



## Review

# Mineral-mediated stability of organic carbon in soil and relevant interaction mechanisms

Zibo Xu<sup>a</sup>, Daniel C.W. Tsang<sup>b,\*</sup><sup>a</sup> Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China<sup>b</sup> Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China

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## ABSTRACT

Soil, the largest terrestrial carbon reservoir, is central to climate change and relevant feedback to environmental health. Minerals are the essential components that contribute to over 60% of soil carbon storage. However, how the interactions between minerals and organic carbon shape the carbon transformation and stability remains poorly understood. Herein, we critically review the primary interactions between organic carbon and soil minerals and the relevant mechanisms, including sorption, redox reaction, co-precipitation, dissolution, polymerization, and catalytic reaction. These interactions, highly complex with the combination of multiple processes, greatly affect the stability of organic carbon through the following processes: (1) formation or deconstruction of the mineral–organic carbon association; (2) oxidative transformation of the organic carbon with minerals; (3) catalytic polymerization of organic carbon with minerals; and (4) varying association stability of organic carbon according to the mineral transformation. Several pieces of evidence related to the carbon turnover and stability during the interaction with soil minerals in the real eco-environment are then demonstrated. We also highlight the current research gaps and outline research priorities, which may map future directions for a deeper mechanisms-based understanding of the soil carbon storage capacity considering its interactions with minerals.

## 1. Introduction

The rising global fossil fuel consumption caused the increase of atmospheric CO<sub>2</sub> concentration from 280 ppm before industrialization to 417.2 ppm in 2022, contributing to global warming with an average increase of 1.07 °C [1–3]. Understanding the fate of carbon is urgently needed to abate global warming for the sake of the eco-environment and human health [1,4–6]. Soils, as dynamic global carbon reservoirs, contain more organic carbon than vegetation and atmospheric carbon pools [7,8]. Therefore, even the release or activation of a small proportion of soil organic carbon (SOC) will significantly affect the atmospheric greenhouse gases and global climate. As reported, approximately 14% of atmospheric CO<sub>2</sub> over the past decade is attributed to the destabilization of SOC [9]. Organic carbon in the soil has a complex composition, including plant, animal, and microorganism residues (e.g., microbial necromass) with different degrees of decomposition/humification, organic substances synthesized through natural and anthropogenic reactions, and biomass of live soil organisms and associated products [7,8,10]. Most organic carbon in soil occurs in close spatial proximity to the soil minerals, i.e., another key component in the soil, including

phyllosilicates and other aluminosilicates, metal oxides, hydroxides, oxyhydroxides, carbonates, and sulfides [11], and will almost inevitably come into contact with mineral surfaces during its cycle [11,12]. The mineral–organic carbon stocks are predicted as 899 Pg C (5%–95% range: 668, 1,074 Pg C) to a depth of 1 m in soil, occupying over 66%–70% of the total SOC [13]. Therefore, the interactions between organic carbon and minerals are crucial to predicting and evaluating carbon's fate in various land uses and, thus, global warming [1,11–16].

Great interest has been drawn towards the interactions between organic carbon and minerals under simulated soil conditions [11,12,15], considering its impact on soil health, fertility, pollutant transformation, and carbon sequestration. The interactions between specific organic carbon and minerals are generally coupled with multiple routes, leading to a complicated impact on the carbon sequestration potential. It has been confirmed that interaction with minerals could significantly change the speciation and properties of the SOC via redox reaction, polymerization, and catalytic reaction, directly affecting its stability and bioavailability [17–21]. In addition, sorption, complexation, and co-precipitation between organic carbon and minerals would form the mineral–organic carbon association, protecting the organic carbon

\* Corresponding author.

E-mail address: [cedan@ust.hk](mailto:cedan@ust.hk) (D.C.W. Tsang).<https://doi.org/10.1016/j.eehl.2023.12.003>

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against degradation [22–25]. The catalytic polymerization of simple organic carbon on mineral surfaces is increasingly considered a crucial step for organic carbon preservation and accumulation in the soil [14, 26]. Meanwhile, organic carbon can alter the mineral structures through chelation, dissolution, co-precipitation, and redox reaction, dramatically affecting their combination with the organic carbon, which is also crucial for the fate of SOC [14, 27–29]. Given the highly variable compositions of both organic carbon and minerals in the soil, precise prediction of the potential interaction process is challenging [30, 31]. Different speciation, even a slight change of the surface functionality, particle size, or crystallinity, will lead to a contrasting interaction route and, thus, distinctive stabilization or destabilization impact.

Regarding soil organic matter, a few critical reviews have been conducted elucidating its nature and dynamics [32, 33], geochemistry processes [34], characterization methods [35], and impact on the fate of trace metals [10] in soil. These reviews provided useful information on the transformation of soil organic matter and its impact on the soil ecology functions, while its interactions with minerals and relevant implications on soil carbon storage remain unclear. Considering the fate and functions of minerals in the soil, its geochemistry process [36] and impact on the element cycling [37] are summarized. Although the interactions between soil organic matter and minerals have been recently reviewed [11, 38], their impact on the stability of organic carbon and relevant mechanisms are still unveiled. Therefore, we provided a critical review to illuminate the interaction mechanisms between minerals and SOC, including sorption, redox reaction, dissolution, co-precipitation, polymerization, and catalytic reaction. More importantly, the impact of these interactions on the fate of SOC was elucidated, including positive stabilization and negative destabilization. We further evaluated several site studies in natural eco-environment systems to evidence the importance of the mineral-organic carbon interactions on soil carbon stability. Accordingly, the existing knowledge gaps and research prospects were discussed and proposed. As the properties and compositions of soil organic matter and minerals have been reviewed in detail in the literature, this critical review focused specifically on their interactions and relevant impact on soil carbon storage.

## 2. Interactions between minerals and SOC

### 2.1. Sorption of SOC on minerals via different mechanisms

Sorption of organic carbon on the minerals has been verified as a vital process for the interactions between organic carbon and minerals in the soil, and the mineral-associated organic carbon has a much lower mineralization ratio than the free (unbound) organic carbon. Various studies reported that minerals, including clay minerals (phyllosilicates), metal oxides, and metal hydroxides, have a higher potential for SOC sorption based on the surface properties (e.g., surface area), and the sorption mechanisms varied based on the mineral speciation and the electrostatic properties (Fig. 1) [11, 39–42]. Soil minerals are divided into two types: permanently charged and variably charged, corresponding to various sorption performances and dynamics (Fig. 1).

For the variably charged minerals, the variety comes from the surface hydroxyl groups (Fig. 1), which can be protonated with increasing acidity in the soil solution. The protonated hydroxyl with a positive charge could attract negatively charged organic carbon through electrostatic interaction and ligand exchange. Therefore, an acidic environment usually facilitates the organic carbon sorption on the mineral oxide or hydroxide [31, 43–45]. By contrast, a negative surface charge occurs on these minerals under the alkalinity environment due to the hydrolysis of hydroxyl groups, which suppress direct sorption. The combination through bridging cations (e.g., calcium) would become the primary process with decreased electrostatic repulsion between negative mineral surface and organic carbon [45].

The permanent charge on the mineral originates from the isomorphous substitution of metals with a different charge (Fig. 1), especially for the

phyllosilicates with rich octahedral aluminum and tetrahedral silicon. A negative charge surface is found in the phyllosilicates after the substitution by fewer charge cations, with a higher capacity to attract cations on the surface to balance the charge, which can serve as the bridging ions for organic carbon sorption. The cation bridging impact has been widely reported for organic carbon sorption on the illite, smectite, or montmorillonites with Ca, Mg, or Fe bridging [46–48], and smectite usually shows a higher capacity than illite and kaolinite due to more negative surface charge and richer cations exchange content [49, 50]. Furthermore, a partial redox reaction might also cause a permanent charge on the mineral surfaces; for instance, the reductive formation of Mn(III) in MnO<sub>2</sub> crystalline leads to a negative surface charge with cations sorption, resulting in a different organic carbon sorption process.

Both permanently charged and variably charged minerals can form non-charge minerals under specific conditions, i.e., suitable pH for the variably charged minerals and permanently neutral charge minerals without isomorphous substitution (Fig. 1). The entropy-driven hydrophobic exclusion or partitioning with van der Waals forces or H-bonding can be the primary sorption mechanism under this situation [31, 46, 51], typically targeting the nonpolar molecules [45].

