Impact of Biogenic Magnetite Formation and Transformation on Biogeochemical Cycles

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Magnetite nanoparticles.
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Magnetite is a redox-active mineral that can form from both abiotic and biotic processes, and plays an active role in different biogeochemical cycles. Biogenic magnetite particles have properties that differ from their abiogenic counterparts in a variety of ways, including their size, chemical purity, magnetic properties, and association with biomass-derived organic matter. These properties directly influence magnetite reactivity—in particular its sorbent and redox behavior—affecting its association with metals, oxyanions, and other compounds in the environment. Biogenic (and abiogenic) magnetite particles are involved in redox processes by storing electrons, functioning as biogeobatteries, and by transferring electrons between microbial cells or between cells and inorganic constituents. Thus, magnetite influences the fate of contaminants and nutrients in the environment.

KEYWORDS: iron; biogeobattery; reactivity; microbial Fe(II) oxidation; microbial Fe(III) reduction; redox biogeochemistry

FORMATION OF BIOGENIC MAGNETITE

Iron is present in almost every environment on Earth, which comes as no surprise due to its high concentration in the Earth's crust. A large fraction of this iron pool enters soils, sediments, and other ecosystems, and is involved in various biogeochemical cycles as mediated by different types of microorganisms. Iron typically exists in two oxidation states: reduced (ferrous iron, Fe(II)) and oxidized (ferric iron, Fe(III)). A number of microorganisms have been identified in recent decades that cycle iron between these oxidation states to live in specific environments (Kappler et al. 2021). While many organisms, including humans, require oxygen (O_2) as an electron acceptor for respiration, Fe(III)-respiring microorganisms are capable of replacing O_2 with Fe(III). In contrast, Fe(II)-oxidizing microorganisms oxidize Fe(II) to Fe(III) as an energy source, coupled with the reduction of either O_2 (acidophilic or microaerophilic Fe(II)-oxidizers), nitrate (nitrate-reducing Fe(II)-oxidizers), or even CO_2 with the addition of light as an energy source (anoxygenic phototrophic Fe(II)-oxidizers) (Kappler et al. 2021). Not only does this microbial iron cycle contribute toward the rusting of cars in scrapyards and ships at the bottom of oceans, it also plays a major role in the formation and transformation of various iron minerals in the environment as well as to magnetic signatures in soils and sediments (FIG. 1).

Fe(II) is fairly soluble at neutral pH in the absence of O_2, reaching µM to low mM concentrations depending on the concentrations of sulfide, bicarbonate, or phosphate. In contrast, at neutral pH, the solubility of Fe(III) is much lower and it is found in the form of Fe(III) (oxyhydr)oxide minerals such as ferrihydrite (simplified formula $Fe(OH)_3$), goethite (α-FeOOH), or hematite (α-Fe$_2$O$_3$). In redox fluctuating or environments with gradients

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FIGURE 1 Examples of habitats where iron plays an active biogeochemical role: the highly acidic, Fe-rich Rio Tinto in Spain (**TOP LEFT**), in a subsurface aquifer sediment in the Hanoi area (Vietnam) (**TOP RIGHT**), in a marine sediment (Kalo Vig, Denmark, **BOTTOM LEFT**), and in a natural Fe-rich spring in the Engadin area, Switzerland (**BOTTOM RIGHT**). PHOTOS: ANDREAS KAPPLER.
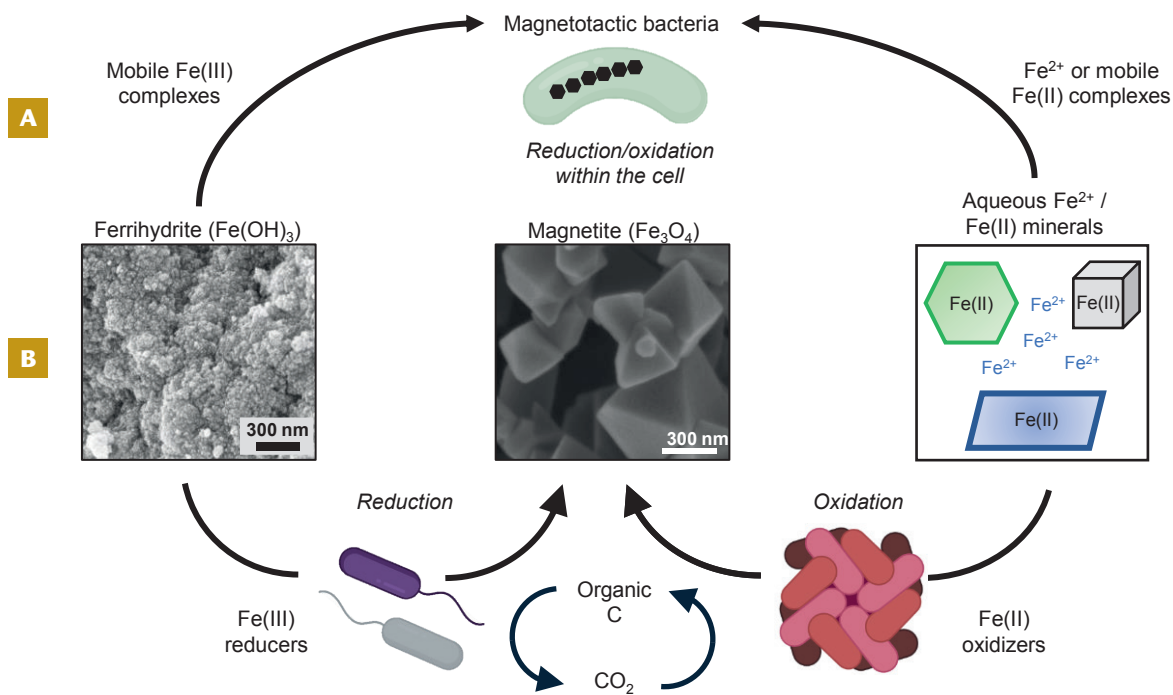
FIGURE 2 (**A**) Magnetotactic bacteria form chains of intracellular magnetite particles. (**B**) Formation of extracellular biogenic magnetite by various Fe(III)-reducing and Fe(II)-oxidizing microorganisms. In addition to the Fe cycle, they also participate in the carbon cycle through carbon fixation and degradation.

