Reviews and syntheses: Iron: A driver of nitrogen bioavailability in soils?

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Abstract. An adequate supply of bioavailable nitrogen (N) is critical to soil microbial communities and plants. Over the last decades, research efforts have rarely considered the importance of reactive iron (Fe) minerals in the processes that produce or consume bioavailable N in soils, compared to other factors such as soil texture, pH, and organic matter (OM). However, Fe is involved in both enzymatic and non-enzymatic reactions that influence the N cycle. More broadly, reactive Fe minerals restrict soil organic matter (SOM) cycling through sorption processes, but also promote SOM decomposition and denitrification in anoxic conditions. By synthesizing available research, we show that Fe plays diverse roles in N bioavailability. Fe affects N bioavailability directly by acting as a sorbent, catalyst, and electron transfer agent, or indirectly by promoting certain soil features, such as aggregate formation and stability, which affect N turnover processes. These roles can lead to different outcomes on N bioavailability, depending on environmental conditions such as soil redox shifts during wet-dry cycles. We provide examples of Fe-N interactions and discuss the possible underlying mechanisms, which can be abiotic or microbially meditated. We also discuss how Fe participates in three complex phenomena that influence N bioavailability: priming, the Birch effect, and freeze-thaw cycle. Furthermore, we highlight how Fe-N bioavailability interactions are influenced by global change and identify methodological constraints that hinder the development of mechanistic understanding of Fe in controlling N bioavailability and highlight the areas of needed research.

1 Introduction

Nitrogen (N) bioavailability is a critical limiting factor for terrestrial ecosystem productivity (Vitousek and Howarth, 1991). The largest pool of N in these ecosystems is found in soils which contain 133–140 Pg of total N globally within the first top 100 cm of soil (Batjes, 1996). A clear description of the factors controlling N bioavailability in soils is needed to design agricultural practices that meet crop demand and mitigate N loss to the environment. A large literature exists on the effects of soil texture, organic matter (OM), mineral N inputs, pH, moisture, and microbial communities on N mineralization. However, emerging theories on soil organic matter (SOM) dynamics are increasingly emphasizing the role of soil mineralogy (Cotrufo et al., 2013; Lehmann and Kleber, 2015; Blankinship et al., 2018; Daly et al., 2021; Whalen et al., 2022). While these reviews have largely focused on carbon (C) cycling, the role of minerals is rarely considered in N cycling (Jilling et al., 2018). Since C and N cycles are interconnected in soils (Gärdenäs et al., 2011; Feng et al., 2019), they should be regulated by the same factors, including mineralogy type (Wade et al., 2018). Increasing evidence shows that Fe specifically represents a major control over N biological transformations, including mineralization (Wade et al., 2018), nitrification (Huang, X. et al., 2016; Han et al., 2018) and denitrification (Wang et al., 2016; Zhu et al., 2014), as well as their abiotic analogous reactions, such as chemo-denitrification (Burger and Venterea, 2011) and Fe-mediated hydroxylamine (NH_2OH) oxidation to nitrous oxide (N_2O) (Bremner et al., 1980). These reactions and others Fig.1, are likely to operate ubiquitously in soils, due to the close proximity between Fe minerals and SOM since most of the latter is contained in association with the former (Wagai and Mayer, 2007; Lalonde et al., 2012).

The characteristic properties of individual Fe minerals and N compounds and how these properties are influenced by the soil environment likely drive the aforementioned reactions as well. First, Fe exists in a variety of polymorphs (Navrotsky et al., 2008) and is a redox-sensitive element that cycles between Fe(II) and Fe(III) states as controlled by soil Eh and pH. While Fe(III) promotes N stabilization within mineral associations, Fe(III) mobilization when it is reduced to Fe(II) can release N into solution. Fe reactivity is also driven by the amount and sign of surface charge, surface topography, particle size, crystallinity (Petridis et al., 2014; Li et al., 2015a) and the presence and the type of organic matter (OM) coverage (Kaiser and Zech, 2000a; Kleber et al., 2007; Boland et al., 2014; Henneberry et al., 2016; Daugherty et al., 2017; Gao et al., 2018; Poggenburg et al., 2018). Second, soil N exists predominantly in organic forms (ON); mostly as protein and peptides, and to a lesser extent as amino-sugars and nucleic acids (Schulten and Schnitzer, 1997; Kögel-Knabner, 2006; Knicker, 2011). Proteins are intrinsically reactive towards soil minerals, due to a number of properties, including hydrophobicity, surface charge distribution, surface area, number and type of functional groups, conformation, and size (Lützow et al., 2006). N from these compounds is generally not directly bioavailable due to molecular size constraints on microbial cell uptake (Schimel and Bennett, 2004). Depolymerization reactions, carried out by the activity of extracellular enzymes, such as peptidases, transform these polymers into soluble, low molecular weight (MW) organic monomers (e.g., short oligopeptides, amino acids (AAs)). Recent research shows that the size of AAs available for mineralization is controlled by peptidase activity, but more so by

protein availability, both of which are affected by the interactions with Fe minerals. Therefore, Fe may drive gross AA

65 production in soils (Noll et al., 2019).
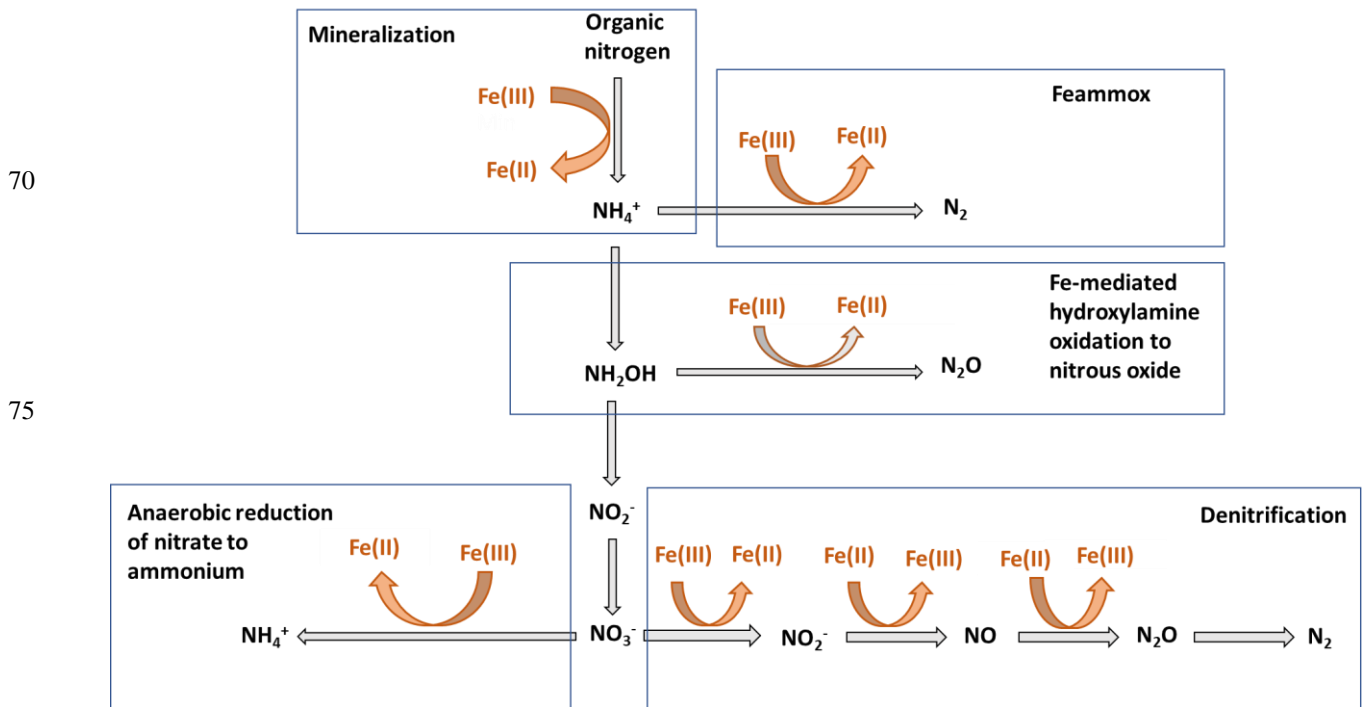
Figure 1: Schematic representation depicting the different stages of the N cycle in which iron plays a role. Adapted from (Zhu-Barker et al. 2016).

80 Therefore, the impact of Fe on N cycling can be significant and should be considered. This review aims to understand the role of Fe in controlling N bioavailability. To do so, we categorize the processes by which Fe affects OM dynamics into four different categories/roles (Fig.2). In the **sorbent role**, OM interacts with Fe(III) through adsorption, coprecipitation or surface coatings (Eusterhues et al., 2005; Wagai and Mayer, 2007; Lalonde et al., 2012). These associations increase OM storage by decreasing its availability to extracellular enzymes and decomposition processes (Lalonde et al., 2012). In fact, the content of

85 Fe minerals is a major predictor of soil sorptive capacity (Mayes et al., 2012). In the **structural role**, Fe minerals participate in the formation of soil aggregates (Zhang, X. et al., 2016) and increase soil structural stability (Barral et al., 1998; Xue et al., 2019). Aggregates can increase OM stability and retention in soils by protecting it from the decomposer community and their enzymes (Van Veen and Kuikman, 1990; Kleber et al., 2021). Moreover, Fe(III) can facilitate the formation of large polymers of OM that promote its stability. Thirdly, Fe's **electron transfer role** depends on its oxidation state. Fe(III) serves as a sink of

90 electrons, while Fe(II) functions as a source of electrons. During anoxic periods, dissimilatory Fe(III) reduction can be coupled with the oxidation of OM, which accounts for significant amount of C loss under anoxic conditions (Roden and Wetzel, 1996; Dubinsky et al., 2010). This process can release previously adsorbed or coprecipitated C, thereby increasing its susceptibility

to degradation. Finally, Fe has a **catalysis role**, whereby Fe acts as a catalyst for the production of reactive oxygen species (ROS), which are potent oxidants of OM. This happens through Fenton reactions that are prevalent in various soils such as cultivated soils (Hall and Silver, 2013; Chen et al., 2020), arctic soils (Trusiak et al., 2018) and desert soils (Hall et al., 2012; Georgiou et al., 2015). These reactions are an overlooked but potentially important pathway for OM transformation in soils and sediments and N bioavailability (Lipson et al., 2010; Wang et al., 2017; Trusiak et al., 2018; Merino et al., 2020; Kleber et al., 2021).

While these roles of Fe in controlling C cycling have been studied extensively, their effects on N bioavailability are not well explored. This review seeks to underpin these suggested relationships and provide mechanistic descriptions of how Fe controls N bioavailability in soils. Moreover, we detail how Fe participates in three complex phenomena that influence N bioavailability: priming, the Birch effect, and freeze-thaw cycle. And finally, we explore how Fe-N bioavailability interactions are influenced by global change. This information is needed to construct reliable models with improved predictive power of N cycling in terrestrial ecosystems (Wade et al., 2018), and will offer new possibilities for land management.
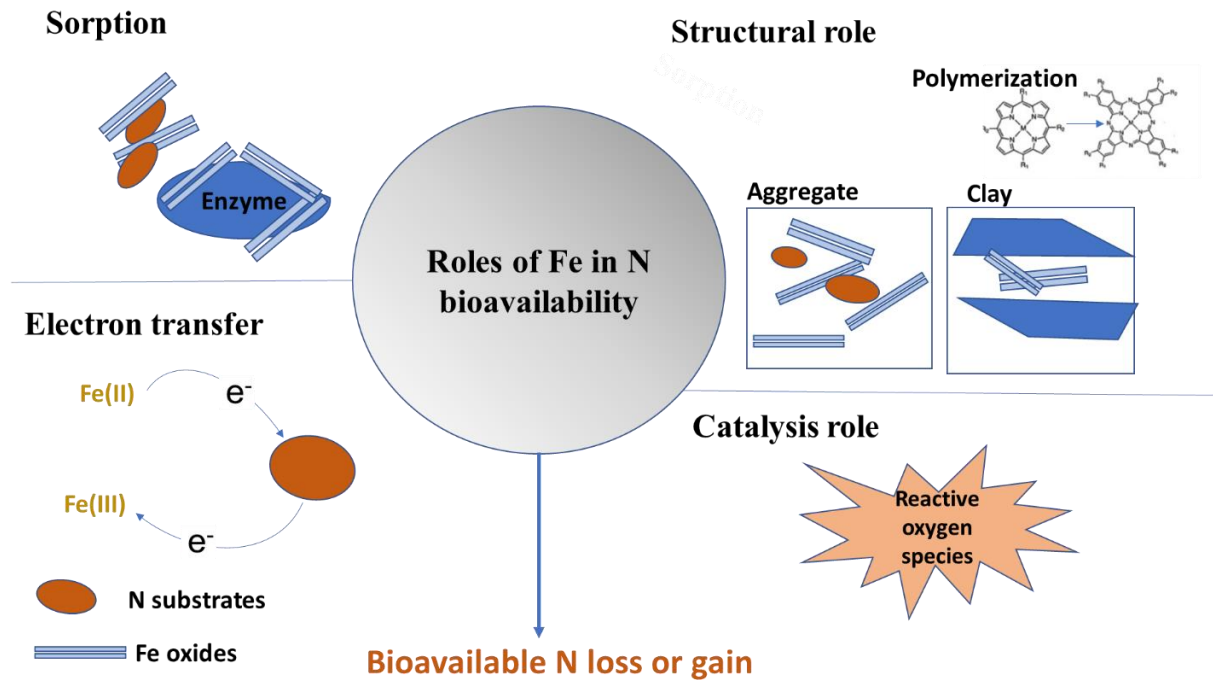
Figure 2: Roles of Fe in N bioavailability.

2 Roles of Fe in controlling N bioavailability

2.1 Sorbent role

125   This section aims to elucidate how Fe as a sorbent interacts with both inorganic N (ammonium: NH_4^+ and nitrate: NO_3^-) and ON and how these interactions modulate N bioavailability. The opposite process of sorption, known as desorption, can affect N bioavailability since sorbed N can be released back into soil solution. By comprehending the dynamics of both sorption onto and desorption of N from Fe minerals, we can gain more insights into mechanisms affecting its bioavailability in soils.

2.1.1 ON bioavailability

130   Soil microbes rely heavily on their ability to access ON and the effectiveness of their extracellular enzymes (EE) in breaking it down into assimilable forms. In fact, increased N-acquiring enzyme activities correlate positively with N mineralization. Fe minerals can modulate N bioavailability by controlling both ON accessibility and EE activity through sorption. Nevertheless, the outcomes on N bioavailability are variable and depend on several factors, including soil conditions, the interplay between ON, EE, and Fe mineral surfaces, and the potential for desorption to occur. Here, we discuss these intricate interactions which

135   can result in distinct patterns of N bioavailability across soils.

2.1.1.1 Does extracellular enzymes sorption to Fe oxides affect their participation in N mineralization?

   Soil microbes produce various types of EE, including substrate-specific enzymes (e.g., proteases and aminopeptidases) and non-specific oxidative enzymes (e.g., laccase and peroxidase) to acquire N (Caldwell, 2005; Sinsabaugh et al., 2009; Hassan et al., 2013). While the latter enzymes are typically associated with C cycle, their importance for N mineralization has also

140   been demonstrated (Zhu et al., 2014; Kieloaho et al., 2016). Many of these enzymes become adsorbed to Fe minerals when released in soil. The effect of such immobilization on enzyme activities and consequent N bioavailability remains uncertain due to conflicting reports in the literature. Numerous studies have documented a decrease in enzyme activity combined with increased persistence in soil and resistance to proteolysis (Sarkar and Burns, 1984; Gianfreda et al., 1995; Bayan and Eivazi, 1999; Rani et al., 2000; Tietjen and Wetzel, 2003; Kelleher et al., 2004; Yan et al., 2010; Schimel et al., 2017; Li et al., 2020),

145   while others have reported opposing effects (Quiquampoix and Ratcliffe, 1992; Quiquampoix et al., 1995; Servagent-Noinville et al., 2000). For instance, Fe adsorption reduced the activity of urease (Gianfreda et al., 1995; Bayan and Eivazi, 1999; Li et al., 2020), but increased the activity of N acetyl-glucosaminidase (NAG) (Allison, 2006; Olagoke et al., 2020). These contradicting effects can have multiple explanations. First, enzyme active sites can become occluded upon adsorption, which limits the diffusion of ON towards the binding sites and lower ON decomposition. Site occlusion can be caused by

150   conformational changes in the enzyme structure (Datta et al., 2017), Fe-induced aggregation (Olagoke et al., 2020) or unfavourable attachment orientation on mineral surfaces (Baron et al., 1999; Yang et al., 2019). Second, Fe oxides can inhibit the activity of EE by constraining ON availability. Along a 120-kyr-old chronosequence, Turner et al., (2014) found that Fe oxides inhibited the activities of urease and proteases more strongly than aminopeptidases, possibly due to the preferential adsorption of urea and proteins over peptides (Turner et al., 2014). Third, enzyme activity may be influenced by soil mineral

155   content, as observed by (Olagoke et al., 2020). In mineral-poor soils, enzymes may have higher and more persistent activity due to limited adsorption sites, potentially leading to improved microbial C and N use efficiencies by allowing microbes to

invest in biomass production instead of enzyme production. Finally, a new mechanism was proposed by Chacon et al., (2019) where Fe minerals, specifically goethite, can induce abiotic protein fragmentation with subsequent loss of activity (Chacon et al., 2019), but further investigation is needed to determine its occurrence in soil and its implications for enzyme activity and N bioavailability. Beyond sorption, reduced metals, which are prevalent in waterlogged soil, have been found to exert an inhibitory or stimulating effects on enzyme activity. Specifically, $Fe(II)$ stimulated the activity of oxidative enzymes (Van Bodegom et al., 2005; Sinsabaugh, 2010), but strongly inhibited that of urease (Gotoh and Patrick Jr, 1974; Tabatabai, 1977; Pulford and Tabatabai, 1988; Gu et al., 2019). Amidase activity, on the other hand, appeared to be unaffected by waterlogging (Pulford and Tabatabai, 1988). In the light of the current state of knowledge, there is a need for more research to comprehend how the intricate relationships between Fe minerals and enzymes regulate N bioavailability in soils.