The sorption process generally starts with the formation of monolayer coverage on the mineral surface through the above-mentioned mechanism, which then converts into a multilayer molecular architecture, driven by complex biological and chemical processes [52]. The hydrophobic interactions between organic carbon and the involvement of cations might be responsible for the organic layer thickening [52]. This process can be evidenced by online high-resolution mass spectrometry, which revealed that aromatic carbon was first sorbed on the iron minerals, and the non-aromatic organic carbon would be sorbed on the formed carbon layer afterward [53]. The key factor for organic carbon sorption changes from mineral surface chemistry to organic-organic interaction. Moreover, continuous and competitive sorption/desorption with different organic carbon and inorganic ions was reported, and thus, organic carbon with higher affinity tended to be preserved on the mineral surfaces [53, 54]. The dominant process is often time-dependent and related to the interaction duration (field age).

Accordingly, the surface charge and properties of the minerals greatly affect the organic carbon sorption, and the sorption process and mechanisms are also controlled by environmental conditions, co-existing moieties, and concerned duration. The sorption mechanisms of organic carbon on the minerals typically determine its stability in the soil environment, which will be further elaborated in the following sections.

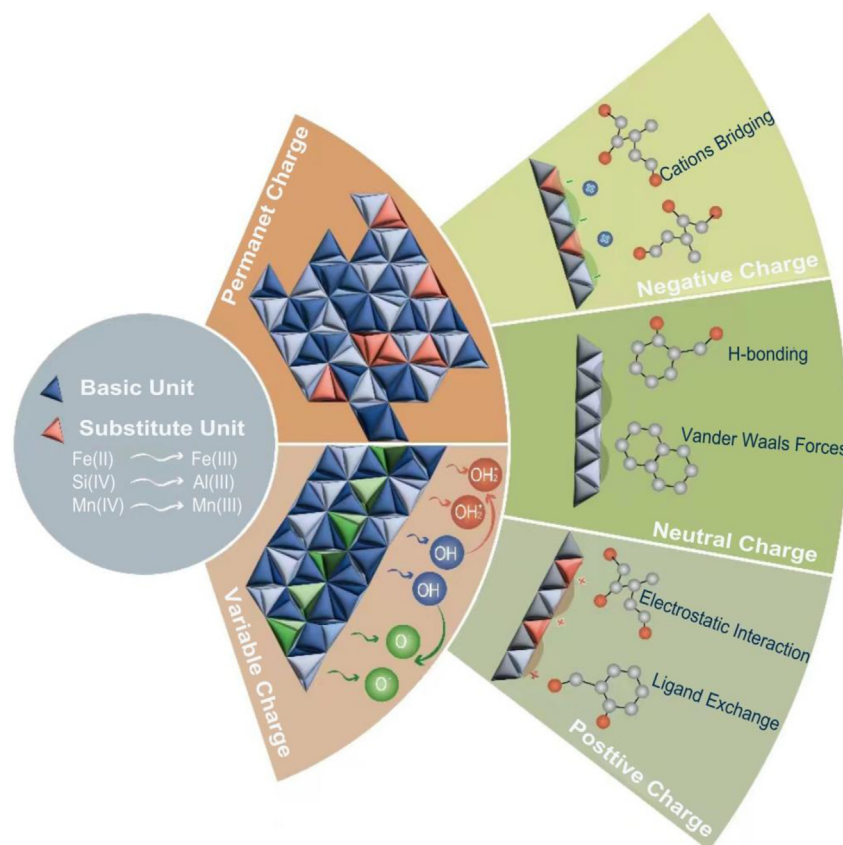
### 2.2. Redox reactions between organic carbon and redox-active minerals

The direct electron transfer reactions between organic carbon and minerals, as well as the indirect processes supported by forming reactive oxygen species (ROS) or microbes, are essential interactions in the soil environment (Fig. 2).

#### 2.2.1. Direct electron transfer between organic carbon and minerals

Although organic carbon contains a variety of surface functionalities from oxidizing to reducing [55], it usually serves as the electron donor during the redox reaction with soil minerals, leading to the reduction of mineral metals (Fig. 2). This direct redox reaction typically requires the approaching of dissolved organic matter (DOM) on the mineral surfaces, which can be achieved by the above-mentioned sorption process or direct incorporation (e.g., pyrogenic carbon with minerals [56]).

A variety of organic carbon can serve as the electron-donating moiety for the reduction of minerals (i.e., Fe and Mn minerals, phyllosilicates). Humic acids, low-molecular-weight organic acids (LMWOAs), proteins, phenols, anilines, and pyrogenic carbon have been proven to donate electrons for mineral reduction. During the reduction process, the hydroquinone/phenol,  $\alpha$ -hydroxyl, and N/S-containing moieties (e.g.,  $-\text{NH}_2$ ) were the primary electron-donating moieties on the organic carbon [57–63], which undergo oxidative transformation to form



**Fig. 1.** Sorption mechanisms of soil organic carbon on minerals with different properties. Basic units (e.g., tetrahedral silicon or iron oxide) will be substituted by different minerals (substitute units) through the exchange or reduction process [e.g., Fe(III) to Fe(II) or Si(IV) to Al(III)], thus leading to a permanent charge. In addition, the surface hydroxyl group will be protonated to form a variable charge. Different surface charges will affect the sorption process and mechanisms.

compounds with higher oxygen but lower hydrogen content [63]. However, some studies reported contrasting transformation with the decrease of oxygen after the redox reaction due to the difference in DOM [63–65], indicating the composition-dependent oxidation pathway of DOM. Oxidation or even mineralization with the broken aromatic ring or carbon chain happens during the redox reactions, characterized by changes in molecular size, O, and H contents [18,45,63–66].

Minerals, especially iron hydro(oxide) and manganese oxide, can accept the electrons originating from the organic carbon. The hosted Fe(III) or Mn(IV) can be reduced to the Fe(II) or Mn(III)/Mn(II), accompanied by the metal release (reductive dissolution), defects formation, and/or mineral transformation process [66–72]. For instance, introducing organic acids can modify the relative rates of olation and oxolation reactions, causing the transformation of ferrihydrite into goethite, magnetite, and lepidocrocite, facilitated by the formed Fe(II) [67]. Similarly, partial reduction of Birnessite by organic carbon can increase the proportion of Mn(II, III) on the edge sites of Birnessite and further lead to the formation of MnOOH and Mn<sub>3</sub>O<sub>4</sub> [18,20,66,70,73,74].

### 2.2.2. Redox-related transformation with the formation of ROS

Redox reactions between soil minerals and organic carbon can be achieved by the generated ROS (Fig. 2). Mineral-derived ROS, including hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), superoxide (O<sub>2</sub><sup>•-</sup>/HO<sub>2</sub>), and hydroxyl radical (HO<sup>•</sup>), are crucial players during the oxidation of SOC, leading to the decrease of molecular size and increase of oxygen-containing functional groups, or even mineralization [75–81], depending on the reactants and conditions [11,82,83]. For instance, the exposure to <sup>1</sup>O<sub>2</sub> removed the organic carbon with an O/C > 0.3 and primarily resulted in the increase of oxygen, while the exposure to O<sub>2</sub><sup>•-</sup> removed organic carbon with less

oxygen (O/C < 0.3) and produced aliphatic formula (H/C > 1.5) [82]. Hydroxyl radicals (HO<sup>•</sup>) are unselective and robust oxidants with high reaction rates and a good ability to oxidize almost all SOC [84,85]. It can stimulate organic carbon decomposition by generating black carbon-like carbon, alicyclic aliphatic compounds, or even CO<sub>2</sub> [86,87]. Based on the studies in floodplain soils, abiotic Fe-mediated radicals can significantly enhance the oxidative depolymerization of SOC, and its impact is higher than the fungal-mediated oxidation process [88]. It is worth noting that most studies concerning the degradation of organic carbon by ROS in the soil focused on the pollutant degradation process, while its impact on the oxidation/degradation of soil organic matter needs more investigation.

The production of ROS with minerals is mainly achieved via water or O<sub>2</sub> reaction at the defects sites, or through interactions with mineral-adsorbed Fe(II)/Mn(III) biologically or non-biologically [76,78,83,85,89–101], or via the photochemical redox reaction [102–107] (Fig. 2). The extent of contribution of ROS through different routes is greatly affected by the soil condition, such as O<sub>2</sub> content, pH, and light exposure, while quantitative contribution analysis is still limited in general. A recent study by Shu et al. indicated that the formation of ROS with ferrihydrite under sunlight was contributed by water oxidation (5.0%), dissolved oxygen reduction (40.9%), and photolysis of Fe(III)-hydroxyl complex (54.1%) [102], while further investment is highly needed. The formation types, contents, and mechanisms of different ROS under various conditions are almost unknown, and the co-existence of organic carbon would make the generation route even more complex.

