



Photochemistry of iron in aquatic environments

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Light energy is a driver for many biogeochemical element cycles in aquatic systems. The sunlight-induced photochemical reduction of ferric iron (Fe(III)) photoreduction to ferrous iron (Fe(II)) by either direct ligand-to-metal charge transfer or by photochemically produced radicals can be an important source of dissolved Fe_{aq}²⁺ in aqueous and sedimentary environments. Reactive oxygen species (ROS) are formed by a variety of light-dependent reactions. Those ROS can oxidize Fe(II) or reduce Fe(III), and due to their high reactivity they are key oxidants in aquatic systems where they influence many other biogeochemical cycles. In oxic waters with circumneutral pH, the produced Fe(II) reaches nanomolar concentrations and serves as a nutrient, whereas in acidic waters, freshwater and marine sediments, which are rich in Fe(II), the photochemically formed Fe(II) can reach concentrations of up to 100 micromolar and be used as additional electron donor for acidophilic aerobic, microaerophilic, phototrophic and, if nitrate is present, for nitrate-reducing Fe(II)-oxidizing bacteria. Therefore, Fe(III) photoreduction may not only control the primary productivity in the oceans but has a tremendous impact on Fe cycling in the littoral zone of freshwater and marine environments. In this review, we summarize photochemical reactions involving Fe, discuss the role of ROS in Fe cycling, and highlight the importance of photoreductive processes in the environment.

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Environmental significance

Light drives a series of physico-chemical reactions in natural environments and it has a huge impact on the development of microbial life. Iron is required as trace element for almost any kind of living organisms and its provision in aquatic environments is controlled by iron(III) photoreduction. Here we summarize the current knowledge of the reaction network that connects light and aquatic environments *via* the redox cycling of iron and the consecutive formation of reactive oxygen species.

Light availability on Earth

The sun provides our planet with light and thereby with enormous amounts of energy.^{1,2} Light is electromagnetic radiation, propagating as wave through space.³ It consists of a wide range of wavelengths (electromagnetic spectrum) ranging from the very short and energy-rich gamma rays (<0.01 nm) to the very long and energy-poor radio waves (>10 cm). The visible light (VIS) of the electromagnetic spectrum covers only a narrow band of wavelengths ranging from 400 nm (violet) to 700 nm (red).³ Large parts of the electromagnetic spectrum coming from the sun are reflected or absorbed in the atmosphere, *e.g.* by ozone, aerosols or water vapor, before reaching the Earth's surface.^{4,5} Especially shorter wavelength radiation (<400 nm), which has the potential to photochemically damage cells,^{6,7} is absorbed in the atmosphere to a great extent (Fig. 1).⁴ On a cloudless day, typically 3–5% of the total surface irradiance is ultraviolet A (UVA; 320–400 nm) and

ultraviolet B (UVB; 280–320 nm) light,^{8–10} but the percentage depends on latitude, season, time of the day and absorbing substances in the atmosphere such as ozone.⁹ Light can also be seen as particles of energy (photons)¹¹ and light intensity can be denoted as photon flux in $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ (microeinstein) or as spectral irradiance in $\text{W m}^{-2} \text{nm}^{-1}$ giving the power of a particular wavelength of light.¹ The photon flux reaching the Earth's surface during the day is on average a few hundred¹ to 2000 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ under full sunlight.^{12,13} In lakes or in the ocean, the light intensity decreases exponentially with water depth by absorption and scattering⁴ and the light penetration depth into the water depends on concentration and composition of attenuating substances such as phytoplankton, particles or dissolved organic molecules in the water column as well as on wavelength (Fig. 1).⁷ In the clearest natural waters, visible light reaches a depth of 170 m with 1% of the surface irradiance remaining, whereas in highly turbid waters, this threshold is already reached in a few meters depth.^{7,14} The infrared wavelength region (IR, 700 nm to 100 μm) of the electromagnetic spectrum is absorbed most strongly in the water column, followed by ultraviolet (UV) light (1 nm to 400 nm) if the concentration of attenuating substances is low.^{15,16} The greatest transparency of clear ocean water lies with 480 nm in the blue region of the VIS range¹⁵ and