2.1.1.2 Does the sorption of ON to Fe oxides affect their bioavailability?

Many studies have demonstrated that poorly crystalline Fe minerals, such as ferrihydrite, control the sorption of ON in soils (Kaiser and Zech, 2000b; Dümig et al., 2012; Keiluweit et al., 2012; Dippold et al., 2014). Indeed, Fe minerals interact with a wide range of N-containing moieties via adsorption or coprecipitation processes; the latter process incorporates N into organo-mineral associations (MAOM), which are essential for OM stabilization (Leinweber and Schulten, 2000; Keiluweit et al., 2012; Swenson et al., 2015; Heckman et al., 2018; Zhao et al., 2020). During these processes, Fe can form strong chemical bonds with N-containing moieties; for instance, goethite forms stronger bond with the SOM functional group ammonia (NH_3^+) than with carboxylate, phosphate, or methyl groups (Newcomb et al., 2017). The bond strength between N and mineral surfaces varies considerably across different environments due to differences in binding mechanisms, mineral and N properties, soil properties such as pH and ion strength, and the presence of antecedent SOM on mineral surfaces (Lützow et al., 2006). However, protein may adsorb irreversibly to mineral surfaces over a wide range of solution pH and resist desorption (Hlady and Buijs, 1996; Yu et al., 2013); desorption is perceived to be a necessary step for EE to proceed with N mineralization. Similarly, nucleic acid molecules persist for a long time on clay minerals (Yu et al., 2013) and are shielded from degradation. Advances in spectroscopic techniques have generated new conceptual models of organo-mineral associations, such as "the zonal structure model of organo-mineral associations", which postulates that organic compounds self-organize on mineral particle surfaces (Kleber et al., 2007). In this model, amphiphilic SOM compounds with N-bearing and oxidized functional groups directly interact with mineral surfaces to form "the contact zone", whereas hydrophobic groups face outwards creating a region of high hydrophobicity, "the hydrophobic zone". Additional organic molecules attach to this zone, forming an outer layer termed "the kinetic zone". Multiple recent observations support this model, including (1) the preferential enrichment of N-containing moieties on Fe mineral surfaces (Kopittke et al., 2018; Possinger et al., 2020), (2) the preferential adsorption of N compounds over other organic compound classes on Fe mineral surfaces (Gao et al., 2017) and (3) the partial sorption of some organic compounds, including AAs, to Fe minerals (Amelung et al., 2002; Dippold et al., 2014). This model has implications for N bioavailability, because, in contrast to the contact zone, the weakly sorbed N in the kinetic zone likely exchanges with soil solution and is more available. Recent research on the chemical composition of C and N at the organo-

190 organic and organo-mineral interfaces of the model found that alkyl C and less N occurred at the former, whereas oxidized C and more N occurred at the latter (Possinger et al., 2020). The authors of this study hypothesized that the processes stabilizing C and N at these interfaces are different, considering that the association between SOM rich in O/N-alkyl C and Fe oxides explained the stabilization of O/N-alkyl C in soils (Schöning et al., 2005). In addition to protecting a fraction of bioavailable N, Vogel et al., (2014, 2015) found that sorption can retard the movement of N in soils, thereby increasing N retention by

195 decreasing its accessibility to degradation mechanisms. More insight is needed to advance the understanding of ON bioavailability from organo-mineral associations.

2.1.1.3 Desorption of ON from Fe minerals

The desorption of ON from Fe-organic associations occurs due to several destabilization mechanisms, including surface displacement by competitive sorption, oxidative and reductive dissolution of Fe minerals (Kleber et al., 2015) and local

200 disequilibrium in soil chemistry. Once released, ON may become accessible to microbial degradation or diffuse into microbial cells. The following is a discussion of the different destabilization mechanisms of Fe-organic associations in soils and factors influencing them:

(a) ON desorption by oxidation and reductive dissolution of Fe minerals

The oxidation and the reduction of Fe minerals, in response to variations in soil pH and redox conditions, can significantly

205 compromise the stability of Fe-organo associations and release Fe and OM into soil solution as a consequence. In fact, Fe reduction can decrease mineral sorption capacity and releases Fe ions, which can lower soil pH, and promote the solubilization of Fe-mineral associations. However, the extent of OM mobilized remains unpredictable due to knowledge gaps related to mineral resistance mechanisms to reduction and their controlling factors in soils. For instance, short-range order (SRO) Fe oxides can resist both chemical and microbial reduction, due to coprecipitation of Fe with SRO aluminosilicates or physical

210 protection within microaggregates (Henneberry et al., 2012; Shimizu et al., 2013; Eusterhues et al., 2014; Filimonova et al., 2016; Suda and Makino, 2016; Coward et al., 2018; Tamrat et al., 2019). Conversely, Fe oxidation can also solubilize Fe-organo associations by decreasing pH or generating hydroxyl radicals through Fenton chemistry, which oxidize OM abiotically. In addition to these effects, redox alterations to mineral properties can also affect OM cycling. For instance, the transformation of amorphous Fe minerals to more crystalline forms can promote long-term OM stabilization and decrease its

215 turnover rates (Hall et al., 2018), since crystalline forms are more resistant to reduction. Chen et al (2020) also found that crystalline forms were not associated with C release from Fe associations (Chen et al., 2020).

(b) N desorption by local disequilibrium in soil chemistry

OM in soils can be desorbed from mineral surfaces due to the establishment of local disequilibrium conditions. Such conditions result from depletion of DOM in the soil solution, due to microbial uptake, for example, promote the release of OM from

220 MAOM until DOM concentrations in the soil solution are in equilibrium with sorbed OM. This process is likely affected by the strength of bonds between N and Fe minerals; in fact, interaction forces vary considerably: strong interactions are favored by polyvalent cation bridges and ligand exchange whereas weak interactions occur by hydrogen bonds or van der Waals

(Kleber et al., 2015). While the relationship between particular binding mechanism and N desorption from minerals has not yet been established in real soil conditions, multiple studies in model systems demonstrated that OM bound by ligand exchange was more resistant to desorption than other mechanisms (Wang and Lee, 1993; Gu et al., 1994; Gu et al., 1995; Mikutta et al., 2007). Therefore, it will be likely less affected by the dynamic equilibria principle and less N will be made available (Kleber et al., 2015).

(c) N desorption by surface displacement via competitive sorption

ON associated with Fe can be displaced by the input of highly sorptive organic compounds. For instance, Scott and Rothstein (2014) observed that weakly bound, N-rich hydrophilic compounds were easily displaced by stronger binding compounds (e.g. hydrophobic compounds), leading to the downward migration of N to subsurface and mineral horizons.

(d) Is desorption of N from organo-mineral associations a prerequisite to N mineralization?

As mentioned earlier, desorption of protein from mineral surfaces is often perceived to be the primary pathway by which ON becomes accessible to microbial degradation (Schimel and Bennett, 2004). However, protein adsorption to Fe minerals is an irreversible process (Rabe et al., 2011), which restricts proteolytic activity. Recently, the direct proteolysis of protein at the mineral surface was investigated, as ferrihydrite- and goethite-adsorbed protein was found to be degraded without prior desorption (Tian et al., 2020). Substrate-enzyme complexes were formed directly at the surface of minerals. Together with the zonal structure of organo-mineral associations, this finding challenges the long-standing assumption that Fe minerals impair protein bioavailability through acting as a sorbent. The reader is referred to Keiluweit and Kuyper (2020) for a more expanded discussion of this mechanism (Keiluweit and Kuyper, 2020).

2.1.2 Inorganic N bioavailability

Fe plays a crucial role in regulating inorganic N bioavailability in soils, with Fe present in clay minerals being a prominent example of this interconnection. In fact, Fe present in clays accounts for 30-50% of total Fe in soils and sediments and can be located in both the octahedral and tetrahedral sheets of 1:1 and 2:1 clay mineral or exist as coating on their surfaces (Favre et al., 2006; Stucki, 2013). On one hand, the reduction of this Fe has been demonstrated to enable the abiotic fixation of NH_4^+ (Zhang and Scherer, 2000; Deroo et al., 2021). This occurs through increasing negative charge and cation exchange capacity of clays (Pentráková et al., 2013). In addition, the reductive dissolution of coated Fe on clay minerals promotes NH_4^+ diffusion into or out of clay interlayers (Zhang and Scherer, 2000). After de-fixation, the fixed NH_4^+ pool can serve as a source of bioavailable N (Deroo et al., 2021). On the other hand, the oxidation of clay's Fe(II) can be involved in the processes that cause the loss of bioavailable N. For instance, Zhao et al., (2013) found that the oxidation of Fe(II) present in nontronite causes the loss of NO_3^- as dinitrogen (N_2) (Zhao et al., 2013). The potential importance of such processes in N bioavailability should be considered, especially in highly weathered soils with high clay content.

2.2 Structural role of Fe in controlling N bioavailability

This section explores the structural role of Fe in regulating the availability of N. Two aspects are examined; the influence of structural Fe in aggregates on N bioavailability and the polymerization of ON induced by Fe.

2.2.1 Fe, soil aggregates and N bioavailability

Fe oxides play a critical role in the formation and the stability of microaggregate in soils, which ultimately affect N bioavailability. These oxides serve as nuclei for microaggregate formation and a binding agent forming bridges between them (Barral et al., 1998; Pronk et al., 2012; Peng et al., 2015; Wei et al., 2016). In fact, it was shown that the partial or complete removal of mineral-forming components, for example due to Fe reduction, can initiate aggregate turnover and destabilization (Michalet, 1993; Cornell and Schwertmann, 2003). The relative importance of Fe in aggregate stability depends on several properties, such as Fe mineral and SOM content, mineral identity and degree of crystallinity, and soil redox conditions, which are expected to affect N bioavailability. In particular, Fe promotes the formation and stability of aggregates in soils with low OM and high Fe content (Barral et al., 1998; Wu et al., 2016). Duiker et al., (2003) showed that poorly crystalline Fe minerals are more important than crystalline minerals for aggregate stabilization (Duiker et al., 2003).

Many studies suggest that Fe mediated micro-aggregation may slow down or suppress N mineralization and stabilize OM. For example, Silva et al., (2015) reported that applying Fe-rich biosolids in a tropical soil chronosequence induced rapid formation of microaggregates and significantly increased SOC (Silva et al., 2015). Similarly, Bugeja and Castellano (2018) observed positive correlation between ammonium oxalate-extractable Fe (AmOx-F) and C and N in microaggregates, indicating that Fe and microaggregate stabilization are interconnected (Bugeja and Castellano, 2018). Mendes et al (1999) showed that readily mineralizable N levels correlate positively with increased aggregate size in soils (Mendes et al., 1999). In addition, numerous studies reported the accumulation of N in microaggregates (Golchin et al., 1994; Rodionov et al., 2001). For instance, Wagai et al., (2020) observed joint accumulation of OM with low C:N ratio and pedogenic Fe and Al oxides in the meso-density fractions (1.8–2.4 $\mathrm{g\,cm^{-3}}$) of five soil orders collected from different climate zones. These observations are explained by the fact that microaggregate-N is relatively more persistent than macroaggregate-N because microaggregates' turnover is relatively slow and not available to microbial degradation, which provides longer-term stabilization of OM (Cambardella and Elliott, 1993; Six et al., 2002). We also hypothesize that there is another pathway by which Fe-promoted aggregation may decrease N mineralization, based on the information that aggregates of different sizes influence microbial community composition differently and therefore the activities of N mineralization enzymes (Muruganandam et al., 2009). Therefore, it will be useful to examine the distribution and the activities of these enzymes among soil aggregate size classes along a gradient of increasing Fe mineral content in soils.

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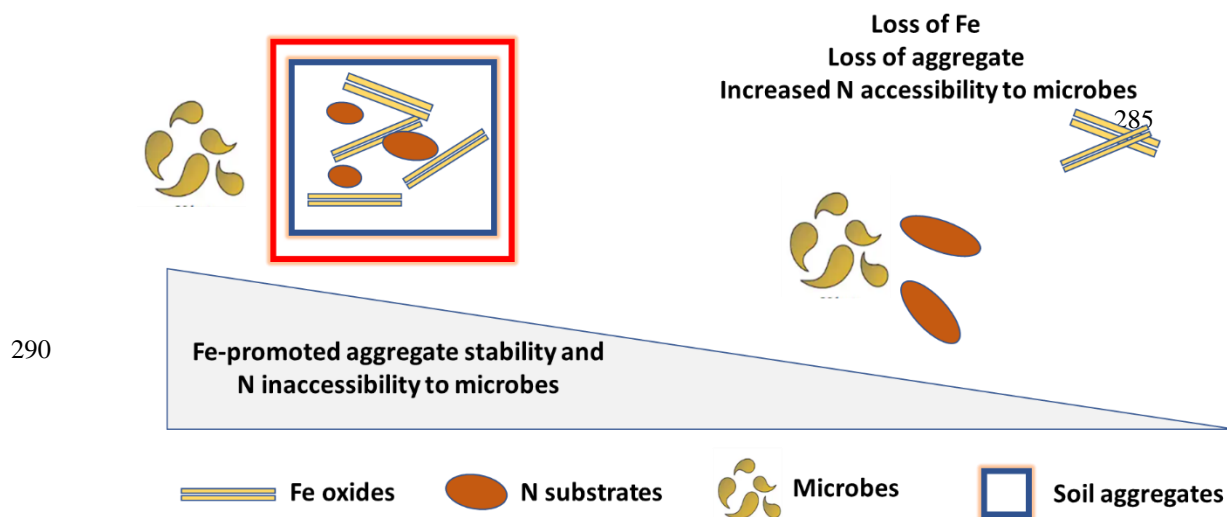

295 **Figure 3. Schematic representation of the effects of Fe-promoted aggregate formation and stability on N accessibility to microbial degradation.**

2.2.2 Does Fe-induced ON polymerization increase the recalcitrance of N?

Little is known about Fe (mineral)-induced OM polymerization in soils. Some evidence exist that Fe oxides induce both C and N polymerization of SOM (Piccolo et al., 2011; Li, C. et al., 2012; Johnson et al., 2015; Zou et al., 2020) . In a long-term organic fertilization experiment, Yu et al., (2020) proposed that the Fe-catalyzed formation of reactive oxygen species (ROS) allows C monomers to recombine into large, recalcitrant C biopolymers through the formation of intramolecular bonds. A similar process was observed by Piccolo et al., (2011). Similarly, hydrohematite, maghemite, lepidocrocite and hematite can induce the oxidative polymerization of hydroquinone, with rates depending on the type of minerals (Huang, 1990). Synthetic ferrihydrite and goethite were demonstrated to induce peptide bond formation between aspartate chains (Matrajt and Blanot, 2004), as well as the abiotic formation of AAs from simple organics such as pyruvate and glyoxylate (Barge et al., 2019). The environmental conditions in these experiments were similar to those occurring in natural systems such as in Fe-containing sediments (Barge et al., 2019). More studies of abiotic polymerization by minerals must be envisaged to understand its relevance to N bioavailability in soils.