The co-existing organic carbon content will affect the generation route and pathway of ROS by the minerals, mainly through its combination with the minerals [77,78,85,93]. With the increased ratio of organic carbon to Fe, the main electron transfer pathway could change

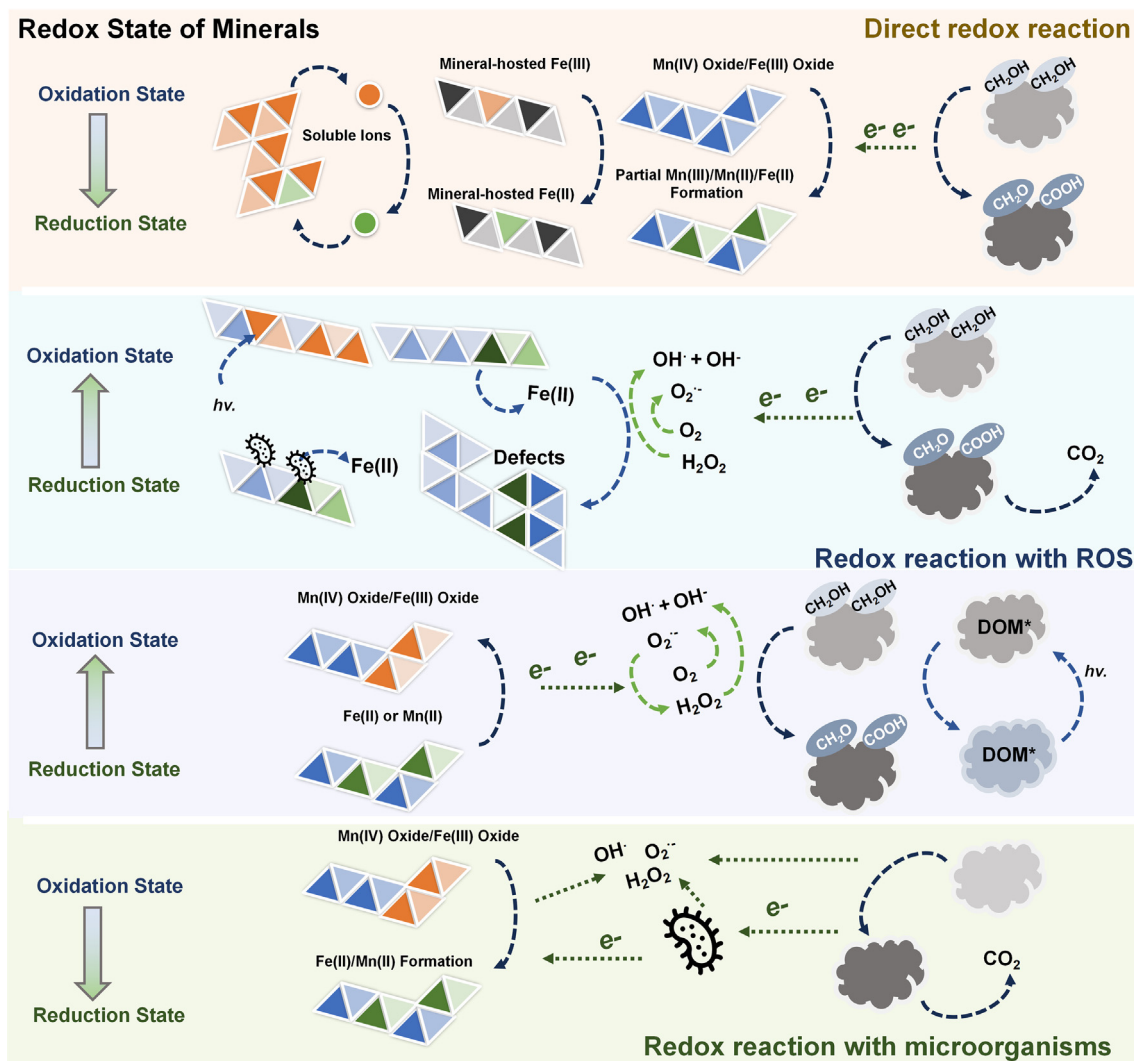


Fig. 2. Redox reactions between organic carbon and minerals with the support of reactive oxygen species (ROS) and microorganisms. The redox reaction will cause the oxidative degradation of soil organic carbon with either oxidation or reduction of soil minerals.

with the variation of electron donor from dissolved inorganic Fe(II) and surface-adsorbed Fe(II) to the organic carbon-complexed Fe(II) and reduced organic carbon, resulting in the increased yield of  $\cdot\text{OH}$  compared to  $\text{H}_2\text{O}_2$  [85]. Moreover, complexation with organic carbon leads to homogeneous ROS generation pathways [through oxidation of aqueous Fe(II)–organic carbon species] compared to only heterogeneous [through oxidation of structural Fe(II)] with soil minerals, commonly causing a higher generation ratio [77]. Similarly, organic carbon would markedly alter the interactions with manganese oxides with the  $\text{O}_2$ , resulting in the contrasting transformation route with distinct oxidation products [78]. For the photochemical process, the chelation impact from organic carbon would significantly affect the photochemical reactivity of the minerals through the photo-induced metal–ligand charge transfer with photogeneration of ROS [102,108–110]. Furthermore, the light-screening impact of organic carbon might inhibit the photoreaction of minerals [79,111].

Another potential interaction pathway was the impact of organic carbon-derived ROS [112–115] on mineral transformation. The active fractions in DOM can absorb solar energy and transform to the excited-state DOM ( $\text{DOM}^*$ ) [116,117], which consequently induces the production of various ROS [112–114,118], together with several poorly identified organic radicals [119]. The reduced form of dissolved organic carbon has been proven to generate radicals under dark conditions [96,

120,121]. The composition of dissolved organic carbon is closely related to the amount and composition of ROS generated [55,114,121,122]. For instance, lower-molecular-weight fractions in the dissolved organic carbon were found to have higher ROS quantum yields [122,123]. Other studies indicated that the production of  $\text{O}_2^{\cdot-}$  and  $\text{HO}^{\cdot}$  were determined by the hydrophobic fractions, whereas  $^1\text{O}_2$  generation was controlled by the hydrophilic fraction [118]. In addition to the dissolved organic carbon, biochar and other pyrogenic carbon are essential sources for ROS generation during their interactions with  $\text{O}_2$  in the soil environment [124, 125], with the released (dissolved) fraction of biochar contributing to ROS generation with or without sunlight [126–128].

The generated ROS is recognized to impose a dominant effect on the transformation of soil minerals with redox-related transformation. Oxidation of Fe(II) by the generated ROS was reported to promote mineral transformation, such as the transformation of ferrihydrite to goethite, lepidocrocite, and schwertmannite [101,102,129]. Green rust was also reported to be oxidized by ROS, forming goethite and lepidocrocite with the other incorporated metals [130]. Similarly, the oxidation of  $\text{Mn}^{2+}$  by the photo-generated  $\text{O}_2^{\cdot-}$  [131] or bio-generated  $\text{O}_2^{\cdot-}$  [132] could lead to the formation of Birnessite and low-valence manganese oxides.

As both minerals and organic carbon can generate ROS and interact with ROS, the interactions of mineral and organic carbon will further

influence ROS generation and transformation. For example, Fe(II) would cause the generation of reduced dissolved organic carbon, which is crucial for ROS generation. As the reverse route, reducing Fe(III) by dissolved organic carbon can also be responsible for ROS formation. Therefore, the interactions between minerals and organic carbon with ROS are intertwined and reciprocal in the soil environment. Further studies are recommended to evaluate and quantify the time-dependent contribution (e.g., kinetics) and related transformation (e.g., thermodynamics) of both SOC and minerals in bilateral directions.