of O_2, where both Fe(III) reduction and Fe(II) oxidation occur in close temporal or spatial proximity, the formation of mixed-valent iron minerals such as green rust (e.g., carbonate green rust ($Fe^{II}_4Fe^{III}_2(OH)_{12}[CO_3]\cdot3H_2O$)) and magnetite ($Fe_3O_4$) are common (Usman et al. 2018). Magnetite has an ideal stoichiometric Fe(II)/Fe(III) ratio of 1:2. Consequently, the formation of magnetite requires the co-existence of Fe(III) and Fe(II) during the precipitation process, which is facilitated when dissolved Fe(II) sorbs to short-range ordered (SRO) Fe(III) oxyhydroxide minerals. The mechanistic pathways that enable adsorption of Fe(II) on SRO Fe(III) phases thereby promote magnetite formation.

Because magnetite contains both Fe(II) and Fe(III), both microbial Fe(III) reduction and Fe(II) oxidation can, in principle, induce the formation of biogenic magnetite. However, the formation of magnetite by Fe(II)-oxidizing bacteria has been described very rarely (Miot et al. 2014 and references therein) (FIG. 2). The nitrate-reducing Fe(II)-oxidizer *Acidovorax* sp. BoFeN1 produces magnetite during Fe(II) oxidation in the presence of green rust and existing magnetite particles (Miot et al. 2014). Potentially small amounts of magnetite are formed by the phototrophic Fe(II)-oxidizer *Rhodopseudomonas palustris* TIE-1 and the nitrate-reducing Fe(II)-oxidizer *Dechlorosoma suillum* (Miot et al. 2014 and references therein). In contrast to the nitrate-reducing and phototrophic Fe(II)-oxidizers that live in anoxic conditions, magnetite formation has not been described for microaerophilic Fe(II)-oxidizers (using O_2 as electron acceptor for Fe(II) oxidation under microoxic conditions, i.e., conditions with low O_2 concentrations). It is probably challenging to form magnetite in Fe(II)-oxidizing laboratory cultures because high cell numbers (10^7–10^9 cells/mL) are usually involved in such experiments. These high cell numbers lead to fast Fe(II) oxidation that prevents sufficient accumulation of sorbed Fe(II) on precipitating Fe(III) minerals. However, in natural systems, magnetite formation via Fe(II)-oxidizers may be more favorable as Fe(II)-oxidizer cell numbers tend to be lower and those cells likely also have lower metabolic oxidation rates due to limitations in substrates, nutrients, and less favorable physiochemical conditions.

In contrast to the microbial Fe(II) oxidation route, an excess of Fe(III) minerals is already present during the microbial Fe(III) mineral reduction route. During reduction, Fe(II) rapidly adsorbs to existing Fe(III) mineral surfaces and can induce mineral transformation. The rate of Fe(III) mineral reduction—particularly for the mineral ferrihydrite—can determine the type of secondary mineral that forms. Very low reduction rates and the associated low concentrations of Fe(II) induce a dissolution–reprecipitation transformation of ferrihydrite to goethite, while very rapid reduction rates can dissolve the Fe(III) mineral more quickly than magnetite can form. This leads to either the release of aqueous Fe^{2+} or—depending on the type of anions present—the precipitation of Fe(II) minerals such as siderite, vivianite, and mackinawite. Ferrihydrite is efficiently converted to magnetite at intermediate reduction rates. In addition to Fe(III) reduction rates, the total amount of Fe(III) minerals present and the presence of other environmentally relevant components, such as natural organic matter (humic substances) or phosphate, can influence the interactions between Fe(II) and the mineral surface, thus limiting or even preventing the formation of magnetite.