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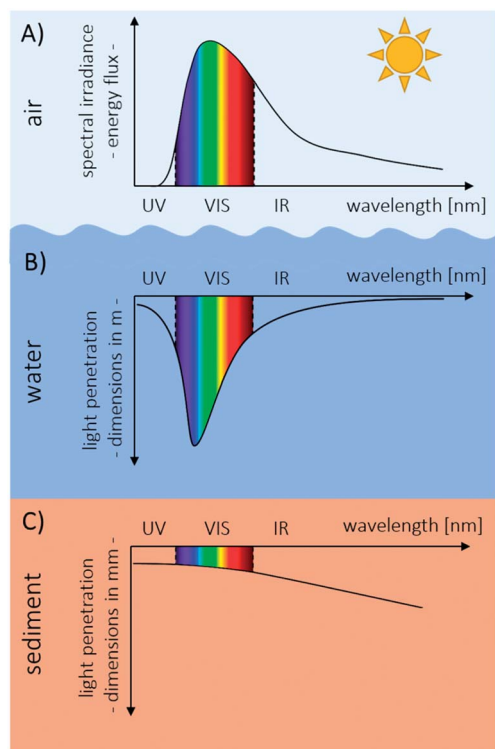


Fig. 1 (A) Simplified daylight spectrum as energy flux reaching the Earth's surface; (B) and (C) Qualitative light penetration into water or sediment (here: pure sand) showing the relative depth, where 1% remains of the spectral energy flux at the water or sediment surface, respectively.

light attenuation in water generally increases with longer wavelengths.¹⁴ Reaching the sediment surface, *e.g.* in littoral waters, light is penetrating into the sediment, depending on particle size and composition.¹⁷ While UV light usually only penetrates some hundreds of micrometers into the sediment,^{18,19} light in the VIS range can penetrate several millimeters whereby light penetration depth decreases with decreasing grain size.¹⁷ Directly on the sediment surface, the scalar irradiance (*i.e.* the light coming from all directions at one point)¹⁷ can be up to 280% of the incident irradiance due to scattering effects of the sediment particles.¹⁷ In contrast to the water column, light in the range of 450 to 500 nm (blue) is attenuated most strongly in sediments and attenuation decreases towards longer wavelengths, lowest in the IR region (Fig. 1).¹⁷

Impact of light in aquatic environments

The most important biochemical process in aquatic environments that is relying on light is oxygenic photosynthesis. During this process, plants or cyanobacteria absorb solar energy of specific wavelength regions in light-harvesting pigments by structures called chromophores,^{20,21} convert light energy into chemical energy (ATP) and further by CO₂ fixation into biomass and release oxygen (O₂) as a by-product.¹³ Additionally, anoxygenic phototrophic microorganisms such as green sulphur, purple sulphur or purple non-sulphur bacteria, use light as energy source for their metabolisms. Instead of water, they use

reduced inorganic or organic compounds as electron donor, *e.g.* sulfide, hydrogen or ferrous iron (Fe(II)) (anoxygenic photosynthesis).^{22–25} However, light is not only the energy source of such microbially catalyzed reactions but also provides energy for purely photochemical processes in the environment. Light can photochemically degrade larger molecules of dissolved organic matter (DOM), especially in the UV region (280–400 nm),^{16,26–28} resulting in the production of a variety of organic molecules with reduced molecular weight^{27,29,30} or in the production of dissolved inorganic carbon (photochemical mineralization of DOM).^{27,31,32} The photochemically formed products can have different chemical properties with increased or decreased bioavailability.^{26,27,29,33–36} Light-induced dissolution of particulate organic matter from resuspended sediments releases significant amounts of dissolved organic carbon (DOC) into the water column, especially in coastal or estuarine regions that receive large sediment plumes.^{28,37–39} Reactive oxygen species (ROS) such as singlet oxygen (¹O₂), superoxide (O₂^{•−}), hydroxyl radical (OH[•]) and hydrogen peroxide (H₂O₂) can form during photolysis of DOM,^{20,40–45} which have tremendous implications on different biogeochemical processes due to their high reactivity.^{26,43,46–48} Photochemically produced superoxide or H₂O₂ are able to reduce for instance manganese oxides⁴⁹ and the photo-reduction of manganese oxides by dissolved organic substances induced by sunlight is an important reaction for maintaining dissolved Mn(II) concentrations in seawater for supply of manganese to phytoplankton.^{50,51}

Besides the importance of light in the cycling of carbon or manganese, light is also a driving force in the Fe redox cycle of aquatic environments and sediments as it is able to photochemically induce the reduction of Fe(III) to Fe(II) (Fe(III) photoreduction). Light induced reactions are shown in Fig. 2. In this review, we summarize photochemical processes of Fe in aquatic ecosystems including the mechanisms responsible for light-induced reduction of Fe(III) and discuss the consequences of these photochemical reactions for biogeochemical Fe cycling.