### 2.2.3. Microorganisms-induced electron transfer between organic carbon and minerals

Mineral redox transformation involving microorganisms is widely reported, with organic carbon usually serving as the carbon or electron source of microorganisms (Fig. 2). For iron minerals, the transitions between Fe(II) and Fe(III) can be triggered by the microorganisms with alternating reducing and oxidizing conditions, which is altered by shifts of electron donors (e.g., reduced organic carbon) and acceptors (e.g., O<sub>2</sub>) [133–137]. Under anaerobic conditions, Fe(III) (hydro)oxides can be reduced by dissimilatory Fe-reducing bacteria [138–140], while Fe(II) can be oxidized by the Fe-oxidizing bacteria [141,142]. Similarly, the redox transformation of Mn can be controlled by the microorganisms for either Mn(II) oxidation [132,143,144] or Mn(IV) reduction [144–147]. Certain organic matter types, such as pyrogenic carbon, might inhibit the reductive transformation and crystallization of minerals during the microorganism-induced transformation process [148].

As SOC typically serves as the electron donor, the bio-reductive transformation of minerals is the critical redox reaction, with the induced transformation by the reduced metal ions [e.g., Fe(II) or Mn(III)] also being crucial. *Geobacter* can reduce lepidocrocite and ferrihydrite with magnetite formation together with SOC [133,149], also causing the oxidation and mineralization of organic carbon (e.g., sucrose to acetate and inorganic carbon [136]). The reductive formation of Fe(II) with microorganisms would catalyze subsequent mineral transformation [140,150] (e.g., ferrihydrite to goethite, lepidocrocite, siderite, or mackinawite), with a variable formation preference compared to the non-biological transformation [140]. In addition, Mn(IV)-reducing bacteria respire Mn(IV) using various organic compounds as electron donors, leading to the reductive dissolution of MnO<sub>2</sub>, but this process is restricted by the co-existing electron-accepting moieties [18]. This reductive transformation/dissolution with microorganisms (e.g., *Shewanella oneidensis* MR-1) and organic carbon (e.g., lactate) might generate MnOOH through inherent redox reactions, and/or further form manganese(II) phosphate and carbonate by the re-precipitation [151]. Reconstruction of microbial community structures might occur during the biogeochemical redox processes, e.g., the *Clostridium*-like, *Geobacter*-like, and *Dehalococcoides*-like organisms were enriched during the Fe(III) reduction, SO<sub>4</sub><sup>2-</sup> reduction, and organic carbon dichlorination [152].

Reactive oxygen species, e.g., O<sub>2</sub><sup>•-</sup> and HO<sup>•</sup>, generated by the microbial community-mediated redox transformations of minerals [83,153,154], affect the carbon cycling. Both bacteria [155] and fungi [154] are essential microorganisms for producing ROS with soil minerals. For instance, the dominant bacterial community in the rhizosphere [156] and detritusphere [157], including *Proteobacteria* clades, *Bacteroidetes*, *Actinobacteria*, and *Firmicutes*, determined the O<sub>2</sub><sup>•-</sup> production [155]. Similarly, *Geobacter*, *Paucimonas*, *Rhodocyclaceae\_K82*, and *Desulfotomaculum* strongly affect HO<sup>•</sup> production, with the latter two species being important in soils with rich minerals [158]. For fungi, Ascomycota fungus (*Trichoderma guizhouense*) and Ascomycete filamentous fungus (*Stilbella aciculosa*) are proven to induce the formation of O<sub>2</sub><sup>•-</sup> and H<sub>2</sub>O<sub>2</sub> with Fe and/or Mn minerals [154,159]. These ROS will affect organic carbon degradation, as discussed in the previous section.

It is worth noting that the current studies about biological mineral transformation mainly involve easily degradable organic carbon, such as aliphatic carbon with low molecular weights (e.g., glucose, sucrose, and lactic acid), while typical SOC contains large amounts of aromatic carbon

with high molecular weights. These organic carbons, including both humic substances and (dissolved) biochar, often show a high electron shuttle nature to accelerate the electron transfer with microorganisms based on the latest research findings [160–166]. However, its potential as both an electron shuttle and direct electron donor for the microorganisms is seldom evaluated [160,167], and more investigation about its transformation afterward is needed.

### 2.3. Mineral dissolution caused by chelation and/or reduction of organic carbon

Mineral dissolution is an essential geochemistry process that is crucial for the fate and relevant transformation/functionality of organic carbon and minerals (Fig. 3) [168–173]. Chelation and sorption of organic carbon, especially LMWOAs, is vital in mineral dissolution [168,174–177]. The dissolution of minerals begins with the adsorption/approaching of organic acids on their surface, followed by the protonation of hydroxyl groups on the mineral surface and the formation of organic coordination complexes on the inner surface. This inevitably leads to the continuous weakening (destabilization) of the metal–oxygen bonds, thus promoting the dissolution of the minerals [169,170,172,178–180]. Using hematite and oxalate as an example, the proton transfer from HC<sub>2</sub>O<sub>4</sub> to the surface –OH of hematite via a proton-coupled electron transfer is found as the first step of the dissolution process, enhancing the acidity of the hematite surface. Meanwhile, the strength of Fe–O bonds on the hematite surface would decrease to the same level as that of Fe(III)-H<sub>2</sub>O cluster formed between homogeneous Fe(III) and H<sub>2</sub>O [178]. Afterward, these weakened Fe–O bonds on the hematite surface can be broken with the resultant iron dissolution as Fe(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O) clusters. Similar results are observed during the dissolution of phyllosilicates, as oxalic acid can be readily complexed with silicon and aluminum ions to achieve feldspar dissolution [180].

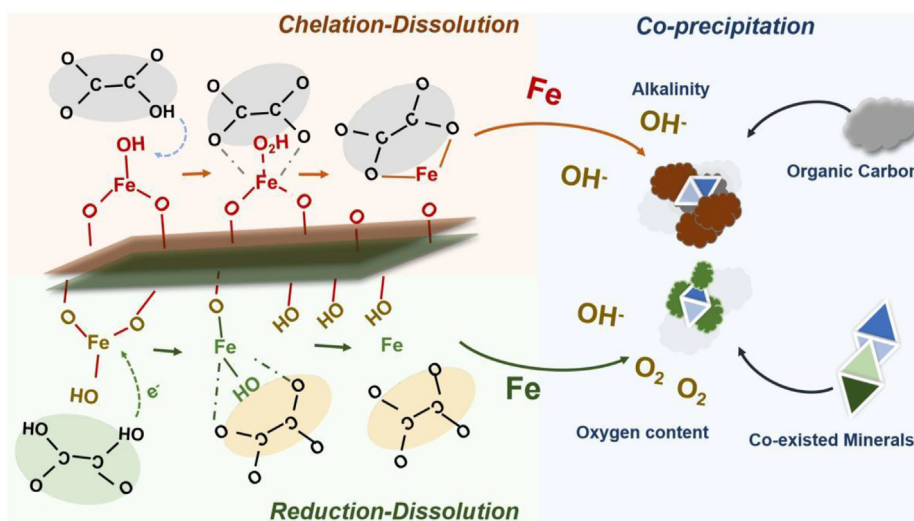
In addition to the sorption-chelation process, the reductive dissolution of minerals might happen with organic carbon. According to the redox processes mentioned above, organic carbon can reduce the minerals directly or through the photo/biological reduction processes, forming highly soluble Fe(II) or Mn(II) [63,67–69,173,181–186].

Beyond the release of metal ions, the dissolution process might also trigger the mineral transformation with these released metal ions, with potential processes including catalyzed recrystallization [176], transformation through repetitive dissolution-precipitation [181], co-precipitation with other ions [183], or illitization [187], further impacting the fate and properties of both minerals and organic carbon.

### 2.4. Co-precipitation of mineral ions and organic carbon

Co-precipitation is essential for the association between organic carbon and soil minerals, similar to the sorption process. In natural environments, co-precipitation of organic carbon with minerals often happens alongside the dissolution and redox reactions due to the varying pH and/or redox conditions (Fig. 3) [188]. For example, in paddy soil, dissolved Fe(II), formed by reduction under flooding conditions, can be quickly oxidized to relatively insoluble Fe(III) precipitates with the co-precipitation of high-concentration organic carbon [188,189].

Compared to the sorption process, co-precipitation forms a mixture of pure oxyhydroxides, organic carbon-rich oxyhydroxides, and precipitated mineral–organic complexes, playing a much more critical role in the carbon and mineral element cycling [188,190–194]. Co-precipitation of organic carbon and minerals is not only a non-specific physical encapsulation of organic carbon but may also cause a bi-directional set of reactions that lead to spatial separation and transformation of mineral and carbon phases [195,196]. Mineral properties would be significantly altered during the co-precipitation process, such as smaller particle size, lower structural order with rich defects, and more functionality, and thus, its reactivity significantly changes [189,193,197–201].