2.3 Catalytic role of Fe in controlling N bioavailability

Emerging research has revealed that ROS derived from Fe-catalyzed Fenton reactions (Box 2) are implicated in N mineralization. These reactions may involve abiotic or coupled biotic-abiotic processes causing N to mineralize, as explained below. In desert soils, the reaction of light with hematite generates ROS, which can oxidize AAs to nitrous oxide (N_2O) (Georgiou et al., 2015) and N oxide gases (Hall et al., 2012). Compared to soil containing water, desert soils accumulate

photogenerated superoxides and peroxidases via complexation of $O_2^{\cdot-}$ with surface transition metal oxides. When these soils

315 are wetted, the accumulated ROS are subjected to dismutation and hydrolysis leading to the generation of $HO^{\cdot}$ and subsequent OM oxidation. While this mechanism is strictly abiotic, soil microorganisms in diverse ecosystems were found to use Fe-generated $HO^{\cdot}$ to acquire organic C and N (Diaz et al., 2013; Shah et al., 2016; Zhang, J. et al., 2016; Op De Beeck et al., 2018). For instance, a boreal forest fungus (*Paxillus involutus*) may use radical oxidation to stimulate N mineralization in various ways (Op De Beeck et al., 2018): (1) to liberate NH_4^+ from amine groups of proteins, peptides, and amino acids

320 according to mechanisms reviewed in Stadtman and Levine (2003), (2) to facilitate the accessibility of protein-N in SOM complexes to proteolytic degradation and (3) to enhance protein vulnerability to proteolysis and increase the activity of proteolytic enzymes (Zhang, J. et al., 2016).

Despite their involvement in N liberation, ROS may promote the formation of stable and protective Fe-associated OM complexes. In a long-term fertilization experiment conducted by Yu et al., (2020), Fe mobilized by Fenton reactions formed

325 new short-range order (SRO) Fe minerals, which promoted C and N storage. Moreover, ROS generated from catalytic reactions involving Fe can also cause enzyme oxidation and subsequent loss of activity (Huang et al., 2013).

Box 1: Fe-catalyzed Fenton reactions

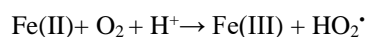
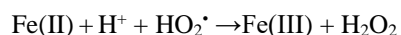
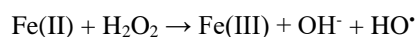
Most Fe minerals, such as ferrihydrite, goethite, hematite, magnetite, and pyrite, can catalyze Fenton-like reactions (Kwan and Voelker, 2003; Garrido-Ramírez et al., 2010). Fe-catalyzed Fenton reactions are mainly driven by fluctuating redox conditions (Xu et al., 2013), oxygenation of Fe^{II}- bearing minerals (Tong et al., 2016) and photochemistry (Georgiou et al., 2015). Despite having a short lifetime in soil (Apel and Hirt, 2004), ROS, such as $HO^{\cdot}$ ($E^o = 2.8$ V), are non-selective and strong oxidants of OM (Gligorovski et al., 2015).

Photoreduction of Fe(III)-ligand (L) complexes : Fe(III)-L + hv -> Fe(II) + L*

Reactions of Fe meditated ROS generation:

$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + HO^{\cdot}$

$Fe(II) + H^+ + HO_2^{\cdot} \rightarrow Fe(III) + H_2O_2$

$Fe(II) + O_2 + H^+ \rightarrow Fe(III) + HO_2^{\cdot}$

2.4 Electron transfer role of Fe in N bioavailability

Electron transfer to Fe(III) oxides, both biotically or abiotically, is a critical step in many processes favoring the gain or the

330 loss of N from soils and sediments (Sahrawat, 2004; Ding et al., 2014). The ability of Fe(III) minerals to accept electrons, or their 'reducibility', varies greatly with crystallinity, particle size, solution pH, ambient Fe(II) concentration, the presence of adsorbates and aggregation level (Roden, 2004, 2006). Here, we explore relationships between mineral reducibility and anaerobic NH_4^+ oxidation associated with Fe reduction (Feammox) and anaerobic OM oxidation to illustrate two examples of N processes that are involved in bioavailable N production and loss. Starting with Feammox, this process occurs mostly in

335 acidic soils and has been estimated to metabolize 7.8−61 kg NH_4^+ /ha/year in paddy soils, accounting for about 3.9 %−31 %

of N fertilizer loss (Ding et al., 2014). The terminal products of this process are either N_2, NO_2^- or NO_3^- with N_2 as the dominant product (Yang et al., 2012). Feammox rates are strongly positively correlated with the concentrations of microbially reducible Fe(III) (Ding et al., 2014; Li et al., 2015b; Ding et al., 2019; Ding et al., 2020). Moreover, Fe(III) enhances the activity, distribution and diversity of microbial communities involved in Feammox (Huang, S. et al., 2016; Ding et al., 2017). A series

340 of incubation studies investigated the effects of different Fe sources on Feammox, and the results demonstrated that only ferrihydrite and goethite, not ferric chloride, lepidocrocite, hematite, or magnetite, served as electron acceptors for Feammox (Huang and Jaffé, 2015, 2018). These observations can be explained by a possible accumulation of free Fe(II), which halted Feammox, or due to the limited ability of Fe-reducers in reducing certain minerals (Huang et al., 2014). It is notable that chelates (Park et al., 2009) and electron shuttles (Zhou et al., 2016) can facilitate electron transfer to Fe(III) minerals (Fig. 3),

345 which enhances their reduction rates and related N processes. For instance, the addition of electron shuttles increased potential N loss by Feammox by 17–340% compared to no addition (Zhou et al., 2016). Similar to Feammox, NH_4^+ production rates in submerged soils and sediments were found to be strongly correlated with reducible Fe(II) production rates (Sahrawat and Narteh, 2001; Sahrawat, 2004).

The electron-donating capacity of Fe minerals is also involved in N bioavailability. In fact, many Fe(II) species, including

350 soluble Fe(II)- and Fe(III)-bearing minerals such as siderite and magnetite, can act as electron donors (Benz et al., 1998; Chaudhuri et al., 2001) for NO_3^- reduction coupled with Fe oxidation, which promotes the loss of NO_3^- as gases. For denitrification, it was found that N_2O emissions from flooded soils with contrasting Fe(II) levels were regulated by Fe(II) electron donating capacity: the electrons donated reached 16.2% and 32.9% in soils with low and high Fe(II) content, respectively. Soil with high Fe(II) content emitted less N_2O and more N_2, suggesting an improved denitrification efficiency

355 due to an electron flow which exceeded the demand for N_2O production (Wang et al., 2016).

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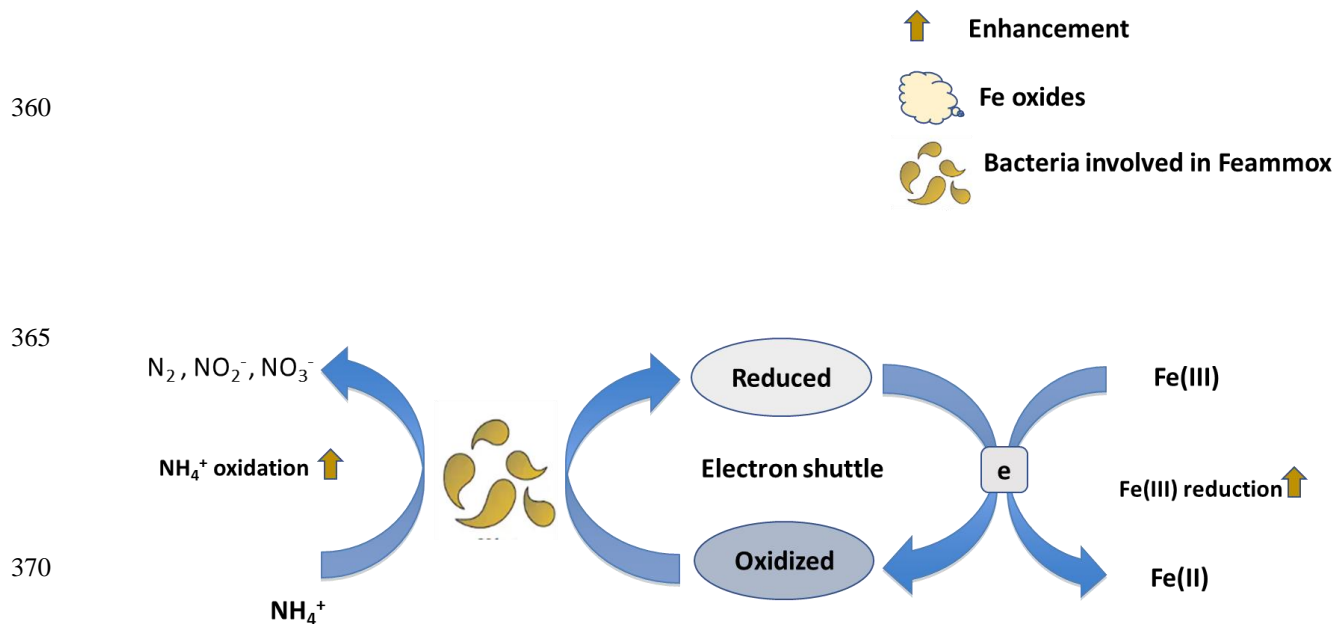
Figure 4. Electron shuttles enhance Fe reduction and NH$_4^+$ oxidation (Feammox) rates.

3 Involvement of Fe in soil phenomena that affect N bioavailability

375   This section is concerned with the role of Fe in the three phenomena that affect N bioavailability in soils: priming, The Birch effect and freeze-thaw cycles. Priming occurs when new input of labile C influences (positive or negative) the decomposition of native SOM (Kuzyakov et al., 2000). The Birch effect is a short-term pulse in C and N mineralization caused by soil drying and rewetting. The freeze-thaw cycles refer to the alternation between freezing and thawing temperatures in a soil which can liberate decomposable OM and accelerate soil respiration. We offer this perspective to facilitate understanding of the
380   mechanisms by which Fe affects N bioavailability through these three phenomena.

3.1 Priming

3.1.1 Fe- mediated priming in soils under oxidizing conditions

Investigations of the patterns and drivers of priming across both local and broad geographical scales indicate that SOM stabilization mechanisms, including associations with Fe oxides, regulate priming and explain most of its variation (Chen et
385   al., 2019; Jeewani et al., 2021). Positive priming, where new inputs increase SOM mineralization, is negatively related to MAOM concentration due to Fe constraining microbial access to sorbed organics to microbial degradation (Bruun et al., 2010; Porras et al., 2018). In the rhizosphere, plant and microbial exudates can disrupt Fe-organic associations by both chemical and biological mechanisms. Chemical mechanisms include stripping Fe from associations through surface complexation,

facilitating Fe reduction (Zinder et al., 1986; Keiluweit et al., 2015; Ding et al., 2021) and displacing sorbed organics into the soil solution (Zinder et al., 1986; Keiluweit et al., 2015; Ding et al., 2021). Biological mechanisms stimulate the production of N-acquiring enzymes as microbes are supplied with carbon and energy (Jilling et al., 2018; Yuan et al., 2018; Jiang et al., 2021; Jilling et al., 2021). Such mechanisms enhance positive priming by increasing the accessibility of C and N to microbes and facilitating N mining. However, the susceptibility of Fe-organic associations to these mechanisms varies; for example, ferrihydrite associations are affected by both chemical and biological processes, while goethite associations are more susceptible to chemical processes (Li, H. et al., 2021). Therefore, the ability of microbes and plant communities to trigger specific destabilization mechanisms of the dominant mineral in their environment affects how much N can be made available from mineral associations (Jilling et al., 2018; Li, H. et al., 2021).

Beyond SOM stabilization, Fe oxides may regulate priming by altering microbial community composition, soil C and N content (Heckman et al., 2009; Heckman et al., 2018); potentially by restricting nutrient availability and changing the structural properties of dissolved organic matter (DOM). For instance, the application of goethite to soil limits P and N bioavailability while increasing the aromatic content of water extractable organic matter (WEOM), which may lower the ratio of fungi to bacteria (Heckman et al., 2012). Fungi have low C use efficiency (CUE) (Silva-Sánchez et al., 2019) and are associated with efficient N cycling (Wardle et al., 2004).

3.1.2 Fe-mediated priming in soils under reducing conditions

Recently, Fe-mediated priming in soils under reducing conditions has received growing interest. Dunham-Cheatham (2020) found that glucose application to a soil under anoxic-oxic transition induced a novel type of priming by facilitating the reductive dissolution of Fe^{III}-C associations under anoxic conditions followed by a dramatic increase of OC mineralization when oxic conditions were restored (Dunham-Cheatham et al., 2020). Li, H. et al., (2021) found that the roles of Fe in anaerobic OM mineralization can be shifted by microbial biomass C (MBC). In soil with low MBC, both ferrihydrite and goethite protected the added acetate from decomposition through sorption processes. In soil with high MBC, however, goethite acted as an electron acceptor and increased acetate decomposition, whereas ferrihydrite predominantly adsorbed the added substrate. Priming decreased in both low and high MBC soils, but more in low MBC soil (Li, H. et al., 2021). Lecomte et al., (2018) demonstrated that Fe(III)-reducing microorganisms have a competitive advantage of colonizing plant roots in the rhizosphere due to their capacity of providing Fe(II) for plant nutrition in exchange for C-rich exudates and performing denitrification (Lecomte et al., 2018). These exudates are probably used as a C source in the denitrification process or to destabilize Fe-organic associations and release sorbed C and N (Dunham-Cheatham et al., 2020). More research into Fe-mediated priming in strictly anoxic soils, or at the oxic-anoxic transition, is needed.

3.2 Birch effect

Although many studies have been done on N mineralization and nitrification (Birch, 1958, 1959, 1960, 1964; Wilson and Baldwin, 2008), the studies on the Birch effect have mainly focused on C. The Birch effect for N was described as a rapid

increase in N mineralization rates as an air-dried soil is rewetted. Soil moisture is accompanied by increased NO_3^- production. This pattern is likely explained by multiple interacting mechanisms, including the dissolution of organo-mineral bonds, which increases the accessibility of substrates to microbial degradation. In addition, the highly dynamic nature of wet dry cycles can trigger rapid electron transfer from and to Fe oxides, known as cryptic Fe cycle, which can affect N bioavailability. During the wet period, Fe(III) oxides can be used as an electron acceptor and be reduced to Fe(II), which can abiotically react with NO_3^- to form NH_4^+, or with nitrite (NO_2^-) to form N_2O. This Fe(II) can be converted back to Fe(III) oxides during the dry period, which may sorb OM and protect it against further degradation or generate oxidative radicals through Fenton reactions that break down organics, including N compounds. Cryptic Fe cycle can also induce rapid redox-induced mineral transformations, such as the transformation of amorphous Fe oxides into more crystalline forms decreases soil sorption capacity and nutrient retention (Attygalla et al., 2016; Wilmoth et al., 2018; Chen et al., 2020). Therefore, this cryptic Fe cycle will have a varied effect on the role of Fe in controlling N bioavailability over short spatiotemporal scales, which may either increase or decrease bioavailable N. Further research is needed to detangle these interactions.

3.3 Fe in the context of freeze-thaw cycles: the case of permafrost-affected soils

Permafrost-affected soils store large amounts of OC and ON as a result of SOM stabilization due to freezing of SOM and cryoturbation. Along a permafrost soil chronosequence, Joss et al., (2022) found a high percentage of FeOM in cryoturbated horizons compared to organic or mineral horizons in soil. Cryoturbation also favors the accumulation of SOM with high C:N ratio at deeper soil depths (Treat et al., 2016a), which also may be present as associations with Fe minerals or in particulate organic matter. Upon thawing, this tremendous amount of SOC and total nitrogen (TN) facilitate high gross N turnover rates by heterotrophic processes. For instance, Treat et al.(2016b) observed increased N availability during long thaw seasons in tundra soils, whereas other authors reported higher N_2O emissions from increased denitrification (Cui et al., 2016; Yang et al., 2016; Yang et al., 2018). This is partly because SOC and SOM, previously trapped in FeOM associations, are released and exposed to microbial degradation (Harden et al., 2012; Gentsch et al., 2015; Mueller et al., 2015; Patzner et al., 2020). In fact, Patzner et al., (2020) found that along a thaw gradient, the amount of dissolved organic carbon (DOC) increased as well as the abundance of Fe(III)-reducing bacteria which use Fe(III) as terminal electron acceptor and oxidize OM. The importance of this mechanism in N destabilization likely depends on the extent to which Fe dissolution contributes to soil OM persistence in redox-dynamic permafrost (Patzner et al., 2020). More investigations of Fe control on N bioavailability in permafrost-affected soils are needed, especially with the recent development pointing out that mineral N cycling is as important as ON cycling in the active layers of these soils (Ramm et al., 2022).

4 Impact of global change on Fe-N bioavailability interactions

450 Anticipated future climate scenarios indicate substantial fluctuations in precipitation and temperature patterns, accompanied by increasing levels of atmospheric CO_2. These changes, along with alterations in land use, have the potential to significantly impact Fe-N bioavailability interactions in various ways, which are detailed below.