General mechanisms of Fe photochemistry

In aquatic systems and sediments with circumneutral pH, dissolved Fe(III) (Fe_{aq}³⁺) occurs only complexed with organic molecules due to the poor solubility of Fe(III) and its tendency to precipitate as poorly soluble Fe(III) (oxyhydr)oxides.^{52–55} Depending on the kind of organic ligand, organically complexed Fe(III) can undergo photochemical reactions (i) by direct photon absorption and ligand-to-metal charge transfer (LMCT), at which an electron is transferred from the ligand to the Fe(III),^{44,52,56} or (ii) by indirect, secondary reactions with photochemically produced radicals such as superoxide.^{44,57–59}

The type of organic ligand and its specific functional groups control the overall photochemical reactivity towards LMCT reactions of the dissolved complexes.^{44,60} For instance, the carboxylate group, which is a common functional group of dissolved organic compounds such as citrate or oxalate, is able to complex Fe(III) and to undergo photochemical reactions by photo-induced charge transfer.^{52,61–63} Organic ligands can also interact with Fe(III) (oxyhydr)oxide mineral or colloidal

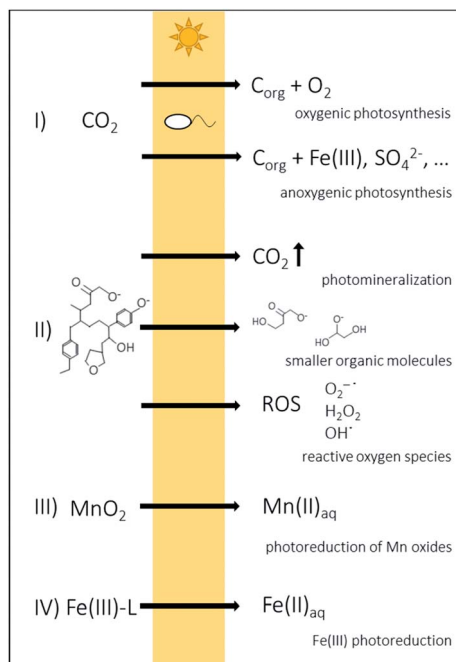
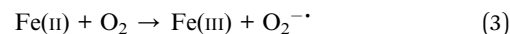
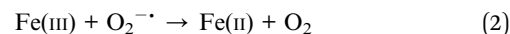
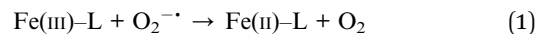


Fig. 2 Illustration of light induced reactions in aquatic environments with reactants on the left and products on the right of the yellow bar indicating a photochemical reaction: (I) oxygenic and anoxygenic photosynthesis (microbially catalyzed), (II) degradation of DOC by light forming CO_2 , smaller organic molecules and/or reactive oxygen species (ROS), (III) photoreduction of manganese oxides (MnO_2), (IV) photoreduction of organically complexed Fe(III) (Fe(III)-L).

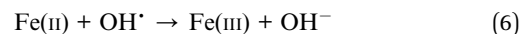
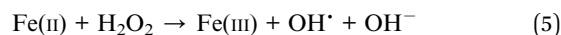
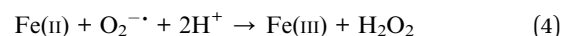
surfaces, where a photochemically mediated charge transfer from the ligand to the surface Fe(III) leads first to a reduction of Fe(III) to Fe(II), followed by either a re-oxidation of Fe(II) or by a dissociation of the formed Fe(II) from the surface leading to mineral dissolution.^{44,64–68} Photoreductive dissolution rates of Fe(III) (oxyhydr)oxides and colloidal Fe particles generally decrease with increasing pH.⁶⁴ For photoreductive mineral dissolution, organic complexation of Fe(III) is not a necessary prerequisite. However, the photochemically induced reduction of inorganic Fe(III)-hydroxo complexes on mineral surfaces by a charge transfer from the surface hydroxide ion to the Fe(III) proceeds less efficient and only at acidic pH.^{64,65,67–71} Therefore, photoreduction of inorganic Fe(III)-hydroxo complexes is not a significant source of Fe(II) in waters above pH 6.5.⁷²