**Fig. 3.** Dissolution of minerals with organic carbon through chelation or reduction; subsequent co-precipitation of soluble metal ions with organic carbon and other minerals (using Fe minerals as an example). Fe on the solid Fe minerals can be extracted by either chelation or reduction process, and the formed Fe ions will be co-precipitated with organic carbon when meeting alkalinity or oxidants.

A high concentration of organic carbon triggers co-precipitation, forming the organic carbon-mineral complexes with homogeneous distribution instead of surface carbon distribution through sorption under lower concentrations [194,202]. The properties and composition of organic carbon would also affect the co-precipitation process. The monodentate carboxyl ligand did not favor the co-precipitation process compared to the polydentate carboxyl ligand [203], thus resulting in the selective accumulation of different organic carbons with the minerals. Similarly, selective retention of lipids and polysaccharide components was observed in the co-precipitates, while proteins were mainly combined with the minerals through the sorption process [204]. The preference for organic carbon (sorption vs co-precipitation) could be the key to the selective accumulation process, and the organic carbon with multiple chelation sites is likely to facilitate the co-precipitation process by bridging multi-mineral particles.

As the dissolution-precipitation and redox reactions of minerals are the premise of the co-precipitation with organic carbon, Fe has been widely investigated (Fig. 3), which can be dissolved under acid or reductive conditions and re-precipitated with oxidants and alkalinity [188,191–195, 197–201,203–207]. The co-precipitation processes form organic carbon-rich ferrihydrite and inhibit its further transformation into crystal iron minerals [193,197–201]. For organic carbon, the co-precipitation with iron minerals will alter its biogeochemical cycling, offering higher stability against leaching, runoff, and biodegradation [194,202,205,207, 208]. Mn minerals can also be co-precipitated with organic carbon during the oxidative precipitation of Mn(II) [18,20], although fewer studies have been reported. Metals such as Ca and Al can be precipitated with alkalinity and involve organic carbon to form co-precipitates, while only several studies reported the formation of Ca-organic carbon [209,210] or Al-organic carbon coprecipitates [48,211], as they assumably often remain in the soluble form in the environment.

Minerals with a low coordination impact with organic carbon and solubility, such as Si minerals, can still be involved in the co-precipitation process of organic carbon and other minerals (e.g., Fe) [211]. During the co-precipitation of organic carbon, Fe, Al, and Si, the formed precipitates are dominated by Si with low organic carbon content, and only 20% Fe will be bound with organic carbon [211]. However, with high organic carbon content, Fe is exclusively linked to organic carbon by monomeric Fe–O–C bonds, while Si and Al form oligomers occluded in the Fe-organic carbon network. The presence of Si in the inorganic structures may change the amount and speciation of organic carbon stabilized by the metallic oligomers.

## 2.5. Polymerization of organic carbon with minerals

Polymerization reactions of organic carbon, aided by minerals, can stabilize due to the increased size/complexity and the higher energy threshold against degradation [18,25,212]. Mn(IV)-oxides, as a strong and efficient oxidant, can accelerate oxidative polymerization of poly-phenols with the combination of semi-quinone radicals, which is referred to as the “browning” process that has been acknowledged as the potential pathway for the abiotic formation of humic substances [20,25,63, 212–214]. In addition, Fe minerals in either soluble ions or solid forms can catalyze the Maillard or oxidative reaction for geo-polymerizing small organic molecules into larger ones [26,215]. Compared to the Fe/Mn minerals, other minerals typically have a lower impact on the oxidative polymerization of organic carbon due to the relatively low oxidation capacity [213]. More studies under field soil conditions are needed to explore and quantify the impact of soil minerals on the polymerization of organic carbons, especially on other polymerization reactions of organic carbon during the interactions with non-redox-active minerals.

## 2.6. Catalytic transformation of organic carbon mediated by minerals

The minerals can act as a catalyst to enhance reaction rates without modifying the overall standard Gibbs energy change in the reaction due to multiple factors [11]. First, minerals can increase the concentration of both organic carbon and oxidants to levels several times higher than those in the bulk solution, thus increasing the reaction rates [40,216, 217]. The degree of orientational freedom of the organic carbon decreases after association with two-dimensional planar mineral surfaces [11,218]. Moreover, minerals can offer empty electron orbitals for the reception of bonding electron pairs of organic carbons (Lewis acid) or serve as the proton donor/acceptor (Bronsted acid/base) to catalyze the reactions of organic carbon [219,220]. Finally, transition metals-based mineral oxides (e.g., iron oxide) or doped minerals (e.g., phyllosilicates with Fe doping) can contribute to catalytic functionality through cycled valence transformation and electron transfer [40,56,59,217,221–223].

Therefore, based on the catalytic mechanisms, various minerals with high organic carbon sorption capacity, extensive binding with organic carbon, and redox-active metals with rich electrons or empty electron orbitals can catalyze the organic carbon transformation [11,220,221, 224], including the above-mentioned redox-related transformation, polymerization, and molecule cleavage of organic carbon [11,25,

224–226]. It is also worth highlighting the potential difficulties in analyzing the mechanisms during the catalysis process of minerals on the organic carbon. As the catalysis reaction is generally accompanied by sorption, bonding, and redox reactions, it is hard to identify the contribution of minerals as the reactants or catalysts during the interactions with organic carbon. A conceptual understanding of these functions and the contributions of soil minerals to organic carbon transformation will be required in the future. Notably, soil enzymes, microbial activity, and soil chemistry play vital roles during the catalytic degradation of organic carbon [227,228]. Only limited studies revealed the roles of soil minerals during this process. Minerals may inhibit the enzyme's catalytic activity through the sorption process [229], and future research is highly needed to reveal this complicated catalytic route.

Accordingly, soil minerals would have complex interactions with organic carbon, changing both minerals and carbon phases. The reactions can be sole sorption, redox, dissolution, complexation, polymerization, catalytic, or a combined process. The primary reactions can be altered due to the variation of mineral properties during the long-term interactions in the field, bringing extra complexity to assessing the potential transformation. These complicated interaction processes will affect the SOC's stability, which will be further discussed in the following sections (Fig. 4).

### 3. Change of organic carbon stability during interactions with minerals

#### 3.1. Protection of SOC by mineral association

Mineral–organic carbon association is widely recognized to stabilize the organic carbon against degradation in the soil environment [22–25, 230–239]. The sorption of organic carbon by minerals is the most crucial pathway for forming mineral–organic carbon association with higher

stability. It is evidenced that various SOC, including dissolved biochar as well as humic and fulvic acids, can be sorbed by minerals with higher chemical-resistance or biological-resistance stability [234,240–243]. The potential sorption mechanisms include complexation, ligand exchange, electrostatic interaction, and/or cation bridging, as stated before [17,23, 234,241,244]. Mineral–organic carbon association can be formed by the co-precipitation process customarily accompanied by entrapping organic carbon in the minerals with secondary mineral formation [18,48,101, 196,208,245–247]. It is worth noting that the participation of microorganisms can be crucial for forming mineral–organic carbon associations, especially in the areas of high density of microbial community (e.g., rhizosphere and biomass-stimulated microbial hotspots), resulting in a higher transformation ratio of organic carbon [248].