Magnetotactic bacteria (MTB) can produce chains of intracellular magnetic particles (either magnetite or greigite, Fe_3S_4) in organelle-like structures, called magnetosomes, within their cytoplasm (FIG. 2; see also Byrne 2023 this issue; Slotznick 2023 this issue). The formation and arrangement of the magnetic particles are tightly controlled by a set of genes that encode the magnetosome—the compartment that hosts the magnetic particles. These bacteria are ubiquitous and phylogenetically diverse, and are often found at oxic–anoxic interfaces where they utilize the magnetic particles to help them navigate along Earth's magnetic field. Recent studies show that MTB also accumulate a large intracellular pool of Fe that is not hosted within magnetic particles (Amor et al. 2020a; 2020b).

In laboratory cultures, Fe(III)-reducers are estimated to produce ~5000 times more extracellular magnetite per dry cell biomass than MTB (Moskowitz et al. 1993). This is partly due to the high level (mM) of solid-phase Fe(III) available to Fe(III)-reducers compared with the low level (µM) of dissolved Fe supplied to MTB. In natural systems, extracellular magnetite formation could be limited in environments with low Fe(III) contents and organic matter. A recent study conservatively estimated that intracellular magnetite formed by MTB accounts for a dissolved Fe removal flux of around 10^5 to 10^8 kg y^{-1}, which is comparable to the global flux of dissolved Fe to the ocean (Amor et al. 2020a). It is presently unknown which of these pathways are the primary route for biogenic magnetite formation; we speculate that the dominance of either extracellular or intracellular pathways will vary based on environmental conditions.

DISTINCT PURITY AND PROPERTIES OF BIOGENIC MAGNETITE

Biogenic magnetite particles, produced either by MTB or by Fe(II)-oxidizing/Fe(III)-reducing bacteria, display distinct properties compared with abiogenic magnetite that influence their redox behavior, reactivities, and involvements in various biogeochemical cycles (see also Slotznick et al. 2023 this issue). The interest in differentiating biogenic and abiogenic magnetite was propelled by the initial assertion that magnetite particles in the meteorite ALH84001 originated from ancient MTB that lived on Mars. Six criteria were proposed as unique features of biogenic magnetite from MTB: (1) single domain size of 30–120 nm with a low aspect ratio, (2) chemical purity, (3) chain arrangement, (4) crystallographic perfection (i.e., low defects), (5) unusual crystal morphology that is not predictable by equilibrium with the surrounding solution, and (6) elongation along the [111] crystal plane. Such features were postulated to arise through millions of years of evolution to optimize the magnetite inclusions for magnetic-based navigation. Unfortunately, these proposed features are not unambiguous because abiogenic magnetite particles display wide variation in properties that can overlap with the size, shape, crystallinity, and trace metal content distributions of MTB-produced magnetite. Additionally, any chain arrangement structure can be lost when the biogenic magnetite particles fossilize and experience diagenetic and metamorphic processes.

To date, the chemical purity and magnetic properties of biogenic magnetite from MTB are the most promising and useful indicators of biogenicity (see also Byrne and Amor 2023 this issue). Amor et al. (2015) determined the partition coefficients of 34 elements between magnetite and aqueous solutions. The generally lower trace element incorporation into MTB-produced magnetite is likely due to active biological exclusion of trace elements within the magnetosome. The authors further suggested that the ratio of strontium to calcium could be particularly useful to determine the biogenicity of magnetite. Recent research has also affirmed that the magnetic properties of MTB magnetite are different from those of abiogenic magnetite, and that these differences can be preserved even after cell death. Confidently attributing these signals as signatures of MTB magnetite is challenging when an environment contains mixtures of magnetite from different origins, but much progress has been made in recent years to deconvolve signatures from magnetite mixtures (see Slotznick et al. 2023 this issue).

In contrast to MTB-produced magnetite, the production of extracellular magnetite by other Fe-metabolizing bacteria tends to produce magnetite particles with a wide size range from ~10 to >100 nm. These are similar in size, shape, and magnetic properties to abiogenic magnetite (Moskowitz et al. 1993). Nonetheless, biogenic magnetite particles can contain unique trace metal signatures such as higher Ni and lower Zn relative to abiogenic magnetite (Han et al. 2021). These trace metal signatures may be influenced by the formation of biogenic magnetite around the cell's microenvironments that are chemically distinct from the bulk solution.

Regardless of their formation pathways, all magnetite particles in the environment are associated with organic matter, with biogenic magnetite especially closely associated with cell-derived organics and extracellular polymeric substances. Even organic-free abiotically lab-synthesized magnetite (as well as other iron minerals) are quickly enveloped by a coating of natural organic matter upon entering the environment (Swindle et al. 2014). Association with organic matter imparts negative charges and/or hydrophobic properties to the surface, either in patches or as a complete coating depending on the carbon/iron ratio of the system, particle size, and the specific organics present. Surface modification can lead to an increased sorption of metal ions and/or organics to biogenic magnetite. At the same time, some of the mineral surface reactive sites can be blocked by organic matter or by organic-induced aggregation.