The rate of photochemical LMCT reactions depends on intrinsic properties of the Fe(III) complex, temperature, pH and ionic strength of the surrounding environment, as well as on the intensity and wavelength of the absorbed light.^{52,56,66,71,73–77} Higher light intensities and lower wavelengths lead to faster Fe(III) photoreduction rates.^{66,69,71,74,78} Thus, light below certain wavelengths with sufficient energy is necessary to induce the photochemical LMCT reaction from a ligand to Fe(III), depending on the molecular structure of the complex. UV and lower wavelengths of the VIS region (<520 nm) of the solar spectrum are able to photochemically reduce Fe(III) complexes.^{69,79}

Reduction of Fe(III) in natural waters at circumneutral pH by photochemically produced radicals is most likely mediated by superoxide by either the reduction of a Fe(III)-ligand complex (Fe(III)-L) to a Fe(II)-ligand complex (Fe(II)-L) (eqn (1)) or by the reduction of Fe(III) which dissociated from a ligand prior to reduction by superoxide (eqn (2)) (Fig. 3).^{57–59,80} Superoxide forms in oxic waters by photochemical reaction of DOM with O_2 ,^{43,81} it can be produced by marine phytoplankton^{80,82,83} or during reaction of Fe(II) with O_2 (eqn (3)) (Fig. 3).^{84,85}



Superoxide can not only reduce Fe(III), but can also serve as oxidant of Fe(II) forming hydrogen peroxide (eqn (4)), which in turn forms hydroxyl radicals after reaction with Fe(II) (Fenton reaction, eqn (5)). Hydroxyl radicals can also oxidize Fe(II) forming hydroxide ions (eqn (6)) (Fig. 3).^{84,86}



As superoxide has the ability to act as both, oxidant or reductant, it plays an important role in the cycling of Fe.⁸⁶ Voelker *et al.*⁵⁸ pointed out that superoxide mediated reduction of dissolved Fe(III) is slower than oxidation of Fe(II) at seawater pH. While on the one hand at low concentrations of dissolved Fe(III), superoxide might accelerate Fe(II) oxidation, it can on the other hand retard Fe(II) oxidation at higher concentrations of dissolved Fe(III).⁸⁶ The kind of organic complexation presumably controls the reactivity of Fe(III) towards superoxide.^{87,88} As superoxide is highly reactive towards other redox-active components, dissolved species such as copper or organic material can have a significant influence on the superoxide mediated Fe redox reaction kinetics.⁸⁶

Light energy is able to photo-oxidize dissolved Fe(II) to dissolved Fe(III) forming dihydrogen gas (eqn (7)).

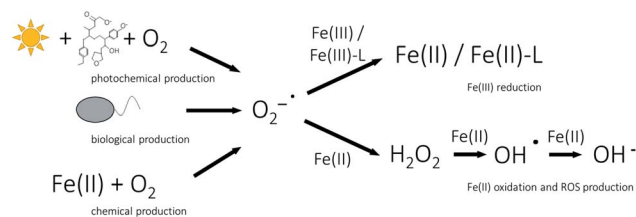
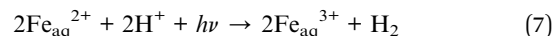


Fig. 3 Superoxide ($\text{O}_2^{\cdot-}$) production processes via photochemical reaction of DOM with O_2 , biological production by marine phytoplankton or during the oxidation of Fe(II) by O_2 as well as superoxide consumption processes via Fe(III) reduction or Fe(II) oxidation.