The primary stabilization mechanisms of mineral–organic carbon association can be physical protection against microorganisms and/or oxidants [22,23,231,232,235,249] and the increase of activation energy barrier during abiotic/biotic degradation [24,25,233,234]. The protection efficacy is highly related to the combination strength of organic carbon and minerals. Organic carbon associated with weaker bonding (e.g., single sorption onto crystalline minerals) is more susceptible to microbial degradation than the intense or ternary combination with amorphous minerals [23,250]. The richness of carboxyl on the organic carbon is also crucial for its stability within the mineral–organic carbon association due to its strong affinity with minerals [196]. Mineral properties, such as the types and contents of clay minerals and Fe (hydro) oxides, will significantly change the stability of the associated organic carbon. For example, 2:1 type montmorillonite with a high Fe content is more effective in carbon fixation than the 1:1 type clay mineral due to the rich combination sites [251]. In short, the binding strength and the site density are the keys to the stability of the mineral–organic carbon association. It is worth noting that the mineral–organic carbon association not only stabilizes organic carbon but is also believed to inhibit mineral

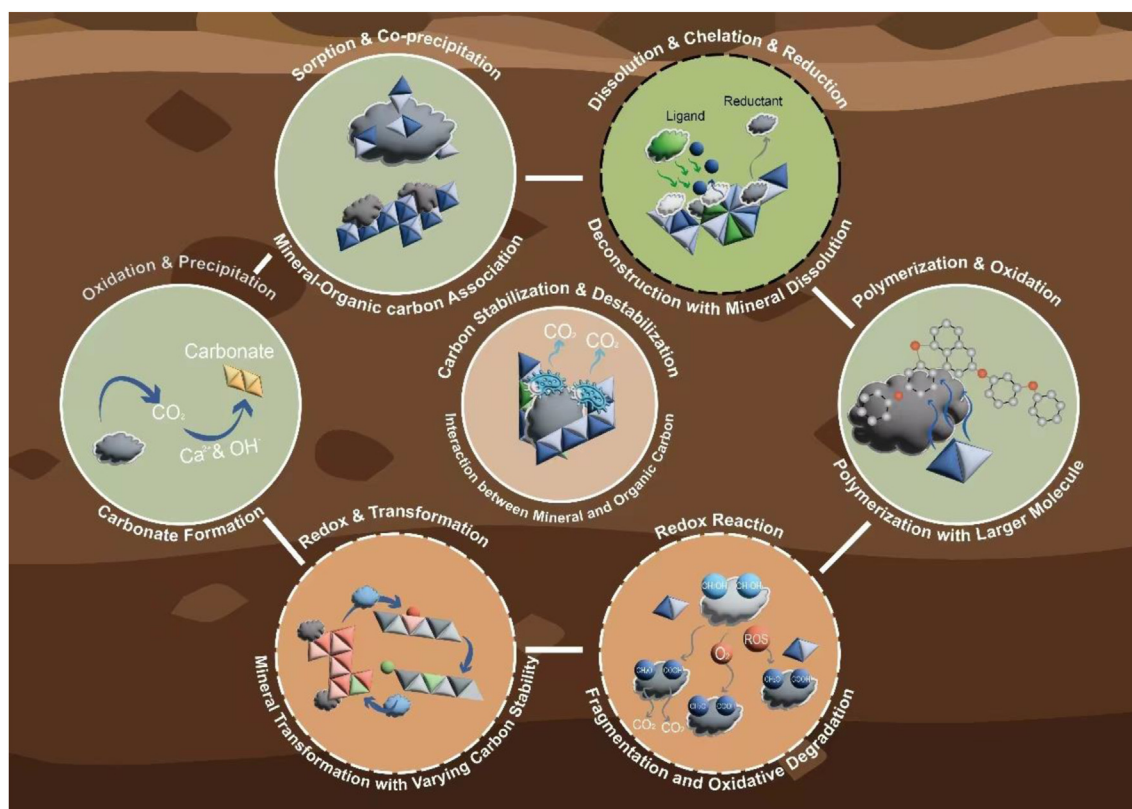


Fig. 4. Conceptual diagram illustrating the stabilizing and destabilizing interactions between minerals and organic carbon in the soil environment.

crystallization and transformation, leading to a higher overall stability [23,148,250].

### 3.2. Mobilization of organic carbon with dissolution of mineral–organic carbon complexes

While the formed mineral–organic carbon association stabilizes carbon, the dissolution of minerals by organic carbon might lead to its destruction, thus causing the mobilization of organic carbon. Organic ligands, such as oxalic acid released from plant roots, can serve as the chelating moiety to dissolve the short-ranged minerals [186,252]. This process will result in the transformation of mineral-associated organic carbon to accessible organic carbon, potentially causing a priming impact with soil microorganisms [17,252,253]. In addition to organic ligands, other root exudates can destabilize the mineral–organic carbon associated with the support of microorganisms [253,254]. Reductive dissolution of Fe or Mn minerals by organic carbon, with or without microorganisms, has been reported, which will cause the release of associated organic carbon [255].

### 3.3. Stabilization of organic carbon via polymerization process

Polymerization could stabilize the organic carbon by increasing its size and complexity, thereby raising the energy threshold in microbial respiration [212,256,257]. For example, Birnessite could enhance the binding and polymerization of small organic carbon (e.g., phenolic monomers) with the formation of large molecules [18,20,214,258]. Iron (hydro)oxides have also been reported to promote the transformation of small molecules to bigger organic molecules, generally accompanied by sorption and co-precipitation, leading to further enhancement of carbon stability [215].

### 3.4. Carbon stability enhancement by the formation of inorganic carbonate

Carbonate is crucial to achieve carbon sequestration, as the inorganic carbonate usually shows higher stability against microbial degradation [259,260]. As it is at the highest state of carbon with a +4 valence state, it cannot be further oxidized and thus exists as a stable form. Although numerous carbon sequestration studies with inorganic carbonate and minerals are conducted for the atmospheric CO<sub>2</sub> precipitation [260–264], relatively few studies reported the potential formation of carbonate, especially with Ca, during the organic carbon oxidation by O<sub>2</sub> or microorganisms [265,266]. For example, the formation of MnCO<sub>3</sub> during the oxidation of organic carbon with Birnessite can be a potential route for carbon preservation [90]. However, the mechanistic understanding of carbonate formation via organic carbon oxidation, particularly the conditions under which the organic carbon can be fully oxidized to CO<sub>2</sub> with the formation of stable carbonate, is not well understood. More studies are needed to unveil the underlying mechanisms for the carbon cycling between organic and inorganic species as well as its stability concerns.

### 3.5. Degradation of organic carbon by direct/indirect oxidation with minerals

Based on the redox processes between organic carbon and soil minerals, organic carbon has a higher possibility of being degraded into organic molecules with smaller size (fragmentation) and richer O functionality [19,45,63–66,75–81,267,268], and these organic carbons usually have lower stability in the soil. Mn(IV) oxide and Fe(III) oxide are widely reported to be dominant for SOC degradation with the oxidative generation of CO<sub>2</sub> and/or labile organic carbon through direct or catalytic redox reaction [18–21,88,238,269–272]. Active mineral-mediated processes promote organic carbon mineralization through redox reactions over its protection in the soil environment [76,273]. For instance,

according to the Swedish forest soil inventory data (n = 2,378), the concentration of exchangeable Mn was negatively associated with the organic carbon content in soil due to the oxidative decomposition of recalcitrant organic carbon by Mn-peroxidases, which overshadowed the protection and production impact [272].

Other interactions between minerals and organic carbon are also crucial for the degradation of organic carbon by minerals. First, sorption, co-precipitation, and/or chelation could alter the possibility of interactions between organic carbon and minerals [198,206]. The dissolution of Fe(II) or Mn(III)/Mn(II) with organic carbon could catalyze the generation of ROS with a higher degradation potential for organic carbon [21,78,269].

Notably, the formed CO<sub>2</sub> might be dissolved and precipitated with metal ions, causing carbonate precipitation with higher stability [90]. The carbonate formation might, to some extent, turn the destabilization of organic carbon into a stabilization process during oxidative degradation. Moreover, organic carbon with higher O content might have a higher potential for forming the mineral–organic carbon association, alleviating the impact of destabilization. It can be concluded that the oxidation and/or degradation degree is crucial for the final stabilization/destabilization impact of organic carbon, which needs quantitative investigation based on the properties and interactions between organic carbon and minerals under varying field-relevant conditions.

### 3.6. Stabilization or destabilization of organic carbon with mineral transformation

Mineral properties change during the mineral transformation process with the organic carbon, affecting the binding affinity and stability of organic carbon [27–29,274]. These changes include surface area [41, 275,276], surface functionality, mineral crystallinity [27,42,277–279], redox state [280–282], and the solubility of minerals [255,283], all regulating its interaction mechanisms with the organic carbon [92,284], causing the stabilization or destabilization process.

Several key mineral transformations with organic carbon in soil will significantly affect these properties. For example, the Fe crystallization process with the organic carbon-generated Fe(II) leads to the transformation of amorphous and short-range-ordered Fe minerals to the crystalline goethite or hematite, which usually shows a lower surface area and thus a lower sorption capacity of organic carbon [42,208,276, 285], resulting in the desorption with afterward oxidation process. Sorption preference will also change during the crystallization [42,286]. Low-crystallinity phases prefer more aromatic and lignin-like components, while higher-crystallinity phases are mainly associated with aliphatic DOM [42], further affecting the organic carbon stabilization with minerals. Moreover, low-crystallinity Fe minerals usually cause a higher and faster mineralization impact of organic carbon due to the higher generation of Fe(II) than the high-crystallinity Fe minerals [282, 287]. Furthermore, some studies suggest that although the mineral crystallization process causes the release of organic carbon, the non-desorbed phase of organic carbon (mainly associated with the co-precipitation process) would become more stable due to the enhanced binding between organic carbon and minerals [288].