Biogenic and abiogenic magnetite particles vary in Fe(II)/Fe(III) ratio, size, organic matter association, and trace metal content, all of which contribute to their wide range of redox potentials (−267 to +253 mV versus standard hydrogen electrode; Bradley and Tratnyek 2019). Abiogenic magnetite is associated with lower redox potentials than magnetically separated magnetite from environmental samples, whereas no correlation has been found between Fe(II)/Fe(III) ratio and redox potential (Bradley and Tratnyek 2019). Particle size potentially contributes to a ~500-mV variation in redox potential within the 1–10-nm radius size range, but this has not been experimentally proven (Kappler et al. 2021). Additional microbial reduction or oxidation of biogenic magnetite can further influence their redox reactivity with implications for environmental remediation (Sundman et al. 2020).

MAGNETITE AS REDOX-ACTIVE CONSTITUENT IN THE ENVIRONMENT

The transfer of electrons between electron donors and acceptors is the central reaction in many biogeochemical processes and, in many cases, controls the rates and extent of turnover of organic substrates. A variety of naturally occurring compounds such as natural organic matter (NOM, humic material), biochar (pyrolyzed biomass), and redox-active mineral particles, such as mackinawite (FeS) and hematite, have been shown to facilitate electron transfer. Magnetite is redox active owing to its mixed-valent nature, i.e., the Fe(II) in magnetite can be oxidized or the Fe(III) can be partially reduced while maintaining the basic mineral structure. Consequently, magnetite can not only store electrons but also act as an electron shuttle to transfer electrons between microbial cells or between cells and external electron acceptors. These external electron acceptors include S, Mn, other Fe minerals, or redox-active trace metals, as well as redox active organics such as (hydro) quinones in NOM. This allows for the potential emergence of conductive networks of mineral–organic matrices in moist aggregates or sediments, linking any range of biological and inorganic entities (Dong et al. 2020 and references therein).
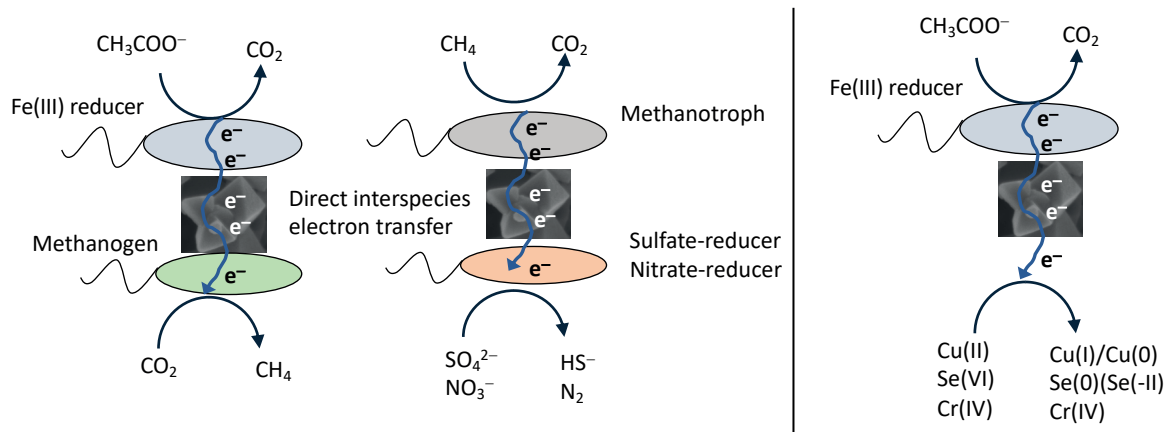
Magnetite facilitates electron transfer between microbial cells in a process called direct interspecies electron transfer (DIET) (Dong et al. 2020; FIG. 3). This is of relevance because in, many cases, the electron transfer between cells (or between cells and solid redox-active constituents) tends to limit the overall turnover rate. For example, methanogens can use DIET to access Fe(III) as electron acceptors (Dong et al. 2020)—via *Geobacter* sp. and perhaps other Fe(III)-reducers—and methane-oxidizers can use magnetite-mediated DIET to stimulate nitrate reduction by denitrifying microorganisms (Liang et al. 2022).

The reduction of Cu(II) by *Geobacter* species was also stimulated by magnetite (Qiu et al. 2020) where the authors suggest magnetite acts as both a geobattery (for storing electrons) and a geoconductor (for transferring electrons as conductor) (FIG. 3). Microbially produced/reduced magnetite can also reduce oxidized selenium (Se) to Se(0) or to Se(−2) and from Cr(VI) to Cr(IV).