While at acidic pH the photo-oxidation of $\text{Fe}_{\text{aq}}^{2+}$ requires UV light with wavelengths in the range of 200–300 nm,^{89–91} the reaction at circumneutral pH is induced also by UV light with higher wavelengths due to the formation of the complex $\text{Fe}(\text{OH})^+$, which is sensitive to wavelengths >300 nm.^{90,92–94} However, it was shown that this reaction does not produce significant amounts of $\text{Fe}(\text{III})$ at seawater conditions.⁹¹ Due to absorption in the atmosphere, *e.g.* by ozone,⁵ only a low flux of UV is reaching the surface of the Earth and the oceans and due to only small concentrations of $\text{Fe}_{\text{aq}}^{2+}$ in oxic waters, the impact of photooxidation of $\text{Fe}(\text{II})$ in the water column and in sediments is presumably negligible.

Fe(III) photoreduction in natural waters

Concentrations of dissolved Fe in oceans are extremely low (pico- to nanomolar range)^{95–98} and Fe is a limiting nutrient for primary production in many regions of the open ocean.^{44,95,99,100} The thermodynamically stable form of Fe in oxic seawater, $\text{Fe}(\text{III})$, precipitates quickly as $\text{Fe}(\text{III})$ (oxyhydr)oxides at circumneutral pH and is therefore removed from the water column.^{44,52} In regions without continental or atmospheric input, Fe concentrations were shown to be only about 100 pM.⁴⁴ More than 99.9% of the dissolved Fe (<0.4 μm) in seawater is present in form of colloids (0.02–0.4 μm) or associated with biologically derived organic ligands of largely unknown identity,^{44,53,60,96,101–103} which keep Fe in solution and control the photochemical reactivity of Fe.^{44,53,104–106} Due to their small size, colloids remain suspended, even though they are distinct from water *via* a surface boundary.¹⁰⁷ Most of Fe colloids in the ocean are also complexed by organic ligands^{108,109} and can contribute up to 90% of the total dissolved Fe pool.^{107,110–112} Due to their particle structure, Fe colloids may have different chemical composition and behavior such as often lower bioavailability than truly soluble Fe (<0.02 μm).^{107,113} Xing *et al.*¹¹⁴ only recently showed that superoxide is able to reduce colloidal $\text{Fe}(\text{III})$. The organic compounds in seawater binding to iron are a mixture of different molecules including polysaccharides and humic substances.^{115,116} A part of these Fe-binding ligands presumably are siderophores,^{78,96,101,104} that were produced and excreted by microorganisms for Fe acquisition under Fe-limiting conditions.^{117,118} Siderophores strongly bind to $\text{Fe}(\text{III})$ and solubilize it from Fe minerals or colloids.^{119,120} Depending on the functional groups binding to $\text{Fe}(\text{III})$, $\text{Fe}(\text{III})$ –siderophore complexes containing α -hydroxy carboxylate groups can undergo direct LMCT reactions leading to a reduction of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ and an oxidation of the siderophore.¹⁰⁴ Extensive studies on siderophores and their photochemical reactivity based on functional groups can be found in the literature.^{44,104,115,121–124} The photoproducted $\text{Fe}(\text{II})$ can subsequently be complexed with an $\text{Fe}(\text{II})$ ligand ($\text{Fe}(\text{II})$ –L) present in seawater. Organic ligands do not only influence the photochemical but also the redox behavior of $\text{Fe}(\text{II})$. Depending on the characteristics, molecular composition and origin of the organic ligands, oxidation rates of $\text{Fe}(\text{II})$ by O_2 or H_2O_2 can be accelerated or slowed down.^{125–128} For instance, complexation of $\text{Fe}(\text{II})$ by more aromatic humic substances has been shown to slow down $\text{Fe}(\text{II})$ oxidation.¹²⁵

Therefore, organic complexation of $\text{Fe}(\text{II})$ can lead to a stabilization of $\text{Fe}(\text{II})$ in water with the organic ligands serving as redox buffer and complexant and retain elevated $\text{Fe}(\text{II})$ –L concentrations in surface waters.^{125,129,130}