4.1 Impact of variability in precipitation and temperature

455 The extreme variation in precipitation can lead to increasing the occurrence of Birch effect and potential disruption of the dynamic of N availability in soils. Fe plays multiple roles in this process; in drier soils, Fe can protect ON from decomposition through the formation of stable Fe-organic associations. However, the reaction of Fe with light can induce Fenton reactions, leading to ON decomposition (Georgiou et al., 2015). In wetter soil, the destabilization of ON can increase as a result of fluctuations in redox conditions, potential occurrence of cryptic Fe cycling and modifications of mineral properties. In addition

460 to precipitation, climate change is causing temperature to rise sharply leading to extensive thawing of permafrost soils. As a consequence, redox-meditated heterotrophic N turnover processes and the destabilization of Fe-organic associations are expected to increase ON loss from these soils. Furthermore, rising temperatures will increase microbial metabolism which will subsequently destabilize SOM.

4.2 Impact of elevated atmospheric CO_2

465 The effects of rising atmospheric CO_2 concentration (eCO_2) levels on Fe-N bioavailability interactions are not well understood. Recent research showed that eCO_2 stimulates root and microbial respiration, which can decrease soil redox potential causing Fe reduction to proceed (Cheng et al., 2010). The production of Fe(II), which increased by 64% under eCO_2 treatment, caused substantial losses of NH_4^+ via Feammox in a 15-year free-air CO_2 enrichment (FACE) study in rice paddy systems. Feammox

470 was meditated by autotrophic anaerobes that may use soil CO_2 as C source to couple anaerobic ammonium oxidation and Fe reduction (Xu, C. et al., 2020). eCO_2 can also increase the destabilization of MAON via priming, as, eCO_2 increases root biomass and associated exudate production at deeper soil depths, enabling the liberation of large amount of deep soil N from these associations (Iversen, 2010). This increased turnover of N from MAOM would probably be substantial under future eCO_2.

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4.3 Impact of land use change

Land use change involving the conversion to agriculture can decrease SON (García-Oliva et al., 2006). We hypothesize that this decline in SON is influenced by the effects of land use change on Fe cycling. For example, it was observed that the crystallinity of Fe oxides increased when forests were converted to agricultural fields in the Southern Piedmont, USA (Li and

480 Richter, 2012). Additionally, Tan et al., (2019) showed that land use change from fallow to paddy soils promoted Fe reduction

by decreasing soil pH and increasing the electron shuttling capacity of SOM (Tan et al., 2019), which may accelerate N turnover by processes such as Feammox.

To conclude, global change affects the roles of Fe in N bioavailability which may in turn affect the balance between Fe-meditated SON destabilization and protection

485 **5 Synthesis and outlook**

Attempts at understanding controls and drivers of N bioavailability, a fundamental soil ecosystem property, often omit the role of Fe minerals. However, the tendency of proteins to associate strongly with minerals, and the involvement of the latter in both enzymatic and non-enzymatic reactions that influence the N cycle has motivated this review, which specifically focuses on Fe-N bioavailability interactions (Fig. 4). Including Fe in current models of SOM is challenging because the mechanisms by

490 which Fe controls N storage, stabilization, bioavailability, and loss are complex and remain incompletely understood. This is because the present knowledge is, on one hand, based on OM-mineral correlations, which is a simplistic approach since correlations tend to be specific for certain soil conditions and types (Wagai et al., 2020; Kleber et al., 2021), and on the other hand, knowledge is impeded by limitations in the analytical framework used to explore these interactions. In this section, we highlight challenges and opportunities for future research.

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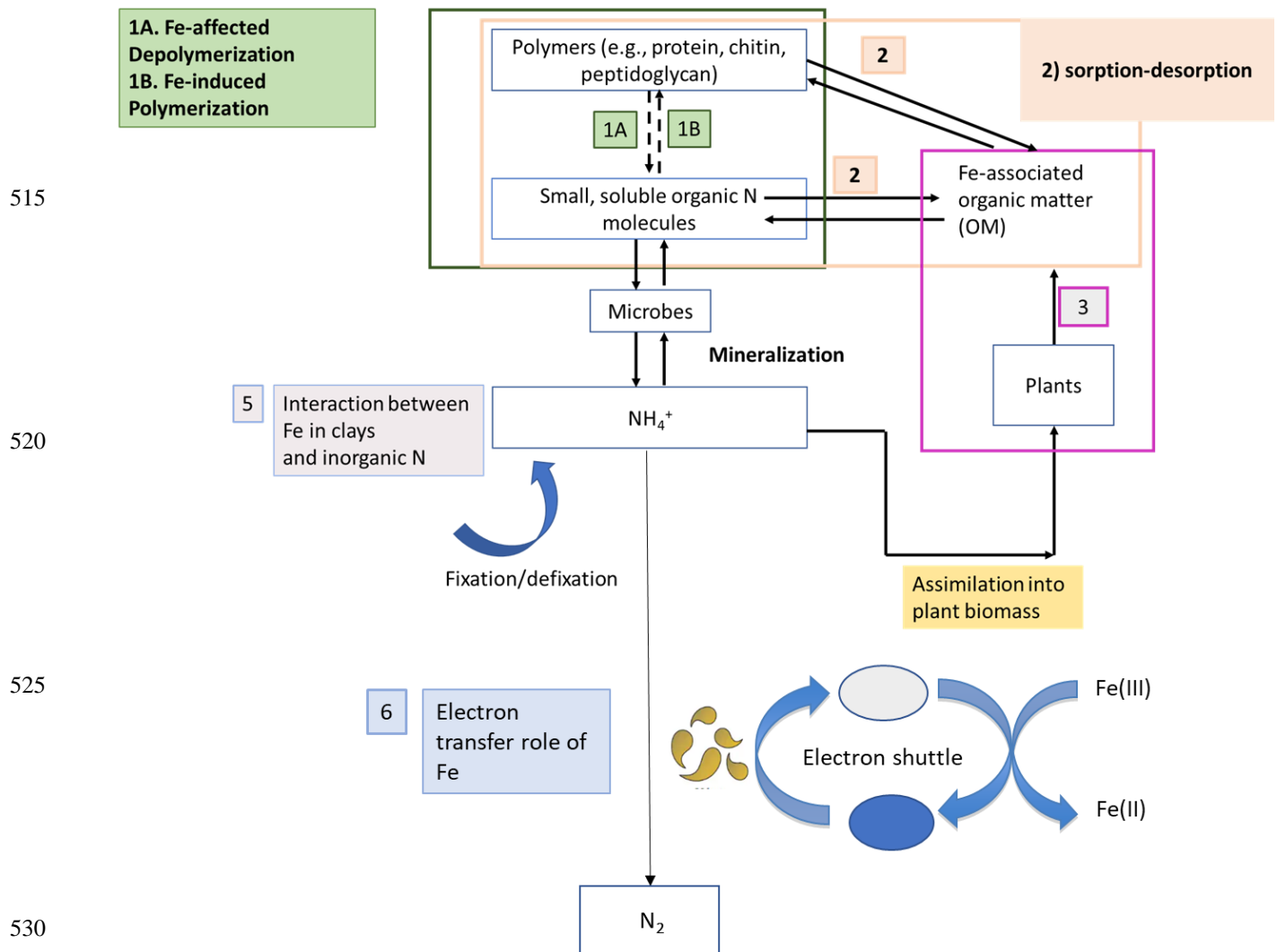
Figure 5. Fe affects N bioavailability in soils. This figure doesn't specify soil conditions under which an Fe role may proceed.

8.1 Sorbent role of Fe in controlling N bioavailability

8.1.1 Organic nitrogen

The sorbent role of Fe in controlling N bioavailability is multifaceted. Sorption can protect ON from decomposition by reducing the activity of enzymes and limiting the accessibility of ON to degradation mechanisms. However, a fraction of sorbed ON is bioavailable (Bird et al., 2002; Kleber et al., 2007), or can be made available by processes such as priming or displacement by competitive organics. Thus, the concept of "sorptive stabilization" of N substrates does not stand as a conclusive explanation for ON persistence in soils and should rather be revisited. In this context, sorption to Fe minerals may

540 impose spatial constraints on the accessibility of ON substances to microbes, as sorption can locate ON in physically isolated spaces such as micropores, microaggregates, or microdomains of densely arranged clays which slows down its decomposition and decreases its bioavailability (Kleber et al., 2021).

Research on Fe-mediated ON depolymerization has mostly focused on proteins (Wanek et al., 2010; Noll et al., 2019; Reuter et al., 2020), since proteins alone constitute 60% or more of the N in plant and microbial cells (Fuchs, 1999) and are strongly

545 sorbed to Fe surfaces. However, not all soil and mineral-associated N is protein. Rather, N exists in a variety of chemical forms including microbial cell wall compounds. Using Fourier transform infrared spectroscopy (FTIR) and isotope pool dilution (IPD), multiple studies have shown the importance of microbial cell wall depolymerization in the delivery of soil N (Hu et al., 2017; Hu et al., 2018; Hu et al., 2020). In addition, depolymerization of membrane lipids and nucleic acids is not yet characterized despite the detection of their degradation products in soils (Warren, 2021). This leads to the following question:

550 how important is the chemical form of Fe-associated N in determining soil N bioavailability? This is relevant since the molecular characteristic of different N forms influences the type and strength of bonding with minerals, which may affect N bioavailability. For instance, Fe oxyhydroxides binds amino sugars more strongly than proteins in boreal forests (Keiluweit and Kuyper, 2020), likely allowing less mineralization from the former compared to the latter compounds.

555 **8.1.2 Inorganic nitrogen**

Despite a small number of studies relating structural Fe in clays and aggregates to N bioavailability, the dynamics of these interactions and relevant mechanisms remain elusive. Several questions remain to be resolved, including: are the original structure and physico-chemical characteristics of clay minerals restored upon reoxidation of its structural Fe? If so, what are the implications for NH_4^+ release and fixation and other processes that influence loss and gain of bioavailable N?

560 **8.2 Structural role of Fe in controlling N bioavailability**

Research is needed to comprehend the implications of Fe's structural role in controlling N bioavailability and its potential influence on soil dynamics and nutrient cycling processes. Specifically, it remains uncertain how significant is the loss of Fe, through solubilization and reduction, to microaggregate instability and N bioavailability in soils. Furthermore, the relevance and occurrence of Fe-induced carbon ON polymerization in soils still require confirmation, as observations of this phenomenon

565 have thus far been limited to laboratory settings.

8.3 The role of Fe as a catalyst in controlling N bioavailability

Assessing the importance of Fe-meditated ROS generation in N bioavailability is a formidable challenge. In fact, despite being common in soils, ROS have extremely short lifetimes and are highly reactive towards other soil constituents such as carbonates and bromide (Kleber et al., 2021), which complicate their detection in soils. They are produced by both abiotic and biotic

570 pathways, and the contribution of each pathway to N bioavailability remains elusive. Additionally, rates and mechanisms of ROS production from these two pathways are still not known. Such information is particularly important to understand N

dynamics in environments conducive to ROS formation, such as oxic/anoxic zones, environments with intense solar radiation or in boreal forests where fungi use ROS based mechanisms to access Fe-sorbed N. In contrast to their decomposition role, Yu et al.(2020) found an important role of Fe-mediated ROS production in OM polymerization, which increases the recalcitrance of OM and its resistance to degradation mechanisms (Yu et al., 2020). This finding sheds light on other controls and pathways relevant to N bioavailability. For example, under what conditions can the role of Fe-mediated ROS generation on N bioavailability be shifted from decomposition to protection? And how will this evolve in a changing world where solar radiation is becoming more intense and the frequencies of extreme events (e.g., droughts, rain) is increasing?

8.4 Electron transfer role of Fe in controlling N bioavailability

The capacity of Fe to act as an electron acceptor and donor can affect bioavailable N loss from soils by processes such as Feammox and denitrification. To further understand these processes, more research is needed on cryptic Fe cycling and the controls over the oxidation-reduction dynamics of Fe in soil, since preservation of oxidized Fe promotes N stabilization within mineral associations. For instance, the effects of added electron shuttles on the extent and the rate of Fe(III) reduction and associated loss of N via Feammox have been investigated, however, the capacity of SOM and organo-Fe associations to transfer electrons has received less attention (Sposito, 2011; Xu, Z. et al., 2020). The characterization and mapping of spatiotemporal redox heterogeneity also deserves attention (Wilmoth, 2021).

8.5 Varied analytical approach is needed to characterize Fe-N interactions

To understand the roles of Fe in controlling N bioavailability, a varied analytical approach must be adopted to enable a more holistic and multidimensional view of these interactions, considering all the possible outcomes of Fe reactions on N as driven by the physico-chemical and biological characteristics of soil and management. This approach is essential to provide realistic turnover rates of N and decipher the underlying mechanisms of Fe-N reactions in soil, in contrast to controlled lab experiments which do not represent soil in its complexity and heterogeneity. This approach should also capture variations in the processes of interest within multiscale and time dimensions. Here, we present most common and powerful techniques that can be combined in the framework of this varied approach to understand Fe-N interactions. Note that an extensive list of techniques is out of the scope of this review.

8.5.1 Imaging techniques

Techniques such as Synchrotron XAS and Synchrotron X-ray allow the identification and the characterization of structural and chemical properties of minerals as well as their oxidation states. They can also be used to determine the speciation of SON and dissolved organic nitrogen (DON) as well as the structural characteristics of soil, such as pore size and pore connectivity. These information could help, for example, to characterize the fine-scale redox heterogeneity (Wilmoth, 2021) that affects Fe cycling and its interconnection with N bioavailability. In addition, these techniques are used to observe and investigate the 3D structure of organo-Fe minerals in soils. Kleber et al., (2021) called for using them in studies of enzyme activity because they

allow the investigation of the natural structure of organo-mineral associations without alteration (Kleber et al., 2021). However, while using advanced imaging techniques reveals information at fine scales, upscaling such data is challenging (Wagai et al., 2020).

8.5.2 Microbial techniques

They provide information on the identity of microbial taxa regulating soil biogeochemical processes in question. They include techniques such as metatranscriptomics which can be used to distinguish the biological from the abiotic pathways used to direct redox reactions (Wilmoth, 2021), and metagenomics that were used recently to explore coupled nutrients interactions, including coupled Fe-N reactions (Ma et al., 2021).

8.5.3 Isotope techniques

Isotopes can be used to determine gross rates and the investigation of the pathways and mechanisms of the processes in question. They can also be used to determine OM pools with varying turnover rates. Stable isotope probing, which is a high-resolution technique, can also be used to trace the microbial uptake of N as affected by Fe minerals as well as its fate in soil environments.

8.5.4 Molecular characterization techniques

These techniques, which include FTIR, allow the identification of different soil organic molecules and the analysis of their bonding mode and strength with minerals.

8.6 Concluding Comment

As a final commentary on Fe-N bioavailability interactions, we propose the following questions: how much N can be mobilized by Fe-related mechanisms? What are the controls on these interactions? And how important are certain mechanisms relative to others in securing N bioavailability in the context of global change? Do reactions observed in laboratory settings occur naturally in soils? We also urge the field to develop new methods and techniques, such as those capable of detecting low concentrations of ROS and their fate in soil environment, or the products of mineral-induced OM polymerization.

Author contributions

IS conducted the literature review and wrote the manuscript, XZB, PL and WH proofread, edited, reviewed, provided guidance and advice on manuscript development.

Competing interests

The authors declare that they have no conflict of interest.

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References

Allison, S. D.: Soil minerals and humic acids alter enzyme stability: implications for ecosystem processes, Biogeochemistry, 81, 361–373, doi:10.1007/s10533-006-9046-2, 2006.

Amelung, W., Lobe, I., and Du Preez, C. C.: Fate of microbial residues in sandy soils of the South African Highveld as
640 influenced by prolonged arable cropping, Eur. J. Soil. Sci., 53, 29–35, doi:10.1046/j.1365-2389.2002.00428.x, 2002.

Apel, K. and Hirt, H.: Reactive oxygen species: metabolism, oxidative stress, and signal transduction, Annu. Rev. Plant. Bio., 55, 373–99, doi:10.1146/annurev.arplant.55.031903.141701, 2004.

Attygalla, N. W., Baldwin, D. S., Silvester, E., Kappen, P., and Whitworth, K. L.: The severity of sediment desiccation affects the adsorption characteristics and speciation of phosphorus, Environ. Sci-Proc. Imp., 18, 64–71, doi:10.1039/c5em00523j,
645 2016.

Barge, L. M., Flores, E., Baum, M. M., VanderVelde, D. G., and Russell, M. J.: Redox and pH gradients drive amino acid synthesis in iron oxyhydroxide mineral systems, P. Natl. Acad. Sci., 116, 4828–4833, doi:10.1073/pnas.1812098116, 2019.

Baron, M. H., Revault, M., Servagent-Noinville, S., Abadie, J., and Quiquampoix, H.: Chymotrypsin adsorption on montmorillonite: enzymatic activity and kinetic FTIR structural analysis, J. Colloid. Interface. Sci., 214, 319–332,
650 doi:10.1006/jcis.1999.6189, 1999.