In contrast to the mineral crystallization with generated Fe(II), several interactions between minerals and organic carbon will inhibit further crystallization and growth of minerals, leading to a higher fixation impact with organic carbon. Interaction or association with organic carbon might facilitate the formation of short-range-ordered minerals and thus higher organic carbon stabilization [27,278,279,289]. For instance, the presence of pyrogenic carbon inhibited the biotransformation of ferrihydrite to the crystal goethite and magnetite, thus maintaining a higher sorption capacity [148]. A loose and porous structure could be found in the mineral growth with the organic carbon due to the inhibited crystallization process, resulting in potent carbon sequestration potential [289].



The redox-related transformation of soil minerals with organic carbon [20,63,66,67,69,208] will greatly affect its interactions with organic carbon. For instance,  $\text{MnO}_2$ ,  $\text{MnOOH}$ , and  $\text{Mn}_3\text{O}_4$ , formed by the redox-related transformation of Mn oxides, have different fractionation and sorption preferences on the organic carbon [290]. In addition, the reductive transformation of iron minerals by organic carbon and microorganisms might drive the release and mobilization of iron and organic carbon, especially under thaw conditions, thus destroying the organic carbon–mineral sink [255]. However, current studies provide limited information about the minerals' stabilization or destabilization impact after redox-related transformation. Most of the studies focused on the change of organic carbon during the redox interactions with minerals, while the resulting minerals can also have a distinct carbon fixation impact and warrant more consideration in future studies.

Therefore, the existence of soil minerals might either protect or destabilize the organic carbon based on the properties and the interaction processes (Fig. 4). The combination of organic carbon and minerals through sorption, complexation, and/or co-precipitation often increases the stability of organic carbon. Moreover, generating stable carbonate or polymerized carbon can enhance carbon sequestration. However, the redox reactions between organic carbon and minerals usually lead to the oxidative transformation of organic carbon as a destabilization process. Furthermore, the transformation of minerals during the interactions with organic carbon would alter its properties and indirectly impact the organic carbon stabilization/destabilization.

#### 4. Case study about organic carbon–minerals interactions in eco-environment

In addition to the lab-scale experiments and related mechanistic findings (Fig. 4), the interactions between organic carbon and minerals, widely observed in the real eco-environment, have recognized their impacts on carbon stability. Nine site studies worldwide are introduced in this section as evidence and illustration of the significant impact of carbon–mineral interactions on carbon stability. Either stabilization or destabilization impact of the organic carbon has been revealed in these field studies due to distinctive interactions between minerals and organic carbon.

##### 4.1. Organic carbon–iron mineral association in Siberian permafrost

According to the study by Martens et al. [291], at the Siberian permafrost, approximately 33%–74% of the organic carbon is associated with small-sized mineral particles. The high content of reactive iron minerals [i.e., poorly crystalline Fe (oxyhydr)oxides] mainly stabilizes the organic carbon through sorption by forming the mineral–organic carbon association, especially during cold and dry climates. In warmer and wetter conditions, the organic carbon can be destabilized with the decomposition of mineral-associated organic carbon due to the decrease of Fe (oxyhydr)oxides and redox-related interactions [273,291], which can be evidenced by 30% higher  $\text{CO}_2$  production. It is also found that more organic carbon is stabilized through the co-precipitation with iron minerals instead of sorption under varying oxic conditions (wetter) than dryer climates, potentially related to the redox-related dissolution process of organic carbon and Fe minerals.

##### 4.2. Organic carbon–iron mineral association in thaw gradient at Stordalen mire

The reductive dissolution of iron minerals and the related mobilization of carbon is found in the thaw gradient at Stordalen mire [255]. Organic carbon is primarily bound to reactive Fe minerals in the studied sites, accounting for 9.9%–14.8% of total SOC. However, reductive transformation and mobilization of Fe(III) in the deeper layers by organic carbon and Fe-reducing bacteria first occur with waterlogging, and these Fe(II) will be re-oxidized by  $\text{O}_2$  close to the surface with the formation of

Fe(III) precipitates. This redox-related dissolution/precipitation will cause the mobilization of associated carbon. As confirmed by the site studies, 9.9%–39.4% of organic carbon bound to the reactive Fe will be released during the reductive dissolution of iron minerals, and its contribution to the carbon loss is significantly higher than organic carbon degradation.

##### 4.3. Organic carbon–clay–iron oxides in Eastern Usambara Mountains of Northeast Tanzania

Soil samples collected from nine sites with different clay and iron oxide content are selected to evaluate the interaction among clay minerals, iron oxides, and organic carbon, as well as the organic carbon stability in the Eastern Usambara Mountains [292]. Mineral-associated organic carbon accounts for up to 81% of the bulk organic carbon in the soil environment, and the larger amount of mineral-associated organic carbon persists in soil due to the soil weathering with decreasing aluminous clay (kaolinite, gibbsite) to Fe oxide (goethite, hematite) ratio. Iron oxides act as the binding sites to combine negative clay minerals and organic carbon, forming mineral-associated organic carbon with high stability against chemical or biological degradation. Over 36% of organic carbon associated with the soil minerals can be preserved even after a strong chemical oxidation process, evidencing its high stability and protection efficacy on the soil minerals.

##### 4.4. Organic carbon–iron mineral association with redox cycling in Arctic tundra soil

In tundra soil, the organic horizons are enriched with poorly crystalline and crystalline iron oxides due to the upward translocation of Fe from anoxic mineral horizons resulting from the redox cycling of Fe(II)/Fe(III) together with dissolution and precipitation [293,294]. These newly formed ferrihydrites and other iron minerals, often present as coatings on the mineral grains with the organic carbon, generate 63% of the mineral-associated carbon. Association with iron minerals can inhibit organic carbon degradation by binding the low-molecular-weight organic carbon, stabilizing the soil aggregates, and forming thick protective coatings.

##### 4.5. Organic carbon–clay minerals from permafrost-affected soils in the Spitsbergen

According to the soil collected from the central part of Spitsbergen (Svalbard, High Arctic) [295], it is found that 10%–15% organic carbon can be intercalated in swelling clay minerals through the sorption process. The entrapping of organic carbon within the interlayers of swelling clay minerals is facilitated by the acidic nature of this soil, and this entrapped organic carbon shows a higher stability against chemical and thermal oxidation in the soil, leading to lower mineralization during the thawing process.

##### 4.6. Change of mineral–organic carbon association in the Kohala region of northern Hawaii

A significant loss of Fe is found in the soil collected from the Kohala region, where high rainfall leads to the reductive dissolution of Fe minerals, causing the destabilization of the Fe–organic carbon association [296]. The released organic carbon will combine with Al minerals to form a new mineral–organic carbon association, also found in the soil with a similar saturation situation [297]. The transition of organic carbon occurs during this reductive transformation of Fe, and lower carboxylic carbon with higher alkyl/O-alkyl carbon exists in the newly formed organic carbon.

These interactions and transformations of organic carbon and minerals significantly affect carbon stability, and the carbon mineralization ratio can be over two times higher after frequent saturation [297]. According to

the study conducted in the Kohala region, older carbon in the Fe-organic carbon will be destabilized during the Fe depletion process, rendering previously stabilized carbon available again for rapid degradation and irreversibly causing the loss of the organic carbon, including long-chain fatty acids [298]. It is worth noting that Si, Al, and Ti are found to be combined with organic carbon during the destruction of Fe-organic carbon association with the formation of a new mineral–organic carbon pool.

#### 4.7. Decomposition of organic carbon with manganese in temperate rainforests

Based on the soil carbon and Mn dataset from a podzolization gradient, an inverse power relationship between carbon and manganese content across temperate rainforests is observed [299], potentially related to the decomposition impact caused by Mn-peroxidase enzymes. The soil carbon content decreased from ~120 T/ha to 40 T/ha with the increase of exchangeable Mn content to 100 kg/ha. Similar results are reported by another Mn fertilization study in northeastern China (45°20'N, 127°34'E) [300], where Mn concentrations are positively correlated with decomposition rates of the lignin-contained substrate, playing the dominant role in the forest system [301]. The decomposition effect of Mn varies with the composition of organic carbon, and the lignin-rich substrate is preferred to be decomposed by Mn-peroxidase, leading to the generation of minor and slowly decomposing fractions with different stability for degradation.