The storage and release of electrons in magnetite can be temporally and spatially decoupled, leading to the description of magnetite as a "biogeobattery" (FIG. 4). As a consequence, under fluctuating redox conditions (including redox variations accompanying diurnal light–dark cycles), different groups of microorganisms can use magnetite either as an electron source or sink. For instance, the phototrophic Fe(II)-oxidizing bacterium *Rhodopseudomonas palustris* TIE-1 oxidizes Fe(II) in magnetite and uses the electrons for CO_2 fixation by photosynthesis under anoxic conditions in the light, whereas under anoxic conditions in the dark, *Geobacter sulfurreducens* can reduce the Fe(III) in magnetite and thus recharge the biogeobattery again for the next daylight period (Dong et al. 2020 and references therein). The use of magnetite as a biogeobattery is not limited to these organisms, but can also be coupled to magnetite reduction by *Shewanella oneidensis* MR-1, which alternates with magnetite oxidation by the nitrate-reducing Fe(II)-oxidizer *Acidovorax* sp. BoFeN1. A biogeobattery, such as magnetite, has potential biotechnological significance owing to its connection to N-cycling and N-removal from wastewater—the oxidation of ammonium to N_2 can be coupled to the reduction of magnetite while the electrons stored from this process can then be used by nitrate-reducing microorganisms, converting the nitrate into harmless N_2 (Li et al. 2022). Magnetite biogeobatteries can also be of broader environmental relevance because the recharging of the battery can occur not only directly by microbial reduction but also by interaction of the magnetite with aqueous Fe(II) (Peng et al. 2018).

BIOGENIC MAGNETITE INFLUENCE ON BIOGEOCHEMICAL CYCLES OF CARBON, NUTRIENTS, AND CONTAMINANTS

Abiogenic and biogenic magnetite interact with pollutant, nutrient, and biogeochemical elemental cycles in the same manner as other Fe (oxyhydr)oxide minerals, while additionally engaging in both reductive and oxidative reactions. As in other Fe (oxyhydr)oxides, the surface of magnetite has three primary chemical arrangements (surface functional groups) where reactions with aqueous ions can take place. These arrangements include the positively charged $\equiv$Fe-OH^{2+}, uncharged $\equiv$Fe-OH^0, and negatively charged Fe-O$^-$ functional groups, where $\equiv$Fe indicates an Fe atom on the surface. The proportion of these functional groups changes with solution pH (Danielsen and Hayes 2004).

Magnetite also exhibits a similar range of particle sizes (and thus specific surface areas) as other Fe (oxyhydr)oxides, extending from highly reactive nano-scale magnetite particles (10 nm) that are most common in biogenic forms to bulk minerals formed in hydrothermal systems as large as 10 mm (Cornell and Schwertmann 1996). The mineral not only attracts cations and anions (especially Ca^{2+}, Cl^-, NO_3^-, and NH_4^+) through typical electrostatic forces, but also forms strong (inner-sphere) bonds with C, P, Pb, Cu, Cu, Cd, Cr, U, Pd, and Pt (Usman et al. 2018 and references therein). The affinity of ions and other constituents for Fe (oxyhydr)oxide minerals (including magnetite) is directly proportional to mineral surface area and the density of surface functional groups. Magnetite has a similar density of functional groups and affinities for ions and soluble constituents as other Fe (oxyhydr)oxides; for instance, all Fe phases have largely similar attraction of P when the functional group density and surface area are similar (Daou et al. 2007). Importantly then, the small particle size (and thus high surface area to volume ratio) of biogenic magnetite positions it as a strong sorbent amongst the Fe (oxyhydr)oxides.

In much the same manner as other Fe (oxyhydr)oxides, magnetite serves as an electron acceptor, but also exhibits unique redox properties, reflecting its mixed-valence redox condition. Magnetite can acquire $\equiv$Fe(III)OFe(II)$^+$ or $\equiv$Fe(III)OFe(II)OH surface moieties (Danielsen and Hayes 2004) either by sorption of Fe^{2+} or exposure of octahedral ferrous sites. In either case, it appears the initially surface-adsorbed Fe(II) is incorporated into the magnetite mineral structure, often developing a surface layer with a higher Fe(II)/Fe(III) ratio than the ratio in the bulk phase (Gorski et al. 2010). Magnetite's stochiometric redox ratio has also been shown to govern the rate and extent of its redox reactivity (Gorski et al. 2010); this increased Fe(II)/
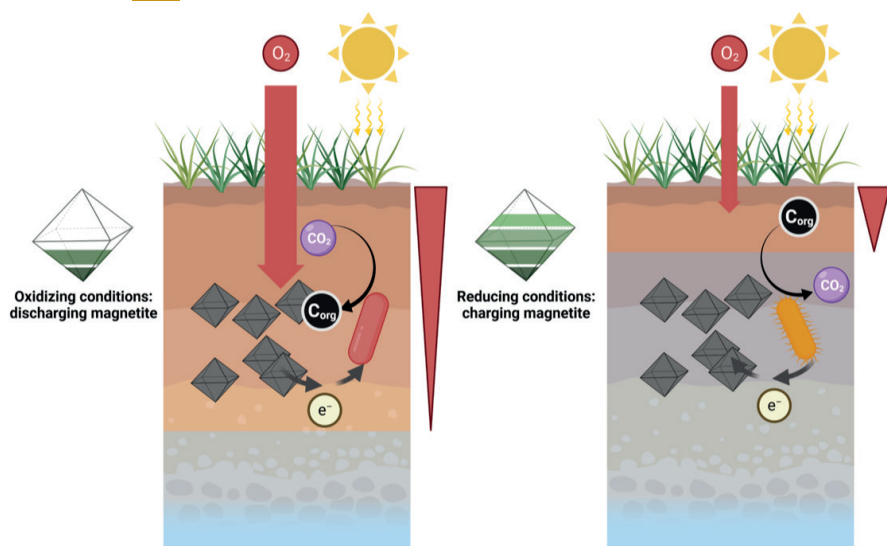
FIGURE 4 Magnetite functioning as biogeobattery: magnetite becomes discharged under oxidizing conditions (**LEFT**) where Fe(II)-oxidizing microorganisms (e.g., using O_2 reduction, nitrate reduction, or photosynthesis for Fe(II) oxidation) use electrons stored as reduced iron (Fe(II)) in magnetite for CO_2 fixation. Under reducing conditions (**RIGHT**), e.g., after soil flooding when O_2 diffusion into the soil is limited, Fe(III)-reducing microorganisms recharge the magnetite by dumping electrons into the magnetite and thus increasing its Fe(II)/Fe(III) ratio.