Barral, M. T., Arias, M., and Guérif, J.: Effects of iron and organic matter on the porosity and structural stability of soil aggregates, Soil. Till. Res., 46, 261–272, doi:10.1016/s0167-1987(98)00092-0, 1998.

Batjes N.H.: Total carbon and nitrogen in the soils of the world, Eur. J. Soil Sci., 47, 151–163, doi:10.1111/j.1365-2389.1996.tb01386.x, 1996.

655 Bayan, M. R. and Eivazi, F.: Selected enzyme activities as affected by free iron oxides and clay particle size, Commun. Soil. Sci. Plan., 30, 1561–1571, doi:10.1080/00103629909370308, 1999.

Benz, M., Brune, A., and Schink, B.: Anaerobic and aerobic oxidation of ferrous iron at neutral pH by chemoheterotrophic nitrate-reducing bacteria, Arch. Microbiol., 169, 159–165, doi:10.1007/s002030050555, 1998.

Birch, H. F.: The effect of soil drying on humus decomposition and nitrogen availability, Plant. Soil., 10, 9–31,
660 doi:10.1007/bf01343734, 1958.

Birch, H. F.: Further observations on humus decomposition and nitrification, Plant. Soil., 11, 262–286, doi:10.1007/bf01435157, 1959.

Birch, H. F.: Nitrification in soils after different periods of dryness, Plant. Soil., 12, 81–96, doi:10.1007/bf01377763, 1960.

Birch, H. F.: Mineralisation of plant nitrogen following alternate wet and dry conditions. Plant. Soil., 20, 43–49, doi:10.1007/bf01378096, 1964.

Bird, J.A., van Kessel, C., and Horwath W. R.: Nitrogen dynamics in humic fractions under alternative straw management in temperate rice, Soil Sci. Soc. Am. J. 66, 478–488, doi:10.2136/sssaj2002.4780, 2002.

Blankinship, J. C., Berhe, A. A., Crow, S. E., Druhan, J. L., Heckman, K. A., Keiluweit, M., Lawrence, C. R., Marín-Spiotta, E., Plante, A. F., Rasmussen, C., Schädel, C., Schimel, J. P., Sierra, C. A., Thompson, A., Wagai, R., and Wieder W. R. Improving understanding of soil organic matter dynamics by triangulating theories, measurements, and models, Biogeochemistry, 140, 1–13, doi:10.1007/s10533-018-0478-2, 2018.

Boland, D. D., Collins, R. N., Miller, C. J., Glover, C. J., and Waite, T. D.: Effect of solution and solid-phase conditions on the Fe(II)-accelerated transformation of ferrihydrite to lepidocrocite and goethite, Environ. Sci. Technol., 48, 5477–5485, doi:10.1021/es4043275, 2014.

Bremner J.M., Blackmer A.M., and Waring S.A.: Formation of nitrous oxide and dinitrogen by chemical decomposition of hydroxylamine in soils, Soil. Biol. Biochem., 12, 263–269, doi:10.1016/0038-0717(80)90072-3, 1980.

Bruun, T. B., Elberling, B., and Christensen, B. T.: Lability of soil organic carbon in tropical soils with different clay minerals, Soil. Biol. Biochem., 42, 888–895, doi:10.1016/j.soilbio.2010.01.009, 2010.

Bugeja, S. and Castellano, M.: Physicochemical organic matter stabilization across a restored grassland chronosequence, Soil. Sci. Soc. Am. J. 82, 1559–1567, doi:10.2136/sssaj2018.07.0259, 2018.

Burger, M. and Venterea, R. T.: Effects of nitrogen fertilizer types on nitrous oxide emissions, in: understanding greenhouse gas emissions from agricultural management, edited by: Guo, L., Gunasekara, A. S., McConnell, L. L., American Chemical Society, 1072, 179–202, doi:10.1021/bk-2011-1072, 2011.

Caldwell, B. A.: Enzyme activities as a component of soil biodiversity: A review, Pedobiologia, 49, 637–644, doi:10.1016/j.pedobi.2005.06.003, 2005.

Cambardella, C. A. and Elliott, E. T.: Carbon and nitrogen distribution in aggregates from cultivated and native grassland soils, Soil. Sci. Soc. Am. J., 57, 1071–1076, doi:10.2136/sssaj1993.03615995005700040032x, 1993.

Chacon, S. S., Reardon, P. N., Burgess, C. J., Purvine, S., Chu, R. K., Clauss, T. R., Walter, E., Myrold, D. D., Washton, N., and Kleber, M.: Mineral surfaces as agents of environmental proteolysis: mechanisms and controls, Environ. Sci. Technol., 53, 3018–3026, doi:10.1021/acs.est.8b05583, 2019.

Chaudhuri, S. K., Lack, J. G., and Coates, J. D.: Biogenic magnetite formation through anaerobic biooxidation of Fe(II), Appl. Environ. Microbiol., 67, 2844–8, doi:10.1128/aem.67.6.2844-2848.2001, 2001.

Chen, C., Hall, S. J., Coward, E., and Thompson, A.: Iron-mediated organic matter decomposition in humid soils can counteract protection. Nat. Commun., 11, 1–13, doi:10.1038/s41467-020-16071-5, 2020.

695   Chen, L., Liu, L., Qin, S., Yang, G., Fang, K., Zhu, B., Kuzyakov, Y., Chen, P., Xu, Y., and Yang, Y.: Regulation of priming effect by soil organic matter stability over a broad geographic scale. Nat. Commun., 10, 5112, doi:10.1038/s41467-019-13119-z, 2019.

Cheng, L., Zhu, J., Chen, G., Zheng, X., Oh, N. H., Rufty, T. W., Richter, D., and Hu, S.: Atmospheric CO2 enrichment facilitates cation release from soil, Ecol. Lett., 13, 284–91, doi:10.1111/j.1461-0248.2009.01421.x, 2010.

700   Cornell, R. M. and Schwertmann, U.: The iron oxides: structure, properties, reactions, occurrences, and uses, Weinheim : Wiley-vch, 664, doi:10.1002/3527602097, 2003.

Cotrufo, M.F., Wallenstein, M.D., Boot, C.M., Denef, K. and Paul, E.: The Microbial Efficiency-Matrix Stabilization (MEMS) framework integrates plant litter decomposition with soil organic matter stabilization: do labile plant inputs form stable soil organic matter?, Glob. Change. Biol., 19, 988–995, doi:10.1111/gcb.12113, 2013.

705   Coward, E. K., Thompson, A., and Plante, A. F.: Contrasting Fe speciation in two humid forest soils: Insight into organomineral associations in redox-active environments, Geochim. Cosmochim. Ac., 238, 68–84, doi:10.1016/j.gca.2018.07.007, 2018.

Cui, Q., Song, C., Wang, X., Shi, F., Wang, L., and Guo, Y.: Rapid N2O fluxes at high level of nitrate nitrogen addition during freeze-thaw events in boreal peatlands of northeast China. Atmos. Environ., 135, 1–8, doi:10.1016/j.atmosenv.2016.03.053, 2016.

710   Daly, A. B., Jilling, A., Bowles, T. M., Buchkowski, R. W., Frey, S. D., Kallenbach, C. M., Keiluweit, M., Mooshammer, M., Schimel J. P., and Grandy A. S.: A holistic framework integrating plant-microbe-mineral regulation of soil bioavailable nitrogen. Biogeochemistry, 154, 211–229, doi:10.1007/s10533-021-00793-9, 2021.

Datta, R., Anand, S., Moulick, A., Baraniya, D., Imran Pathan, S., Rejsek, K., Vranová, V., Sharma, M., Sharma, D., Kelkar, A., and Formánek, P.: How enzymes are adsorbed on soil solid phase and factors limiting its activity: A Review, Int. Agrophys.,
715   31, 287–302, doi:10.1515/intag-2016-0049, 2017.

Daugherty, E. E., Gilbert, B., Nico, P. S., and Borch, T.: Complexation and Redox Buffering of Iron(II) by Dissolved Organic Matter, Environ. Sci. Technol., 51, 11096–11104, doi:10.1021/acs.est.7b03152, 2017.

Deroo, H., Akter, M., Mendoza, O., Boeckx, P., and Sleutel, S.: Control of paddy soil redox condition on gross and net ammonium fixation and defixation, Geoderma, 400, 115151, doi:10.1016/j.geoderma.2021.115151, 2021.

720   Diaz, J. M., Hansel, C. M., Voelker, B. M., Mendes, C. M., Andeer, P. F., and Zhang, T.: Widespread production of extracellular superoxide by heterotrophic bacteria, Science, 340, 1223–1226, doi:10.1126/science.1237331, 2013.

Ding, B., Li, Z., and Qin, Y.: Nitrogen loss from anaerobic ammonium oxidation coupled to Iron(III) reduction in a riparian zone, Environ. Pollut., 231, 379–386, doi:10.1016/j.envpol.2017.08.027, 2017.

Ding, B., Chen, Z., Li, Z., Qin, Y., and Chen, S.: Nitrogen loss through anaerobic ammonium oxidation coupled to Iron
725   reduction from ecosystem habitats in the Taihu estuary region. Sci.Total. Environ., 662, 600–606, doi:10.1016/j.scitotenv.2019.01.231, 2019.

Ding, B., Qin, Y., Luo, W., and Li, Z.: Spatial and seasonal distributions of Feammox from ecosystem habitats in the Wanshan region of the Taihu watershed, China, Chemosphere, 239, 124742, doi:10.1016/j.chemosphere.2019.124742, 2020.

Ding, L. J., An, X. L., Li, S., Zhang, G. L., and Zhu, Y. G.: Nitrogen Loss through Anaerobic Ammonium Oxidation Coupled

730   to Iron Reduction from Paddy Soils in a Chronosequence. Environ. Sci. Technol., 48, 10641–10647, doi:10.1021/es503113s, 2014.

Ding, Y., Ye, Q., Liu, M., Shi, Z., and Liang, Y.: Reductive release of Fe mineral-associated organic matter accelerated by oxalic acid, Sci. Total. Environ. 763, 142937, doi:10.1016/j.scitotenv.2020.142937, 2021.

Dippold, M., Biryukov, M., and Kuzyakov, Y.: Sorption affects amino acid pathways in soil: Implications from position-

735   specific labeling of alanine. Soil. Biol. Biochem., 72, 180–192, doi:10.1016/j.soilbio.2014.01.015, 2014.

Dubinsky, E. A., Silver, W. L., and Firestone, M. K.: Tropical forest soil microbial communities couple iron and carbon biogeochemistry, Ecology, 91, 2604–2612, doi:10.1890/09-1365.1, 2010.

Duiker, S. W., Rhoton, F. E., Torrent, J., Smeck, N. E., and Lal, R.: Iron (hydr)oxide crystallinity effects on soil aggregation, Soil.Sci. Soc. Am. J., 67, 606–611, doi:10.2136/sssaj2003.6060, 2003.

740   Dümig, A., Häusler, W., Steffens, M., and Kögel-Knabner, I.: Clay fractions from a soil chronosequence after glacier retreat reveal the initial evolution of organo–mineral associations, Geochim Cosmochim. Ac., 85, 1–18, doi:10.1016/j.gca.2012.01.046, 2012.

Dunham-Cheatham, S. M., Zhao, Q., Obrist, D., and Yang, Y.: Unexpected mechanism for glucose-primed soil organic carbon mineralization under an anaerobic–aerobic transition, Geoderma, 376, 114535, doi:10.1016/j.geoderma.2020.114535, 2020.

745   Eusterhues, K., Hädrich, A., Neidhardt, J., Küsel, K., Keller, T., Jandt, K., and Totsche, K.: Reduction of ferrihydrite with adsorbed and coprecipitated organic matter: microbial reduction by Geobacter bremensis vs. abiotic reduction by Na-dithionite, Biogeosciences, 11, 4953–4966, doi:10.5194/bg-11-4953-2014, 2014.

Eusterhues, K., Rumpel, C., and Kögel-Knabner, I.: Organo-mineral associations in sandy acid forest soils: importance of specific surface area, iron oxides and micropores, Eur. J. Soil. Sci., 56, 753–763, doi:10.1111/j.1365-2389.2005.00710.x, 2005.

750   Favre, F., Stucki, J. W., and Boivin, P.: Redox properties of structural Fe in ferruginous smectite. a discussion of the standard potential and its environmental implications, Clay. Clay. Miner., 54, 466–472, doi:10.1346/ccmn.2006.0540407, 2006.

Feng, J., Wei, K., Chen, Z., Lü, X., Tian, J., Wang, C., and Chen, L.: Coupling and decoupling of soil carbon and nutrient cycles across an aridity gradient in the drylands of northern China: evidence from ecoenzymatic stoichiometry, Global. Biogeochem. Cy., 33, 559–569, doi:10.1029/2018gb006112, 2019.

755   Filimonova, S., Kaufhold, S., Wagner, F., Häusler, W., and Kögel-Knabner, I.: The role of allophane nano-structure and Fe oxide speciation for hosting soil organic matter in an allophanic Andosol, Geochim. Cosmochim. Ac. 180, 284–302, doi:10.1016/j.gca.2016.02.033, 2016.

Frey, S. D.: Mycorrhizal fungi as mediators of soil organic matter dynamics, Annu. Rev. Ecol. Evol. S., 50, 237–259, doi:10.1146/annurev-ecolsys-110617-062331, 2019.

760   Fuchs, H.: Das lernende Unternehmen, in: Die Kunst, (k)eine perfekte Führungskraft zu sein, Gabler Verlag, Wiesbaden, 110–110, doi:10.1007/978-3-322-82766-1_40, 1999.

Gao, J., Jansen, B., Cerli, C., Helmus, R., Mikutta, R., Dultz, S., Guggenberger, G., and Kalbitz, K.: Competition and surface conditioning alter the adsorption of phenolic and amino acids on soil minerals. Eur. J. Soil. Sci., 68, 667–677, doi:10.1111/ejss.12459, 2017.

765 Gao, J., Jansen, B., Cerli, C., Helmus, R., Mikutta, R., Dultz, S., Guggenberger, G., Vogel, C., and Kalbitz, K.: Organic matter coatings of soil minerals affect adsorptive interactions with phenolic and amino acids, Eur. J. Soil. Sci., 69, 613–624, doi:10.1111/ejss.12562, 2018.

García-Oliva, F., Lancho, J. F. G., Montaño, N. M., and Islas, P.: Soil carbon and nitrogen dynamics followed by a forest-to-pasture conversion in Western Mexico, Agroforest. Syst., 66, 93–100, doi:10.1007/s10457-005-2917-z, 2006.

770 Gärdenäs, A. I., Ågren, G. I., Bird, J. A., Clarholm, M., Hallin, S., Ineson, P., Kätterer, T., Knicker, H., Nilsson, S. I., Näsholm, T., Ogle, S., Paustian, K., Persson, T., and Stendahl, J.: Knowledge gaps in soil carbon and nitrogen interactions – From molecular to global scale, Soil. Biol. Biochem., 43, 702–717, doi:10.1016/j.soilbio.2010.04.006, 2011.

Garrido-Ramírez, E. G., Theng, B. K., and Mora, M. L.: Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions—a review, Appl. Clay. Sci., 47, 182–192, doi:10.1016/j.clay.2009.11.044, 2010.

775 Gentsch, N., Mikutta, R., Shibistova, O., Wild, B., Schnecker, J., Richter, A., Urich, T., Gittel, A., Šantrůčková, H., Bárta, J., Lashchinskiy, N., Mueller, C. W., Fuß, R., and Guggenberger, G.: Properties and bioavailability of particulate and mineral-associated organic matter in Arctic permafrost soils, Lower Kolyma Region, Russia, Eur. J. Soil. Sci., 66, 722–734, doi:10.1111/ejss.12269, 2015.

Georgiou, C. D., Sun, H. J., McKay, C. P., Grintzalis, K., Papapostolou, I., Zisimopoulos, D., Panagiotidis, K., Zhang, G.,
780 Koutsopoulou, E., Christidis, G. E., and Margiolaki, I.: Evidence for photochemical production of reactive oxygen species in desert soils, Nat. Commun., 6, 1–11, doi:10.1038/ncomms8100, 2015.

Gianfreda, L., Rao, M. A., and Violante, A.: Formation and activity of urease-tannate complexes affected by aluminum, iron, and manganese, Soil. Sci. Soc. Am. J., 59, 805–810, doi:10.2136/sssaj1995.03615995005900030024x, 1995.

Gligorovski, S., Strekowski, R., Barbati, S., and Vione, D.: Environmental implications of hydroxyl radicals (•OH), Chem.
785 Rev., 115, 13051–13092, doi:10.1021/cr500310b, 2015.