#### 4.8. Organic carbon preservation by minerals in Dinghushan Biosphere Reserve in South China

Based on the regression analysis of the relationships between the soil's physical and chemical properties and organic carbon from the acid soils in southern China, organic carbon stabilization is strongly influenced by soil clay fraction through sorption and/or by chemical protection through forming organo–mineral complexes [302]. Moreover, a linear relationship between SOC and Fe/Al oxides indicates the importance of these minerals during the formation of mineral-organic carbon association in this acidic soil. The authors also propose that these acidic soils have a large capacity to accumulate more soil carbon through sorption with soil Fe or Al oxides, as the maximum association capacity has not been achieved. Dosing more organic carbon into these soils combined with a systematic land management process can be a potential choice.

#### 4.9. Organic carbon stability with mineral protection across Tibetan alpine permafrost region

Protecting organic carbon by clay minerals, Ca, and Al/Fe-(hydro) oxides exhibit the most substantial and direct impact on improving the stability across the Tibetan alpine permafrost region [15,303]. Two main interaction processes between organic carbon and minerals determine the stabilization process by restricting substrate accessibility or inhibiting microbial activities [304]. One is bridging polyvalent cations (e.g., Ca) and SOC, especially in alkaline and calcareous soils on the Tibetan Plateau with highly calcareous parent materials. This process is usually accompanied by clay minerals to form a stable mineral-organic association, which is vital in regulating SOC dynamics [304]. The other fundamental process is the association between Fe-/Al-hydroxides and organic carbon, which could contribute to nearly 15% of the total organic carbon pool in the Tibetan Plateau [305]. Microorganisms-derived carbon sources and warmer temperatures may be potential reasons for the massive formation of mineral-organic carbon association in the studied area [15,304]. These studies also indicate the determining role of mineral protection on organic carbon decomposition, which explains over 34.8% of soil carbon preservation, especially during climate change with increasing temperature and heavy precipitation [304,306].

Regardless of the soil conditions, all the site studies confirmed the importance of soil minerals on organic carbon cycling. The

mineral–organic carbon association was the primary stabilization process for the organic carbon in the soil, and the dissolution and deconstruction of minerals will lead to the destabilization of the soil carbon. While the degradation impact of minerals through redox-related reactions seems less crucial in most soil environments, the potential oxidation impact of Mn-minerals was reported in some specific soils with high Mn contents. The potential contribution of other mineral-organic carbon interactions (e.g., polymerization and catalytic reaction) and its stabilization/destabilization impact require further investigation in the natural environment. Moreover, evidence for the mineral transformation and its impact on carbon turnover is still insufficient based on the field studies in real eco-environments.

## 5. Future perspectives

### 5.1. Structure–property–activity relationship for the interactions between organic carbon and minerals

Based on the proposed reaction mechanisms, the interaction route between the organic carbon and minerals is highly variable and mainly depends on the structure and characteristics of both minerals and organic carbon. Different interaction routes can lead to contrasting fate of soil carbon. Current studies mainly evaluate this impact by selecting specific natural organic carbon or minerals without a well-designed control on the properties, speciation, and composition. The currently available results are essential for explaining the interaction mechanisms under specific conditions in the soil environment, but they might be less instrumental in evaluating and predicting the potential interactions and long-term stability in a broad spectrum of soils. The impact of SOC composition, abundance of surface functionality, aromaticity, molecular weight distribution, and so on, on the interactions with soil minerals merits a more profound understanding based on the molecular and nano-sized scale design. Furthermore, the speciation, particle size, crystallinity, and surface properties of the soil minerals will concurrently and significantly affect the interactions with SOC, which needs further exploration in mechanistic studies.

### 5.2. Variation of organic carbon–mineral interactions and carbon stability with time

Many studies evaluated the interaction mechanisms between organic carbon and minerals in the soil environment, but most have only focused on one single snapshot rather than the entire timeline of the interaction process. These studies often span several months or years under relatively stable conditions, which may not always be guaranteed in the natural environment. The interactions between fresh organic carbon and minerals at the initial stage will change their properties, leading to a different interaction route in later stages. Different alternations of the properties and compositions of SOC and minerals might occur in the second stage, causing distinctive interaction processes afterward. In other words, the primary interactions are variable with dynamic equilibrium, which is related to the changes in the environmental situations (e.g., variation of temperature or precipitation). The full-view findings across different stages can help to explain the past (formation route), the present (current content and existing forms), and the future (predicted transformation and long-term stability) of organic carbon and minerals.

### 5.3. Spatiotemporal variability of the interactions between organic carbon and minerals

Many studies have investigated the interactions between organic carbon and minerals under specified conditions based on the studied soil, while its variation is widely overlooked. In addition to the compositions and properties of the organic carbon and minerals, other variability related to the site locations and weather conditions, e.g., soil pH, temperature, water content, co-existing moieties, and redox conditions, can

also significantly affect the interaction processes. Linking the cross-linking properties of soils with the potential interactions between organic carbon and minerals can be a fundamental direction for more accurately evaluating soil carbon storage.

#### 5.4. Increasing soil carbon storage by manipulating its interactions with soil minerals

In addition to the existing literature about the analysis of interactions between organic carbon and minerals in the soil environment, manipulating the interaction and transformation processes to improve the soil carbon storage can serve as a promising direction from engineering and practical perspectives. Based on the machine learning prediction, current mineral-organic carbon stocks only correspond to less than 42% of the mineralogical carbon storage capacity ( $4,596 \pm 453$  Pg C in a depth of 1 m) [13]. Although maximum mineral-organic carbon storage may be unattainable due to climate limitations and other restrictions, active control and engineered changes of the mineral contents and compositions can be a potential and large-scale approach to enhance long-term carbon sequestration. In addition, changing the soil properties (e.g., redox conditions, microbial compositions, and soil acidity) can be another direction to control the interaction processes, which can be accomplished by the designed land uses and soil utilization practices, e.g., tillage, cultivation, fertilization, irrigation, and drainage processes. An in-depth understanding of the interaction mechanisms over a relatively long period and dynamic conditions is necessary to guide the manipulation processes.

#### 5.5. Impacts of mineral-organic carbon interactions on the soil carbon amendment

Organic carbon application, such as manure, straw, biochar, and solid waste, has been widely studied for soil quality improvement, pollutant remediation, carbon storage, and soil fertility enhancement [307–312]. However, the long-term impact of the added organic carbon on the interactions with soil minerals is widely overlooked, especially for the carbon storage process. To increase the soil carbon pool, the exogenous carbon input will inevitably increase the total carbon storage at the initial stage; however, the long-term processes impose a possible uncertainty of negative impacts due to mineral transformations, especially when considering the change of microbial abundance and community with fresh biomass carbon input [17,313,314]. Potential desirable or undesirable alternations of the carbon stability require prudent attention and verification, especially when other applications are the primary targets with carbon amendments (e.g., pollutants immobilization and nutrient enrichment). Using biochar or other carbon-rich materials for soil remediation often claims a potential concomitant advantage for carbon sequestration, but its reliability also needs further confirmation with the consideration of mineral interactions and transformation processes.

## 6. Summary

The interactions between SOC and minerals, including sorption, redox reaction, co-precipitation, dissolution, polymerization, and catalytic reaction, are critical for maintaining the long-term carbon stability of organic carbon in the environment. The following processes can be involved in the carbon stabilization/destabilization: (1) formation or deconstruction of the mineral-organic carbon association; (2) oxidative transformation of the organic carbon with minerals; (3) catalytic polymerization or carbonate formation of organic carbon with minerals; and (4) varying association stability of organic carbon during the mineral transformation. Future research is highly needed to reveal the structure-property-activity relationship, spatiotemporal variability, and soil carbon management based on the interactions between SOC and different minerals, which can deepen our understanding of the mineral-organic carbon interactions and their implications on the soil carbon storage, in pursuit of the global goal of achieving carbon neutrality.

## Author contributions

Z.B.X.: conceptualization, investigation, writing; D.C.W.T.: conceptualization, supervision, resources, project administration, funding acquisition, writing.

## Declaration of competing interests

The authors declare no conflicts of interest.

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