Fe(III) ratio in the surface layer may explain the common observation of increased magnetite reactivity following the addition of aqueous Fe^{2+}, which would rapidly sorb to the surface (Danielsen and Hayes 2004). More oxidized magnetite particles, with lower Fe(II)/Fe(III) ratios, take up more Fe(II) until stoichiometric magnetite forms, after which further aqueous Fe(II) uptake is limited. This mixed-valent aspect of magnetite allows it to serve as both an electron acceptor and donor—as discussed above—thus bridging the redox behavior of Fe (oxyhydr)oxides and ferrous mineral phases. Although Fe-substituted clay minerals can also serve as electron donors and acceptors, the rates of electron transfer are approximately two orders of magnitude faster in magnetite (Alexandrov et al. 2013). Thus, when present, biogenic magnetite is likely to be one of the most potent redox-active mineral phases in soils and sediments, especially considering its lab-documented participation in electron shuttling (DIET) and electron storage (battery) functions.

Extensive work has been done to examine magnetite's participation in—and catalysis of—redox reactions (Usman et al. 2018). Because redox reactions cannot occur unless chemical compounds are first adsorbed on the magnetite surface, factors governing the availability of surface functional groups are important. The degree of deprotonation of Fe-O functional groups (governed largely by pH) not only affects adsorption of chemical compounds (Martínez et al. 2006) but also the products of redox reactions (Danielsen and Hayes 2004). Equally important is the stoichiometry of the magnetite mineral and especially the surface layer, which can become enriched in Fe(II) ions when the mineral is present in aqueous solutions with Fe^{2+}(aq) ions, as discussed above (Gorski et al. 2010). Magnetite has been successfully explored as a catalyst of redox reactions, targeting the contaminants uranium, arsenic, and chromium (Sundman et al. 2020), CCl_4 (Danielsen and Hayes 2004), and even glycophosphate pesticides (Yang et al. 2018), among many other constituents (Gorski et al. 2010).

Magnetite likely plays an important role in biogeochemical and contaminant cycles either when present at relevant concentrations or when its unique redox properties are exploited. Near-shore sediment magnetic properties (and magnetite concentrations) often correlate with trace element concentrations, reflecting co-association of industrial pollution and magnetic particles (e.g., Zhang et al. 2007) that may have originated as zero-valent iron and formed magnetite upon oxidation. Here, the sorbent properties of magnetite likely contribute significantly to the retention of pollutant trace metals, either from the original industrial Fe source or from subsequent environmental exposure. Similarly, many placer sand deposits contain large fractions of magnetite and can influence local biogeochemical cycles through nutrient retention (Zaporski and Yang 2022). While in these above examples magnetite was likely formed abiotically, much of the magnetite found in fine-grained sediments from non-polluted sites is now generally regarded as biogenic, and often termed magnetofossils when used to interpret Earth history (Amor et al. 2020a; Slotznick et al. 2023 this issue). These bio-magnetite minerals are thought to have played a significant role in the biogeochemistry of oxic–anoxic transition zones—both during formation, when they likely were used by organisms for navigation in the Earth magnetic field, and during diagenesis, when they would have served as sorbents for carbon and nutrients or as electron acceptors/donors for respiration or assimilation metabolisms (Amor et al. 2020a).