Godbold, D. L., Hoosbeek, M. R., Lukac, M., Cotrufo, M. F., Janssens, I. A., Ceulemans, R., Polle, A., Velthorst, E. J., Scarascia-Mugnozza, G., De Angelis, P., Miglietta, F., and Peressotti, A.: Mycorrhizal hyphal turnover as a dominant process for carbon input into soil organic matter, Plant. Soil. 281, 15–24, doi:10.1007/s11104-005-3701-6, 2006.

Golchin, A., Oades, J., Skjemstad, J., and Clarke, P.: Soil structure and carbon cycling, Soil. Res., 32, 1043–1068,
790 doi:10.1071/sr9941043, 1994.

Gotoh, S. and Patrick Jr, W. H.: Transformation of iron in a waterlogged soil as influenced by redox potential and pH, Soil. Sci. Soc. Am. J., 38, 66–71, doi:10.2136/sssaj1974.03615995003800010024x, 1974.

Gu, B., Schmitt, J., Chen, Z., Liang, L., and McCarthy, J. F.: Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models, Environ. Sci. Technol., 28, 38–46, doi:10.1021/es00050a007, 1994.

795   Gu, B., Schmitt, J., Chen, Z., Liang, L., and McCarthy, J. F.: Adsorption and desorption of different organic matter fractions on iron oxide, Geochim. Cosmochim. Ac., 59, 219–229, doi:10.1016/0016-7037(94)00282-q, 1995.

Gu, C., Zhang, S., Han, P., Hu, X., Xie, L., Li, Y., Brooks, M., Liao, X., and Qin, L.: Soil enzyme activity in soils subjected to flooding and the effect on nitrogen and phosphorus uptake by oilseed rape, Front. Plant. Sci., 10, 386, doi:10.3389/fpls.2019.00368, 2019.

800   Hall, S. J., and Silver, W. L.: Iron oxidation stimulates organic matter decomposition in humid tropical forest soils, Glob. Change. Biol., 19, 2804–2813, doi:10.1111/gcb.12229, 2013.

Hall, S. J., Silver, W. L., and Amundson, R.: Greenhouse gas fluxes from Atacama Desert soils: a test of biogeochemical potential at the Earth's arid extreme, Biogeochemistry, 111, 303–315, doi:10.1007/s10533-011-9650-7, 2012.

Hall, S. J., Berhe, A. A., and Thompson, A.: Order from disorder: do soil organic matter composition and turnover co-vary
805   with iron phase crystallinity?, Biogeochemistry, 140, 93–110, doi:10.1007/s10533-018-0476-4, 2018.

Han, J., Shi, L., Yakun, W., Chen, Z., and Wu, L.: The regulatory role of endogenous iron on greenhouse gas emissions under intensive nitrogen fertilization in subtropical soils of China. Environ. Sci. Pollut. R., 25, 14511–14520, doi:10.1007/s11356-018-1666-2, 2018.

Harden, J. W., Koven, C. D., Ping, C. L., Hugelius, G., McGuire, A. D., Camill, P., Jorgenson, T., Kuhry, P., Michaelson, G.
810   J., and O'Donnell, J. A.: Field information links permafrost carbon to physical vulnerabilities of thawing, Geophys. Res. Lett., 39, doi:10.1029/2012gl051958, 2012.

Hassan, W., Chen, W., Cai, P., and Huang, Q.: Oxidative enzymes, the ultimate regulator: implications for factors affecting their efficiency, J. Environ. Qual., 42, 1779–90, doi:10.2134/jeq2013.05.0204, 2013.

Heckman, K., Welty-Bernard, A., Rasmussen, C., and Schwartz, E., Geologic controls of soil carbon cycling and microbial
815   dynamics in temperate conifer forests, Chem. Geol., 267, 12–23, doi:10.1016/j.chemgeo.2009.01.004, 2009.

Heckman, K. A., Welty-Bernard, A., Vázquez-Ortega, A., Schwartz, E., Chorover, J., and Rasmussen, C.: The influence of goethite and gibbsite on soluble nutrient dynamics and microbial community composition, Biogeochemistry, 112, 179–195, doi:10.1007/s10533-012-9715-2, 2012.

Heckman, K., Throckmorton, H., Horwath, W. R., Swanston, C. W., and Rasmussen, C.: Variation in the molecular structure
820   and radiocarbon abundance of mineral-associated organic matter across a lithosequence of forest soils, Soil. Syst., 2, 36, doi:10.3390/soilsystems2020036, 2018.

Henneberry, Y. K., Kraus, T. E. C., Nico, P. S., and Horwath, W. R., Structural stability of coprecipitated natural organic matter and ferric iron under reducing conditions, Org. Geochem., 48, 81–89, doi:10.1016/j.orggeochem.2012.04.005, 2012.

Henneberry, Y., Kraus, T. E. C., Krabbenhoft, D. P., and Horwath, W. R.: Investigating the temporal effects of metal-based
825   coagulants to remove mercury from solution in the presence of dissolved organic matter, Environ. Manage., 57, 220–228, doi:10.1007/s00267-015-0601-2, 2016.

Hlady, V. V. and Buijs, J.: Protein adsorption on solid surfaces, Curr. Opin. Biotechnol., 7, 72–77, doi:10.1016/s0958-1669(96)80098-x, 1996.

Hu, Y., Zheng, Q., and Wanek, W.: Flux analysis of free amino sugars and amino acids in soils by isotope tracing with a novel liquid chromatography/high resolution mass spectrometry platform, Anal. Chem. 89, 9192–9200, doi:10.1021/acs.analchem.7b01938, 2017.

Hu, Y., Zheng, Q., Zhang, S., Noll, L., and Wanek, W.: Significant release and microbial utilization of amino sugars and d-amino acid enantiomers from microbial cell wall decomposition in soils, Soil. Biol. Biochem., 123, 115–125, doi:10.1016/j.soilbio.2018.04.024, 2018.

Hu, Y., Zheng, Q., Noll, L., Zhang, S., and Wanek, W.: Direct measurement of the in situ decomposition of microbial-derived soil organic matter, Soil. Biol. Biochem., 141, 107660, doi:10.1016/j.soilbio.2019.107660, 2020.

Huang, P. M.: Role of soil minerals in transformations of natural organics and xenobiotics in soil, In: Soil Biochemistry, Routledge, New York, 29–116, doi:10.1201%2F9780203739389-2, 1990.

Huang, S. and Jaffé, P. R.: Characterization of incubation experiments and development of an enrichment culture capable of ammonium oxidation under iron-reducing conditions, Biogeosciences, 12, 769–779, doi:10.5194/bg-12-769-2015, 2015.

Huang, S. and Jaffé, P. R.: Isolation and characterization of an ammonium-oxidizing iron reducer: *Acidimicrobiaceae* sp. A6, Plos One, 13, e0194007, doi:10.1371/journal.pone.0194007, 2018.

Huang, S., Chen, C., Peng, X., and Jaffé, P. R.: Environmental factors affecting the presence of *Acidimicrobiaceae* and ammonium removal under iron-reducing conditions in soil environments, Soil. Biol. Biochem., 98, 148–158, doi:10.1016/j.soilbio.2016.04.012, 2016.

Huang, X., Kanerva, P., Salovaara, H., Loponen, J., and Sontag-Strohm, T.: Oxidative modification of a proline-rich gliadin peptide, Food. Chem., 141, 2011–2016, doi:10.1016/j.foodchem.2013.05.066, 2013.

Huang, X., Gao, D., Peng, S., and Tao, Y.: Effects of ferrous and manganese ions on anammox process in sequencing batch biofilm reactors, J. Environ. Sci., 26, 1034–1039, doi:10.1016/s1001-0742(13)60531-8, 2014.

Huang, X., Zhu-Barker, X., Horwath, W., Faeflen, S., Luo, H., Xin, X., and Jiang, X.: Effect of iron oxide on nitrification in two agricultural soils with different pH, Biogeosciences, 13, 5609–5617, doi:10.5194/bg-13-5609-2016, 2016.

Iversen, C. M.: Digging deeper: fine-root responses to rising atmospheric CO concentration in forested ecosystems, New Phytol., 186, 346–57, doi:10.1111/j.1469-8137.2009.03122.x, 2010.

Jeewani, P. H., Van Zwieten, L., Zhu, Z., Ge, T., Guggenberger, G., Luo, Y., and Xu, J.: Abiotic and biotic regulation on carbon mineralization and stabilization in paddy soils along iron oxide gradients. *Soil. Biol. Biochem.* 160, 108312, doi:10.1016/j.soilbio.2021.108312, 2021

Jiang, Z., Liu, Y., Yang, J., Brookes, P. C., and Gunina, A.: Rhizosphere priming regulates soil organic carbon and nitrogen mineralization: The significance of abiotic mechanisms, Geoderma, 385, 114877, doi:10.1016/j.geoderma.2020.114877, 2021.

Jilling, A., Keiluweit, M., Contosta, A. R., Frey, S., Schimel, J., Schnecker, J., Smith, R. G., Tiemann, L., and Grandy, A. S.: Minerals in the rhizosphere: overlooked mediators of soil nitrogen availability to plants and microbes, Biogeochemistry, 139, 103–122, doi:10.1007/s10533-018-0459-5, 2018.

Jilling, A., Keiluweit, M., Gutknecht, J. L. M., and Grandy, A. S.: Priming mechanisms providing plants and microbes access to mineral-associated organic matter., Soil. Biol. Biochem., 158, 108265, doi:10.1016/j.soilbio.2021.108265, 2021.

Johnson, K., Purvis, G., Lopez-Capel, E., Peacock, C., Gray, N., Wagner, T., März, C., Bowen, L., Ojeda, J., Finlay, N., Robertson, S., Worrall, F., and Greenwell, C.: Towards a mechanistic understanding of carbon stabilization in manganese oxides, Nat. Commun., 6, 7628, doi:10.1038/ncomms8628, 2015.

Joss, H., Patzner, M. S., Maisch, M., Mueller, C. W., Kappler, A., and Bryce, C.: Cryoturbation impacts iron-organic carbon associations along a permafrost soil chronosequence in northern Alaska, Geoderma, 413, 115738, doi:10.1016/j.geoderma.2022.115738, 2022.

Kaiser, K. and Zech, W.: Dissolved organic matter sorption by mineral constituents of subsoil clay fractions, J. Plant. Nutr. Soil. Sc., 163, 531–535, doi:10.1002/1522-2624(200010)163:5<531::aid-jpln531>3.0.co;2-n, 2000a.

Kaiser, K. and Zech, W. : Sorption of dissolved organic nitrogen by acid subsoil horizons and individual mineral phases, Eur. J. Soil. Sci., 51, 403–411, doi:10.1046/j.1365-2389.2000.00320.x, 2000b.

Keiluweit, M. and Kuyper, T. W.: Proteins unbound – how ectomycorrhizal fungi can tap a vast reservoir of mineral-associated organic nitrogen, New. Phytol., 228, 406–408, doi:10.1111/nph.16796, 2020.

Keiluweit, M., Bougoure, J. J., Zeglin, L. H., Myrold, D. D., Weber, P. K., Pett-Ridge, J., Kleber, M., and Nico, P. S.: Nano-scale investigation of the association of microbial nitrogen residues with iron (hydr)oxides in a forest soil O-horizon, Geochim. Cosmochim. Ac., 95, 213–226, doi:10.1016/j.gca.2012.07.001, 2012.

Keiluweit, M., Bougoure, J. J., Nico, P. S., Pett-Ridge, J., Weber, P. K., and Kleber, M.: Mineral protection of soil carbon counteracted by root exudates, Nat. Clim. Change., 5, 588–595, doi:10.1038/nclimate2580, 2015.

Kelleher, B. P., Willeford, K. O., Simpson, A. J., Simpson, M. J., Stout, R., Rafferty, A., and Kingery, W. L.: Acid phosphatase interactions with organo-mineral complexes: influence on catalytic activity, Biogeochemistry, 71, 285–297, doi:10.1023/b:biog.0000049348.53070.6f, 2004.

Kieloaho, A. J., Pihlatie, M., Dominguez Carrasco, M., Kanerva, S., Parshintsev, J., Riekkola, M. L., Pumpanen, J., and Heinonsalo, J.: Stimulation of soil organic nitrogen pool: The effect of plant and soil organic matter degrading enzymes, Soil. Biol. Biochem., 96, 97–106, doi:10.1016/j.soilbio.2016.01.013, 2016.

Kleber, M., Sollins, P., and Sutton, R.: A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces, Biogeochemistry, 85, 9–24, doi:10.1007/s10533-007-9103-5, 2007.

Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R., and Nico, P. S.: Mineral–organic associations: formation, properties, and relevance in soil environments, in: Advances in Agronomy, edited by: Sparks, D. L., Academic Press, Elsevier, 1–140, doi:10.1016/bs.agron.2014.10.005, 2015.

Kleber, M., Bourg, I. C., Coward, E. K., Hansel, C. M., Myneni, S. C. B., and Nunan, N.: Dynamic interactions at the mineral–organic matter interface, Nat. Rev. Earth. Environ., 2, 402–421, doi:10.1038/s43017-021-00162-y, 2021.

895   Knicker, H.: Soil organic N - An under-rated player for C sequestration in soils?, Soil. Biol. Biochem., 43, 1118–1129, doi:10.1016/j.soilbio.2011.02.020, 2011.

Kögel-Knabner, I.: The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. Soil. Biol. Biochem., 34, 139–162, doi:10.1016/s0038-0717(01)00158-4, 2002.

Kögel-Knabner, I.: Chemical structure of organic N and organic P in soil, in: nucleic acids and proteins in soil, edited by:
900   Nannipieri, P. and Smalla, K., Springer, Berlin, Heidelberg, 23–48, doi:10.1007/3-540-29449-x_2, 2006.

Kopittke, P. M., Hernandez-Soriano, M. C., Dalal, R. C., Finn, D., Menzies, N. W., Hoeschen, C., and Mueller, C. W.: Nitrogen-rich microbial products provide new organo-mineral associations for the stabilization of soil organic matter, Glob. Change. Biol., 24, 1762–1770, doi:10.1111/gcb.14009, 2018.

Kuzyakov, Y., Friedel, J. K., and Stahr, K.: Review of mechanisms and quantification of priming effects, Soil Biol. Biochem.,
905   32, 1485–1498, doi:10.1016/s0038-0717(00)00084-5, 2000.

Kwan, W. P. and Voelker, B. M.: Rates of hydroxyl radical generation and organic compound oxidation in mineral-catalyzed Fenton-like systems, Environ. Sci. Technol., 37, 1150–1158, doi:10.1021/es020874g, 2003.

Lalonde, K., Mucci, A., Ouellet, A., and Gélinas, Y.: Preservation of organic matter in sediments promoted by iron, Nature, 483, 198–200, doi:10.1038/nature10855, 2012.

910   Lecomte, S. M., Achouak, W., Abrouk, D., Heulin, T., Nesme, X., and Haichar, F. E. Z.: Diversifying anaerobic respiration strategies to compete in the rhizosphere. Front. Environ. Sci., 6, doi:10.3389/fenvs.2018.00139, 2018.

Lehmann, J., and Kleber, M.: The contentious nature of soil organic matter, Nature, 528, 60–6, doi:10.1038/nature16069, 2015.

Leinweber, P. and Schulten, H. R.: Nonhydrolyzable forms of soil organic nitrogen: Extractability and composition. J. Plant. Nutr. Soil. Sci., 163, 433–439, doi:10.1002/1522-2624(200008)163:4<433::aid-jpln433>3.0.co;2-f, 2000.

915   Li, C., Zhang, B., Ertunc, T., Schaeffer, A., and Ji, R.: Birnessite-induced binding of phenolic monomers to soil humic substances and nature of the bound residues. Environ. Sci. Technol., 46, 8843–8850, doi:10.1021/es3018732, 2012.

Li, H., Bölscher, T., Winnick, M., Tfaily, M. M., Cardon, Z. G., and Keiluweit, M.: Simple plant and microbial exudates destabilize mineral-associated organic matter via multiple pathways, Environ. Sci. Technol., 55, 3389–3398, doi:10.1021/acs.est.0c04592, 2021.

920   Li, J. and Richter, D. D.: Effects of two-century land use changes on soil iron crystallinity and accumulation in Southeastern Piedmont region, USA, Geoderma, 173–174, 184–191, doi:10.1016/j.geoderma.2011.12.021, 2012.

Li, X., Li, H., and Yang, G.: Promoting the adsorption of metal ions on kaolinite by defect sites: a molecular dynamics study, Sci. Rep-Uk., 5, 14377, doi:10.1038/srep14377, 2015a.

Li, X., Hou, L., Liu, M., Zheng, Y., Yin, G., Lin, X., Cheng, L., Li, Y., and Hu, X.: Evidence of nitrogen loss from anaerobic
925   ammonium oxidation coupled with ferric iron reduction in an intertidal wetland, Environ. Sci. Technol., 49, 11560–11568, doi:10.1021/acs.est.5b03419, 2015b.

