studies at both laboratory and field scales under natural conditions are warranted to determine the types of Fe minerals and the extent to which their redox activity can be enhanced by various organic compounds.

Individual roles of OM in Fe redox processes have been well studied, but their multiple effects simultaneously participating in Fe redox processes are not widely recognized. It is known that OM can serve as dual roles to impact Fe redox cycling, including dual roles of electron donor and shuttle^{23,120,121,125}, electron shuttle and complexant¹²⁶ and electron donor and complexant²⁰⁸. In natural environments, OM likely serves as more than one function, and any combinations of electron acceptor, donor, shuttle, buffer and conductor, as well as its adsorbing, co-precipitating and complexing capacities, are conceivable. Therefore, a combined role can be stronger or weaker than their individual roles, depending on the mode of interaction. Future experiments can be designed to investigate their combined role in moderating Fe redox cycling and environmental processes. Given the complexity of organic compounds and Fe minerals in natural environments, further research

is needed to determine how specific organic compounds alter the reactivity and evolution of Fe minerals under varied environmental conditions.

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