Conventional wisdom suggests that the principal influence of magnetite on carbon cycle dynamics is through its influence on nutrient and organic carbon availability. In most environments, magnetite is not present at sufficient concentrations to be a quantitatively important electron acceptor for organic matter respiration. Even when it is present at concentrations as high as 30 weight percent or more, magnetite appears to have a stronger influence on carbon cycling by controlling phosphorous availability through sorption/desorption reactions (Zaporski and Yang 2022) than as an electron acceptor. However, novel investigations of magnetite's electron-shuttling properties (DIET as one example) in environmental systems are rapidly expanding and may change this perspective. For instance, it appears now that magnetite addition stimulates extracellular secretions that promote DIET performance (Dong et al. 2020). This may help explain observations of magnetite's acceleration of methane production in wastewater systems (Dong et al. 2020 and references within), and suggests that even small amounts of biogenic magnetite may create important linkages in electron shuttling systems in soils or sediments in concert with quinone-containing humic substances. For instance, magnetite can directly catalyze N redox transformations and may help explain N-sequestration to organic forms in forest soils (Matus et al. 2019).

EMERGING/POTENTIAL FUTURE APPLICATIONS OF BIOGENIC MAGNETITE

Magnetite is gaining increasing attention for industrial and environmental applications owing to the combination of its redox activity, conductive properties, natural abundance, and low toxicity. Magnetite electrodes show effective performance as components in lithium-ion batteries and for novel quantification of heavy metal ions

and organic pollutants in natural waters (see Gandarias et al. 2023 this issue). In these applications, the electrode is composed of a magnetite–carbon composite, with the added carbon serving to improve conductivity. Because biogenic magnetite particles are, in essence, already a magnetite–carbon composite, it may be intriguing to explore if biogenic magnetite exhibits better performance than abiogenic magnetite. To date, biogenic magnetite (from thermal alteration of biogenic lepidocrocite formed by *Leptothrix*) has been shown to be a suitable electrode material for lithium batteries (Girginov et al. 2017).

Magnetite is already commonly explored and deployed for remediation purposes, especially in the wastewater industry. Here, the sorbent properties of magnetite—common to all Fe (oxyhydr)oxides—are leveraged to capture contaminants. For instance, magnetite has been extensively explored as a binder for phosphorus in the water treatment and wastewater industries because it can be efficiently recovered via its magnetic properties (Castelo-Grande et al. 2021). Magnetic biosorbents, in which magnetite, ferrite, or other metal or metal nanoparticles are impregnated with biosorbents, is an emerging technology for wastewater treatment (Hassan et al. 2020). The advantage of these materials is that the sorbent can be optimized for the removal of specific contaminants, followed by efficient recovery and recycling of the magnetic particles post-treatment. While most magnetic biosorbents are currently manufactured using abiotic methods, new approaches to produce biogenic magnetite are being explored, for instance, as a method of chromium remediation.

ACKNOWLEDGMENTS

REFERENCES

Alexandrov V, Neumann A, Scherer MM, Rosso KM (2013) Electron exchange and conduction in nontronite from first-principles. The Journal of Physical Chemistry C 117: 2032-2040, doi: 10.1021/jp3110776

Amor M and 10 coauthors (2015) Chemical signature of magnetotactic bacteria. Proceedings of the National Academy of Sciences 112: 1699-1703, doi: 10.1073/pnas.1414112112

Amor M, Tharaud M, Gélabert A, Komeili A (2020a) Single-cell determination of iron content in magnetotactic bacteria: implications for the iron biogeochemical cycle. Environmental Microbiology 22: 823-831, doi: 10.1111/1462-2920.14708

Amor M and 7 coauthors (2020b) Magnetotactic bacteria accumulate a large pool of iron distinct from their magnetite crystals. Applied and Environmental Microbiology 86: 1-20, doi: 10.1128/AEM.01278-20

Bradley MJ, Tratnyek PG (2019) Electrochemical characterization of magnetite with agarose-stabilized powder disk electrodes and potentiometric methods. ACS Earth and Space Chemistry 3: 688-699, doi: 10.1021/acsearthspacechem.8b00200

Byrne JM, Amor M (2023) Biomagnetism: insights into magnetic minerals produced by microorganisms. Elements 19: 208-214

Castelo-Grande T and 6 coauthors (2021) Magnetic water treatment in a wastewater treatment plant: part I - sorption and magnetic particles. Journal of Environmental Management 281: 111872, doi: 10.1016/j.jenvman.2020.111872

Cornell RM, Schwertmann U (1996) The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses. VCH, 572 pp

Danielsen KM, Hayes KF (2004) pH dependence of carbon tetrachloride reductive dechlorination by magnetite. Environmental Science and Technology 38: 4745-4752, doi: 10.1021/es0496874

Daou TJ and 7 coauthors (2007) Phosphate adsorption properties of magnetite-based nanoparticles. Chemistry of Materials 19: 4494-4505, doi: 10.1021/cm071046v

Dong G and 9 coauthors (2020) Recent advances in the roles of minerals for enhanced microbial extracellular electron transfer. Renewable and Sustainable Energy Reviews 134: 110404, doi: 10.1016/j.rser.2020.110404