Li, Y., Shahbaz, M., Zhu, Z., Chen, A., Nannipieri, P., Li, B., Deng, Y., Wu, J., and Ge, T.: Contrasting response of organic carbon mineralisation to iron oxide addition under conditions of low and high microbial biomass in anoxic paddy soil, Biol. Fert. Soil., 57, 117–129, doi:10.1007/s00374-020-01510-8, 2021.

930   Li, Y., Wang, M., Zhang, Y., Koopal, L. K., and Tan, W.: Goethite effects on transport and activity of lysozyme with humic acid in quartz sand, Colloid. Surface. A., 604, 125319, doi:10.1016/j.colsurfa.2020.125319, 2020.

Li, Y., Yu, S., Strong, J., and Wang, H.: Are the biogeochemical cycles of carbon, nitrogen, sulfur, and phosphorus driven by the "Fe-III-Fe-II redox wheel" in dynamic redox environments?, J. Soil. Sediment., 12, 683–693, doi:10.1007/s11368-012-0507-z, 2012.

935   Lipson, D. A., Jha, M., Raab, T. K., and Oechel, W. C.: Reduction of iron (III) and humic substances plays a major role in anaerobic respiration in an Arctic peat soil, J. Geophys. RES-Biogeo., 115, doi:10.1029/2009jg001147, 2010.

Lützow, M. V., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., and Flessa, H.: Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions – a review, Eur. J. Soil. Sci., 57, 426–445, doi:10.1111/j.1365-2389.2006.00809.x, 2006.

940   Ma, B., Stirling, E., Liu, Y., Zhao, K., Zhou, J., Singh, B. K., Tang, C., Dahlgren, R. A., and Xu, J.: Soil biogeochemical cycle couplings inferred from a function-taxon network, Research, 2021, doi:10.34133/2021/7102769, 2021.

Matrajt, G. and Blanot, D.: Properties of synthetic ferrihydrite as an amino acid adsorbent and a promoter of peptide bond formation, Amino Acids, 26, 153–8, doi:10.1007/s00726-003-0047-3, 2004.

Mayes, M. A., Heal, K. R., Brandt, C. C., Phillips, J. R., and Jardine, P. M.: Relation between soil order and sorption of

945   dissolved organic carbon in temperate subsoils, Soil. Sci. Soc. Am. J., 76, 1027–1037, doi:10.2136/sssaj2011.0340, 2012.

Mendes, I. C., Bandick, A. K., Dick, R. P., and Bottomley, P. J.: Microbial biomass and activities in soil aggregates affected by winter cover crops, Soil. Sci. Soc. Am. J., 63, 873–881, doi:10.2136/sssaj1999.634873x, 1999.

Merino, C., Kuzyakov, Y., Godoy, K., Cornejo, P., and Matus, F.: Synergy effect of peroxidase enzymes and Fenton reactions greatly increase the anaerobic oxidation of soil organic matter, Sci. Rep-uk., 10, 1–12, doi:10.1038/s41598-020-67953-z, 2020.

950   Michalet, R.: Hematite identification in pseudo-particles of Moroccan rubified soils, Clay. Miner., 28, 233–242, doi:10.1180/claymin.1993.028.2.05, 1993.

Mikutta, R., Mikutta, C., Kalbitz, K., Scheel, T., Kaiser, K., and Jahn, R.: Biodegradation of forest floor organic matter bound to minerals via different binding mechanisms, Geochim. Cosmochim. Ac., 71, 2569–2590, doi:10.1016/j.gca.2007.03.002, 2007.

955   Mueller, C. W., Rethemeyer, J., Kao-Kniffin, J., Löppmann, S., Hinkel, K. M., and G. Bockheim, J.: Large amounts of labile organic carbon in permafrost soils of northern Alaska, Glob. Change Biol., 21, 2804–2817, doi:10.1111/gcb.12876, 2015.

Muruganandam, S., Israel, D. W., and Robarge, W. P.: Activities of nitrogen-mineralization enzymes associated with soil aggregate size fractions of three tillage systems, Soil. Sci. Soc. Am. J., 73, 751–759, doi:10.2136/sssaj2008.0231, 2009.

Navrotsky, A., Mazeina, L., and Majzlan, J.: Size-driven structural and thermodynamic complexity in iron oxides. Science,

960   319, 1635, doi:10.1126/science.1148614, 2008.

Newcomb, C. J., Qafoku, N. P., Grate, J. W., Bailey, V. L., and De Yoreo, J. J.: Developing a molecular picture of soil organic matter–mineral interactions by quantifying organo–mineral binding, Nat. Commun., 8, 1–8, doi:10.1038/s41467-017-00407-9, 2017.

965 Noll, L., Zhang, S., Zheng, Q., Hu, Y., and Wanek, W.: Wide-spread limitation of soil organic nitrogen transformations by substrate availability and not by extracellular enzyme content, Soil. Biol. Biochem., 133, 37–49, doi:10.1016/j.soilbio.2019.02.016, 2019.

Olagoke, F. K., Kaiser, K., Mikutta, R., Kalbitz, K., and Vogel, C.: Persistent activities of extracellular enzymes adsorbed to soil minerals, Microorganisms, 8, 1796, doi:10.3390/microorganisms8111796, 2020.

Op De Beeck, M., Troein, C., Peterson, C., Persson, P., and Tunlid, A.: Fenton reaction facilitates organic nitrogen acquisition

970 by an ectomycorrhizal fungus, New. Phytol., 218, 335–343, doi:10.1111/nph.14971, 2018.

Park, W., Nam, Y. K., Lee, M. J., and Kim, T. H.: Anaerobic ammonia-oxidation coupled with Fe3+ reduction by an anaerobic culture from a piggery wastewater acclimated to NH4+/Fe3+ medium. Biotechnol. Bioproc. E., 14, 680–685, doi:10.1007/s12257-009-0026-y, 2009.

Patzner, M. S., Mueller, C. W., Malusova, M., Baur, M., Nikeleit, V., Scholten, T., Hoeschen, C., Byrne, J.M., Borch, T.,

975 Kappler, A., and Bryce, C.: Iron mineral dissolution releases iron and associated organic carbon during permafrost thaw. Nat. Commun., 11, 1–11, doi:10.1038/s41467-020-20102-6, 2020.

Peng, X., Yan, X., Zhou, H., Zhang, Y., and Sun, H.: Assessing the contributions of sesquioxides and soil organic matter to aggregation in an Ultisol under long-term fertilization, Soil. Till. Res., 46, 89–98, doi:10.1016/j.still.2014.04.003, 2015.

Pentráková, L., Su, K., Pentrák, M., and Stucki, J. W.: A review of microbial redox interactions with structural Fe in clay

980 minerals, Clay. Miner., 48, 543–560, doi:10.1180/claymin.2013.048.3.10, 2013.

Petridis, L., Ambaye, H., Jagadamma, S., Kilbey, S. M., Lokitz, B. S., Lauter, V., and Mayes, M. A.: Spatial arrangement of organic compounds on a model mineral surface: implications for soil organic matter stabilization. Environ. Sci. Technol., 48, 79–84, doi:10.1021/es403430k, 2014.

Piccolo, A., Spaccini, R., Nebbioso, A., and Mazzei, P.: Carbon sequestration in soil by in situ catalyzed photo-oxidative

985 polymerization of soil organic matter, Environ. Sci. Technol., 45, 6697–6702, doi:10.1021/es201572f, 2011.

Poggenburg, C., Mikutta, R., Schippers, A., Dohrmann, R., and Guggenberger, G.: Impact of natural organic matter coatings on the microbial reduction of iron oxides, Geochim. Cosmochim. Ac., 224, 223–248, doi:10.1016/j.gca.2018.01.004, 2018.

Porras, R. C., Hicks Pries, C. E., Torn, M. S., and Nico, P. S.: Synthetic iron (hydr)oxide-glucose associations in subsurface soil: Effects on decomposability of mineral associated carbon, Sci. Total. Environ., 613–614, 342–351,

990 doi:10.1016/j.scitotenv.2017.08.290, 2018.

Possinger, A. R., Zachman, M. J., Enders, A., Levin, B. D. A., Muller, D. A., Kourkoutis, L. F., and Lehmann, J.: Organo–organic and organo–mineral interfaces in soil at the nanometer scale, Nat. Commun., 11, 6103, doi:10.1038/s41467-020-19792-9, 2020.

Pronk, G., Heister, K., Ding, G. C., Smalla, K., and Kögel-Knabner, I., Development of biogeochemical interfaces in an artificial soil incubation experiment; aggregation and formation of organo-mineral associations, Geoderma, 189–190, 585–594, doi:10.1016/j.geoderma.2012.05.020, 2012.

Pulford, I. D. and Tabatabai, M. A.: Effect of waterlogging on enzyme activities in soils, Soil. Biol. Biochem., 20, 215–219, doi:10.1016/0038-0717(88)90039-9, 1988.

Quiquampoix, H. and Ratcliffe, R. G.: A 31P NMR study of the adsorption of bovine serum albumin on montmorillonite using phosphate and the paramagnetic cation Mn2+: modification of conformation with pH, J. Colloid. Interface. Sci., 148, 343–352, doi:10.1016/0021-9797(92)90173-j, 1992.

Quiquampoix, H., Abadie, J., Baron, M., Leprince, F., Matumoto-Pintro, P., Ratcliffe, R. G., and Staunton, S.: Mechanisms and consequences of protein adsorption on soil mineral surfaces, in: ACS Symposium series, American Chemical Society, 602, 321–333, doi:10.1021/bk-1995-0602.ch023, 1995.

Quiquampoix, H., Staunton, S., Baron, M. H., and Ratcliffe, R. G.: Interpretation of the pH dependence of protein adsorption on clay mineral surfaces and its relevance to the understanding of extracellular enzyme activity in soil, Colloid. Surface. A., 75, 85–93, doi:10.1016/0927-7757(93)80419-f, 1993.

Ramm, E., Liu, C. Ambus, P., Butterbach-Bahl, K., Hu, B., Martikainen, P. J., Marushchak, M. E., Mueller, C. W., Rennenberg, H., Schloter, M., Siljanen, H. M. P., Voigt, C., Werner, C., Biasi, C., and Dannenmann, M., A review of the importance of mineral nitrogen cycling in the plant-soil-microbe system of permafrost-affected soils—changing the paradigm, Environ. Res. Lett., 17, 013004, doi:10.1088/1748-9326/ac417e, 2022.

Rabe, M., Verdes, D. and Seeger, S.: Understanding protein adsorption phenomena at solid surfaces, Advances in colloid and interface science, 162(1–2), 87–106, doi:10.1016/j.cis.2010.12.007, 2011.

Rani, A. S., Das, M. L. M., and Satyanarayana, S.: Preparation and characterization of amyloglucosidase adsorbed on activated charcoal, J. Mol. Cata. B-Enzym., 10, 471–476, doi:10.1016/s1381-1177(99)00116-2, 2000.

Reuter, H., Gensel, J., Elvert, M., and Zak, D.: Evidence for preferential protein depolymerization in wetland soils in response to external nitrogen availability provided by a novel FTIR routine, Biogeosciences, 17, 499–514, doi:10.5194/bg-17-499-2020, 2020.

Roden, E. E.: Analysis of long-term bacterial vs. chemical Fe(III) oxide reduction kinetics. Geochim. Cosmochim. Ac., 68, 3205–3216, doi:10.1016/j.gca.2004.03.028, 2004.

Roden, E. E.: Geochemical and microbiological controls on dissimilatory iron reduction, C. R. Geosci., 338, 456–467, doi:10.1016/j.crte.2006.04.009, 2006.

Roden, E. E. and Wetzel, R. G.: Organic carbon oxidation and suppression of methane production by microbial Fe(III) oxide reduction in vegetated and unvegetated freshwater wetland sediments, Limnol. Oceanogr., 41, 1733–1748, doi:10.4319/lo.1996.41.8.1733, 1996.

Rodionov, A., Amelung, W., Urusevskaja, I., and Zech, W.: Origin of the enriched labile fraction (ELF) in Russian Chernozems with different site history, Geoderma, 102, 299–315, doi:10.1016/s0016-7061(01)00038-6, 2001.

Sahrawat, K. L.: Ammonium production in submerged soils and sediments: the role of reducible iron, Commun.Soil. Sci. Plan., 35, 399–411, doi:10.1081/css-120029721, 2004.

1030   Sahrawat, K. L. and Narteh, L. T.: Organic matter and reducible iron control of ammonium production in submerged soils, Commun.Soil. Sci. Plan., 32, 1543–1550, doi:10.1081/css-100104211, 2001.

Sarkar, J. M. and Burns, R. G.: Synthesis and properties of β-d-glucosidasephenolic copolymers as analogues of soil humic-enzyme complexes, Soil Biol. Biochem., 16, 619–625, doi:10.1016/0038-0717(84)90082-8, 1984.

Schimel, J. P. and Bennett, J.: Nitrogen mineralization: challenges of a changing paradigm, Ecology, 85, 591–602,
1035   doi:10.1890/03-8002, 2004.

Schimel, J., Becerra, C. A., and Blankinship, J.: Estimating decay dynamics for enzyme activities in soils from different ecosystems, Soil. Biol. Biochem., 114, 5–11, doi:10.1016/j.soilbio.2017.06.023, 2017.

Schöning, I., Knicker, H., and Kögel-Knabner, I.: Intimate association between O/N-alkyl carbon and iron oxides in clay fractions of forest soils, Org. Geochem., 36, 1378–1390, doi:10.1016/j.orggeochem.2005.06.005, 2005.

1040   Schulten, H. R. and Schnitzer, M.: The chemistry of soil organic nitrogen: a review, Biol. Fert. Soil., 26, 1–15, doi:10.1007/s003740050335, 1997.

Scott, E. E. and Rothstein, D. E.: The dynamic exchange of dissolved organic matter percolating through six diverse soils, Soil. Biol. Biochem., 69, 83–92, doi:10.1016/j.soilbio.2013.10.052, 2014.

Servagent-Noinville, S., Revault, M., Quiquampoix, H., and Baron, M.: Conformational changes of bovine serum albumin
1045   induced by adsorption on different clay surfaces: FTIR analysis. J. Colloid. Interface. Sci., 221, 273–283, doi:10.1006/jcis.1999.6576, 2000.

Shah, F., Nicolás, C., Bentzer, J., Ellström, M., Smits, M., Rineau, F., Canbäck, B., Floudas, D., Carleer, R., Lackner, G., Braesel, J., Hoffmeister, D., Henrissat, B., Ahrén, D., Johansson, T., Hibbett, D. S., Martin, F., Persson, P., and Tunlid, A.: Ectomycorrhizal fungi decompose soil organic matter using oxidative mechanisms adapted from saprotrophic ancestors, New.
1050   Phytol., 209, 1705–1719, doi:10.1111/nph.13722, 2016.

Shimizu, M., Zhou, J., Schröder, C., Obst, M., Kappler, A., and Borch, T.: Dissimilatory reduction and transformation of ferrihydrite-humic acid coprecipitate, Environ. Sci. Technol., 47, 13375–13384, doi:10.1021/es402812j, 2013.

Silva-Sánchez, A., Soares, M., and Rousk, J.: Testing the dependence of microbial growth and carbon use efficiency on nitrogen availability, pH, and organic matter quality, Soil. Biol. Biochem., 134, 25–35, doi:10.1016/j.soilbio.2019.03.008,
1055   2019.

Silva, L. C., Doane, T. A., Corrêa, R. S., Valverde, V., Pereira, E. I., and Horwath, W. R.: Iron-mediated stabilization of soil carbon amplifies the benefits of ecological restoration in degraded lands, Ecol. Appl., 25, 1226–34, doi:10.1890/14-2151.1, 2015.

Sinsabaugh, R. L.: Phenol oxidase, peroxidase and organic matter dynamics of soil. Soil. Biol. Biochem., 42, 391–404,
1060   doi:10.1016/j.soilbio.2009.10.014, 2010.

Sinsabaugh, R. L., Hill, B. H., and Follstad Shah, J. J.: Ecoenzymatic stoichiometry of microbial organic nutrient acquisition in soil and sediment, Nature, 462, 795–798, doi:10.1038/nature08632, 2009.

Six, J., Feller, C., Denef, K., Ogle, S. M., Sa, J. C. d. M., and Albrecht, A.: Soil organic matter, biota and aggregation in temperate and tropical soils - Effects of no-tillage, Agronomie, 22, 755–775, doi:10.1051/agro:2002043, 2002.

1065 Sposito, G.: Electron shuttling by natural organic matter: twenty years after, in: Aquatic redox chemistry, Am. Chem. S., 113–127, doi:10.1021/bk-2011-1071.ch006, 2011.

Stadtman, E. R. and Levine, R. L.: Free radical-mediated oxidation of free amino acids and amino acid residues in proteins, Amino Acids, 25, 207–18, doi:10.1007/s00726-003-0011-2, 2003.

Stucki, J. W.: Properties and behaviour of iron in clay minerals, in: Developments in clay science, edited by: Bergaya F. and

1070 Lagaly, G., Elsevier, 559–611, doi:10.1016/b978-0-08-098258-8.00018-3, 2013.

Suda, A. and Makino, T.: Functional effects of manganese and iron oxides on the dynamics of trace elements in soils with a special focus on arsenic and cadmium: A review, Geoderma, 270, 68–75, doi:10.1016/j.geoderma.2015.12.017, 2016.

Swenson, T. L., Bowen, B. P., Nico, P. S., and Northen, T. R.: Competitive sorption of microbial metabolites on an iron oxide mineral, Soil Biol. Biochem., 90, 34–41, doi:10.1016/j.soilbio.2015.07.022, 2015.

1075 Tabatabai, M.: Effects of trace elements on urease activity in soils, Soil Biol. Biochem., 9, 9–13, doi:10.1016/0038-0717(77)90054-2, 1977.

Tamrat, W. Z., Rose, J., Grauby, O., Doelsch, E., Levard, C., Chaurand, P., and Basile-Doelsch, I.: Soil organo-mineral associations formed by co-precipitation of Fe, Si and Al in presence of organic ligands, Geochim. Cosmochim. Ac., 260, 15–28, doi:10.1016/j.gca.2019.05.043, 2019.

1080 Tan, W., Yuan, Y., Zhao, X., Dang, Q., Yuan, Y., Li, R., Cui, D., and Xi, B.: Soil solid-phase organic matter-mediated microbial reduction of iron minerals increases with land use change sequence from fallow to paddy fields, Sci.Total. Environ., 676, 378–386, doi:10.1016/j.scitotenv.2019.04.288, 2019.

Tian, Z., Wang, T., Tunlid, A., and Persson, P.: proteolysis of iron oxide-associated bovine serum albumin. Environ. Sci. Technol., 54, 5121–5130, doi:10.1021/acs.est.0c00860, 2020.

1085 Tietjen, T. and Wetzel, R. G.: Extracellular enzyme-clay mineral complexes: Enzyme adsorption, alteration of enzyme activity, and protection from photodegradation, Aquat. Ecol., 37, 331–339, doi:10.1023/b:aeco.0000007044.52801.6b, 2003.

Tong, M., Yuan, S., Ma, S., Jin, M., Liu, D., Cheng, D., Liu, X., Gan, Y., and Wang, Y.: Production of abundant hydroxyl radicals from oxygenation of subsurface sediments, Environ. Sci. Technol., 50, 214–221, doi:10.1021/acs.est.5b04323, 2016.

Treat, C. C., Jones, M. C., Camill, P., Gallego-Sala, A., Garneau, M., Harden, J. W., Hugelius, G., Klein, E. S., Kokfelt, U.,

1090 Kuhry, P., Loisel, J., Mathijssen, P. J. H., O'Donnell, J. A., Oksanen, P. O., Ronkainen, T. M., Sannel, A. B. K., Talbot, J., Tarnocai, C., and Väliranta, M.: Effects of permafrost aggradation on peat properties as determined from a pan-Arctic synthesis of plant macrofossils, J. Geophys. Res-Biogeo., 121, 78–94, doi:10.1002/2015jg003061, 2016a.

Treat, C. C., Wollheim, W. M., Varner, R. K., and Bowden, W. B.: Longer thaw seasons increase nitrogen availability for leaching during fall in tundra soils, Environ. Res. Lett., 11, 064013, doi:10.1088/1748-9326/11/6/064013, 2016b.

1095   Trusiak, A., Treibergs, L. A., Kling, G. W., and Cory, R. M.: The role of iron and reactive oxygen species in the production of CO2 in arctic soil waters, Geochim. Cosmochim. Ac., 224, 80–95, doi:10.1016/j.gca.2017.12.022, 2018.

Turner, S., Schippers, A., Meyer-Stüve, S., Guggenberger, G., Gentsch, N., Dohrmann, R., Condron, L. M., Eger, A., Almond, P. C., Peltzer, D. A., Richardson, S. J., and Mikutta, R.: Mineralogical impact on long-term patterns of soil nitrogen and phosphorus enzyme activities, Soil. Biol. Biochem., 68, 31–43, doi:10.1016/j.soilbio.2013.09.016, 2014.

1100   Van Bodegom, P. M., Broekman, R., Van Dijk, J., Bakker, C., and Aerts, R.: Ferrous iron stimulates phenol oxidase activity and organic matter decomposition in waterlogged wetlands, Biogeochemistry, 76, 69–83, doi:10.1007/s10533-005-2053-x, 2005.

Van Veen, J. A., and Kuikman, P. J.: Soil structural aspects of decomposition of organic matter by micro-organisms, Biogeochemistry, 11, 213–233, doi:10.1007/bf00004497, 1990.

1105   Vitousek, P. M. and Howarth, R. W.: Nitrogen limitation on land and in the sea: How can it occur?, Biogeochemistry, 13, 87–115, doi:10.1007/bf00002772, 1991.

Vogel, C., Mueller, C. W., Höschen, C., Buegger, F., Heister, K., Schulz, S., Schloter, M., and Kögel-Knabner, I.: Submicron structures provide preferential spots for carbon and nitrogen sequestration in soils, Nat. Commun., 5, 1–7, doi:10.1038/ncomms3947, 2014.

1110   Vogel, C., Heister, K., Buegger, F., Tanuwidjaja, I., Haug, S., Schloter, M., and Kögel-Knabner, I.: Clay mineral composition modifies decomposition and sequestration of organic carbon and nitrogen in fine soil fractions, Biol. Fert. Soil., 51, 427–442, doi:10.1007/s00374-014-0987-7, 2015.

Wade, J., Waterhouse, H., Roche, L. M., and Horwath, W. R.: Structural equation modeling reveals iron (hydr)oxides as a strong mediator of N mineralization in California agricultural soils, Geoderma, 315, 120–129, 1115   doi:10.1016/j.geoderma.2017.11.039, 2018.

Wagai, R. and Mayer, L. M.: Sorptive stabilization of organic matter in soils by hydrous iron oxides, Geochim. Cosmochim. Ac., 71, 25–35, doi:10.1016/j.gca.2006.08.047, 2007.

Wagai, R., Kajiura, M., and Asano, M.: Iron and aluminum association with microbially processed organic matter via meso-density aggregate formation across soils: organo-metallic glue hypothesis, Soil, 6, 597–627, doi:10.5194/soil-6-597-2020, 1120   2020.

Wanek, W., Mooshammer, M., Blöchl, A., Hanreich, A., and Richter, A.: Determination of gross rates of amino acid production and immobilization in decomposing leaf litter by a novel 15N isotope pool dilution technique, Soil. Biol. Biochem., 42, 1293–1302, doi:10.1016/j.soilbio.2010.04.001, 2010.

Wang, B., Lerdau, M., and He, Y.: Widespread production of nonmicrobial greenhouse gases in soils. Glob. Change. Biol., 1125   23, 4472–4482, doi:10.1111/gcb.13753, 2017.

Wang, M., Hu, R., Zhao, J., Kuzyakov, Y., and Liu, S.: Iron oxidation affects nitrous oxide emissions via donating electrons to denitrification in paddy soils, Geoderma, 271, 173–180, doi:10.1016/j.geoderma.2016.02.022, 2016.

Wang, X.-C. and Lee, C.: Adsorption and desorption of aliphatic amines, amino acids and acetate by clay minerals and marine sediments, Mar. Chem., 44, 1–23, doi:10.1016/0304-4203(93)90002-6, 1993.

Wardle, D. A., Bardgett, R. D., Klironomos, J. N., Setälä, H., van der Putten, W. H., and Wall, D. H.: Ecological linkages between aboveground and belowground biota, Science, 304, 1629–33, doi:10.1126/science.1094875, 2004.

Warren, C.: What are the products of enzymatic cleavage of organic N?, Soil. Biol.Biochem., 154, 108152, doi:10.1016/j.soilbio.2021.108152, 2021.

Wei, Y., Wu, X., Xia, J., Shen, X., and Cai, C.: Variation of Soil Aggregation along the Weathering Gradient: Comparison of Grain Size Distribution under Different Disruptive Forces, PLOS ONE, 11, e0160960, doi:10.1371/journal.pone.0160960, 2016.

Whalen, E. D., Grandy, A. S., Sokol, N. W., Keiluweit, M., Ernakovich, J., Smith, R. G., and Frey, S. D.: Clarifying the evidence for microbial- and plant-derived soil organic matter, and the path toward a more quantitative understanding, Glob. Change. Biol., 28, 7167–7185, doi: 10.1111/gcb.16413, 2022.

Wilmoth, J. L.: Redox heterogeneity entangles soil and climate interactions, Sustainability, 13, 10084, doi:10.3390/su131810084, 2021.

Wilmoth, J. L., Moran, M. A., and Thompson, A.: Transient O2 pulses direct Fe crystallinity and Fe(III)-reducer gene expression within a soil microbiome, Microbiome, 6, 1–14, doi:10.1186/s40168-018-0574-5, 2018.

Wilson, J. S. and Baldwin, D. S.: Exploring the 'Birch effect' in reservoir sediments: influence of inundation history on aerobic nutrient release, Chem. Ecol., 4, 379–386, doi:10.1080/02757540802497582, 2008.

Wu, X., Cai, C., Wang, J., Wei, Y., and Wang, S.: Spatial variations of aggregate stability in relation to sesquioxides for zonal soils, South-central China, Soil. Till. Res., 157, 11–22, doi:10.1016/j.still.2015.11.005, 2016.

Xu, C., Zhang, K., Zhu, W., Xiao, J., Zhu, C., Zhang, N., Yu, F., Li, S., Zhu, C., Tu, Q., Chen, X., Zhu, J., Hu, S., Koide, R. T., Firestone, M. K., and Cheng, L.: Large losses of ammonium-nitrogen from a rice ecosystem under elevated CO(2), Sci. Adv., 6, doi:10.1126/sciadv.abb7433, 2020.

Xu, J., Sahai, N., Eggleston, C. M., and Schoonen, M. A. A.: Reactive oxygen species at the oxide/water interface: Formation mechanisms and implications for prebiotic chemistry and the origin of life, Earth. Planet. Sc. Lett., 363, 156–167, doi:10.1016/j.epsl.2012.12.008, 2013.

Xu, Z., Yang, Z., Wang, H., and Jiang, J.: Assessing redox properties of natural organic matters with regard to electron exchange capacity and redox-active functional groups, J. Chem., 2020, 1–8, doi:10.1155/2020/2698213, 2020.

Xue, B., Huang, L., Huang, Y., Zhou, F., Li, F., Kubar, K. A., Li, X., Lu, J., and Zhu, J.: Roles of soil organic carbon and iron oxides on aggregate formation and stability in two paddy soils. Soil. Till. R., 187, 161–171, doi:10.1016/j.still.2018.12.010, 2019.

Yan, J., Pan, G., Li, L., Quan, G., Ding, C., and Luo, A.: Adsorption, immobilization, and activity of β-glucosidase on different soil colloids, J. Colloid. Interface. Sci., 348, 565–570, doi:10.1016/j.jcis.2010.04.044, 2010.

Yang, G., Peng, Y., Marushchak, M. E., Chen, Y., Wang, G., Li, F., Zhang, D., Wang, J., Yu, J., Liu, L., Qin, S., Kou, D., and Yang, Y.: Magnitude and pathways of increased nitrous oxide emissions from uplands following permafrost thaw, Environ. Sci. Technol., 52, 9162–9169, doi:10.1021/acs.est.8b02271, 2018.

Yang, W. H., Weber, K. A., and Silver, W. L.: Nitrogen loss from soil through anaerobic ammonium oxidation coupled to iron reduction, Nat. Geosci.,5, 538–541, doi:10.1038/ngeo1530, 2012.

Yang, Z., Gao, J., Yang, M., and Sun, Z.: Effects of freezing intensity on soil solution nitrogen and microbial biomass nitrogen in an alpine grassland ecosystem on the Tibetan Plateau, China, J. Arid. Land., 8, 749–759, doi:10.1007/s40333-016-0012-0, 2016.

Yang, Z., Liao, Y., Fu, X., Zaporski, J., Peters, S., Jamison, M., Liu, Y., Wullschleger, S. D., Graham, D. E., and Gu, B.: Temperature sensitivity of mineral-enzyme interactions on the hydrolysis of cellobiose and indican by β-glucosidase, Sci.Total. Environ., 686, 1194–1201, doi:10.1016/j.scitotenv.2019.05.479, 2019.

Yu, G. H., Sun, F. S., Yang, L., He, X.H., and Polizzotto, M. L.: Influence of biodiversity and iron availability on soil peroxide: Implications for soil carbon stabilization and storage, Land. Degrad. Dev., 31, 463–472, doi:10.1002/ldr.3463, 2020.

Yu, W. H., Li, N., Tong, D. S., Zhou, C. H., Lin, C. X., and Xu, C. Y.: Adsorption of proteins and nucleic acids on clay minerals and their interactions: A review, Appl.Clay. Sci., 80–81, 443–452, doi:10.1016/j.clay.2013.06.003, 2013.

Yuan, Y., Zhao, W., Zhang, Z., Xiao, J., Li, D., Liu, Q., Yin, H., and Yin, H.: Impacts of oxalic acid and glucose additions on N transformation in microcosms via artificial roots, Soil. Biol. Biochem., 121, 16–23, doi:10.1016/j.soilbio.2018.03.002, 2018.

Zhang, J., Presley, G. N., Hammel, K. E., Ryu, J. S., Menke, J. R., Figueroa, M., Hu, D., Orr, G., and Schilling, J. S.: Localizing gene regulation reveals a staggered wood decay mechanism for the brown rot fungus *Postia placenta*.,Proc. Natl. Acad. Sci. USA., 113, 10968–73, doi:10.1073/pnas.1608454113, 2016.

Zhang, X. W., Kong, L. W., Cui, X. L., and Yin, S.: Occurrence characteristics of free iron oxides in soil microstructure: evidence from XRD, SEM and EDS, B. Eng. Geol. Environ., 75, 1493–1503, doi:10.1007/s10064-015-0781-2, 2016.

Zhang, Y. and Scherer, H.: Mechanisms of fixation and release of ammonium in paddy soils after floodingII. Effect of transformation of nitrogen forms on ammonium fixation, Biol. Fert. Soil., 31, 517–521, doi:10.1007/s003740000202, 2000.

Zhao, L., Dong, H., Kukkadapu, R., Agrawal, A., Liu, D., Zhang, J., and Edelmann, R. E.: Biological oxidation of Fe(II) in reduced nontronite coupled with nitrate reduction by *Pseudogulbenkiania* sp. Strain 2002, Geochim. Cosmochim. Act., 119, 231–247, doi:10.1016/j.gca.2013.05.033, 2013.

Zhao, Q., Callister, S. J., Thompson, A. M., Kukkadapu, R. K., Tfaily, M. M., Bramer, L. M., Qafoku, N. P., Bell, S. L., Hobbie, S. E., Seabloom, E. W., Borer, E. T., and Hofmockel, K. S.: Strong mineralogic control of soil organic matter composition in response to nutrient addition across diverse grassland sites, Sci. Total. Environ., 736, 137839, doi:10.1016/j.scitotenv.2020.137839, 2020.

Zhou, G. W., Yang, X. R., Li, H., Marshall, C. W., Zheng, B. X., Yan, Y., Su, J. Q., and Zhu, Y. G.: Electron shuttles enhance anaerobic ammonium oxidation coupled to Iron(III) reduction, Environ. Sci. Technol., 50, 9298–307, doi:10.1021/acs.est.6b02077, 2016.

1195 Zhu, B., Gutknecht, J. L. M., Herman, D. J., Keck, D. C., Firestone, M. K., and Cheng, W.: Rhizosphere priming effects on soil carbon and nitrogen mineralization, Soil. Biol. Biochem., 76, 183–192, doi:10.1016/j.soilbio.2014.04.033, 2014.

Zhu-Barker, X., Cavazos, A. R., Ostrom, N. E., Horwath, W. R., and Glass, J. B.: The importance of abiotic reactions for nitrous oxide production, Biogeochemistry, 126, 251–267, doi:10.1007/s10533-015-0166-4, 2015.

Zinder, B., Furrer, G., and Stumm, W.: The coordination chemistry of weathering: II. Dissolution of Fe(III) oxides, Geochim.

1200 Cosmochim. Ac., 50, 1861–1869, doi:10.1016/0016-7037(86)90244-9, 1986.

Zou, J., Huang, J., Zhang, H., and Yue, D.: Evolution of humic substances in polymerization of polyphenol and amino acid based on non-destructive characterization, Front. Environ. Sci. Eng., 15, doi:10.1007/s11783-020-1297-y, 2020.