Gandarias L, Kimber RL, Ona-Nguema G (2023) Environmental, biomedical, and industrial applications of biogenic magnetite nanoparticles. Elements 19: 228-233

Girginov C and 6 coauthors (2017) A comparative study on application of biogenic hematite and magnetite as electrode materials in hybrid supercapacitors. Journal of Chemical Technology and Metallurgy 52: 557-563

Gorski CA, Nurmi JT, Tratnyek PG, Hofstetter TB, Scherer MM (2010) Redox behavior of magnetite: implications for contaminant reduction. Environmental Science and Technology 44: 55-60, doi: 10.1021/es9016848

Han X and 5 coauthors (2020) Effect of microbial biomass and humic acids on abiotic and biotic magnetite formation. Environmental Science and Technology 54: 4121-4130, doi: 10.1021/acs.est.9b07095

Hassan M, Naidu R, Du J, Liu Y, Qi F (2020) Critical review of magnetic biosorbents: their preparation, application, and regeneration for wastewater treatment. Science of The Total Environment 702: 134893, doi: 10.1016/j.scitotenv.2019.134893

Kappler A and 5 coauthors (2021) An evolving view on biogeochemical cycling of iron. Nature Reviews Microbiology 19: 360-374, doi: 10.1038/s41579-020-00502-7

Li S, Kappler A, Haderlein SB, Zhu YG (2022) Powering biological nitrogen removal from the environment by geobatteries. Trends in Biotechnology 40: 377-380, doi: 10.1016/j.tibtech.2021.10.008

Liang L and 6 coauthors (2022) Magnetite-mediated electrically connected community for shortening startup of methane-dependent denitrification in a membrane biofilm reactor. Chemical Engineering Journal 428: 132004, doi: 10.1016/j.cej.2021.132004

Martínez M, Giménez J, de Pablo J, Rovira M, Duro L (2006) Sorption of selenium(IV) and selenium(VI) onto magnetite. Applied Surface Science 252: 3767-3773, doi: 10.1016/j.apsusc.2005.05.067

Matus F and 8 coauthors (2019) Ferrous wheel hypothesis: abiotic nitrate incorporation into dissolved organic matter. Geochimica et Cosmochimica Acta 245: 514-524, doi: 10.1016/j.gca.2018.11.020

Miot J and 7 coauthors (2014) Formation of single domain magnetite by green rust oxidation promoted by microbial anaerobic nitrate-dependent iron oxidation. Geochimica et Cosmochimica Acta 139: 327-343, doi: 10.1016/j.gca.2014.04.047

Moskowitz BM, Frankel RB, Bazylinski DA (1993) Rock magnetic criteria for the detection of biogenic magnetite. Earth and Planetary Science Letters 120: 283-300, doi: 10.1016/0012-821X(93)90245-5

Peng H and 6 coauthors (2018) Reversible Fe(II) uptake/release by magnetite nanoparticles. Environmental Science: Nano 5: 1545-1555, doi: 10.1039/C8EN00328A

Qiu H and 9 coauthors (2020) The shuttling effects and associated mechanisms of different types of iron oxide nanoparticles for Cu(II) reduction by *Geobacter sulfurreducens*. Journal of Hazardous Materials 393: 122390, doi: 10.1016/j.jhazmat.2020.122390

Slotznick SP, Egli R, Lascu I (2023) Magnetofossils: relics and records of deep time and space. Elements 19: 215-221

Swindle AL, Madden ASE, Cozzarelli IM, Benamara M (2014) Size-dependent reactivity of magnetite nanoparticles: a field-laboratory comparison. Environmental Science and Technology 48: 11413-11420, doi: 10.1021/es500172p

Sundman A and 7 coauthors (2020) Effect of Fe-metabolizing bacteria and humic substances on magnetite nanoparticle reactivity towards arsenic and chromium. Journal of Hazardous Materials 384: 121450, doi: 10.1016/j.jhazmat.2019.121450

Usman M and 7 coauthors (2018) Magnetite and green rust: synthesis, properties and environmental applications of mixed-valent iron minerals. Chemical Reviews 118: 3251-3304, doi: 10.1021/acs.chemrev.7b00224

Yang Y, Deng Q, Yan W, Jing C, Zhang Y (2018) Comparative study of glyphosate removal on goethite and magnetite: adsorption and photo-degradation. Chemical Engineering Journal 352: 581-589, doi: 10.1016/j.cej.2018.07.058

Zaporski J, Yang Z (2022) Effects of magnetite on phosphorus storage and carbon cycling in Lake Michigan shoreline sediments. Applied Geochemistry 140: 105293, doi: 10.1016/j.apgeochem.2022.105293

Zhang W, Yu L, Lu M, Hutchinson SM, Feng H (2007) Magnetic approach to normalizing heavy metal concentrations for particle size effects in intertidal sediments in the Yangtze Estuary, China. Environmental Pollution 147: 238-244, doi: 10.1016/j.envpol.2006.08.003 ∎