$\text{Fe}(\text{II})$ –L or $\text{Fe}_{\text{aq}}^{2+}$ can be taken up by microorganisms.⁷⁸ The chemical and physical speciation of Fe determines its bioavailability.^{54,60} Photochemically induced reduction of $\text{Fe}(\text{III})$ forms $\text{Fe}_{\text{aq}}^{2+}$, $\text{Fe}(\text{II})$ –L and more reactive Fe species, which are generally more bioavailable and are therefore an important nutrient source for phytoplankton in the oceans.^{54,131–133} Instead of being taken up by microorganisms, $\text{Fe}(\text{II})$ can also rapidly be re-oxidized, *e.g.* by O_2 or H_2O_2 ,^{57,72,78,84,134,135} which are the main oxidants of $\text{Fe}(\text{II})$ in seawater.^{84,136} This re-oxidation of $\text{Fe}(\text{II})$ yields $\text{Fe}(\text{III})$ and the formation of ROS, which can further oxidize $\text{Fe}(\text{II})$ or reduce $\text{Fe}(\text{III})$ (eqn (1)–(6)), leading to rapid, light induced cycling of Fe in the oceans.^{54,55,57,78}

Besides direct LMCT reactions, $\text{Fe}(\text{III})$ –organic complexes can also undergo indirect photochemical reactions involving photochemically produced radical species such as superoxide, which is the most likely reductant of $\text{Fe}(\text{III})$ at seawater pH.^{44,57–59,137} As superoxide is formed by photochemical reactions of DOM with O_2 ,^{43,81} the contribution of the indirect photochemical reduction of $\text{Fe}(\text{III})$ *via* superoxide to the overall $\text{Fe}(\text{II})$ concentrations of the ocean is determined by the chemical composition of DOM present in seawater.^{44,54,74} Xing *et al.*¹¹⁴ only recently found that superoxide mediated $\text{Fe}(\text{III})$ reduction mainly is important in natural waters with limited concentrations of Fe binding ligands. In general, the interplay of both $\text{Fe}(\text{III})$ reduction pathways, direct LMCT reactions and indirect $\text{Fe}(\text{III})$ reduction involving superoxide, maintain the $\text{Fe}(\text{II})$ pool of the oceans.^{58,104} The actual $\text{Fe}(\text{III})$ photoreduction rates in the ocean depend on the photosusceptibility of the different organic complexes as well as light intensity and wavelength of the incoming sunlight.^{61,71} Although UVB light is most efficient for $\text{Fe}(\text{III})$ photoreduction,^{138,139} the UVA and VIS regions are quantitatively more important for photochemical $\text{Fe}(\text{II})$ production in the ocean due to their lower atmospheric attenuation and their deeper penetration into the water column of the ocean compared to UVB light.¹³⁹

Despite fast oxidation of $\text{Fe}(\text{II})$ by O_2 , H_2O_2 or other oxidants in the oceans, a steady state concentration of $\text{Fe}(\text{II})$ can build up if rates of light-induced $\text{Fe}(\text{III})$ reduction are high enough.^{52,55,104,140} While $\text{Fe}(\text{III})$ photoreduction leads to significant $\text{Fe}(\text{II})$ concentrations in seawater following diurnal cycles^{131,138,141} and elevated $\text{Fe}(\text{II})$ concentrations near the water surface,^{55,74,96} the combination of both, $\text{Fe}(\text{III})$ photoreduction and $\text{Fe}(\text{II})$ oxidation by O_2 and ROS, largely control the $\text{Fe}(\text{II})$ concentrations in irradiated seawater.⁵⁷

The photochemically induced reduction of $\text{Fe}(\text{III})$ does not only drive Fe cycling in the oceans, but also plays an important role for $\text{Fe}(\text{II})$ availability in freshwater systems.^{74,85,142} Usually, Fe concentrations and DOM in coastal waters but also in freshwater lakes are higher than in the open ocean due to larger particulate inputs,^{74,82,143} with dissolved Fe almost entirely being present in organic complexes.^{54,85,142} In circumneutral lakes, $\text{Fe}(\text{III})$ photoreduction leads to diel cycling of $\text{Fe}(\text{II})$ with maximum concentrations close to the water surface similar as

in the ocean.^{74,142} Both, light-induced LMCT reactions and superoxide mediated reduction of Fe(III) are responsible for the photoproduced Fe(II) concentrations in the investigated circumneutral freshwater lakes.^{74,85} The molecular weight of DOM present influences the extent of Fe(III) photoreduction.^{54,85}

Fe(III) photoreduction in anthropogenically altered waters

Anthropogenic influences such as acid mine drainage can lower the pH of surface waters leading typically to pH values between 2 and 4.⁷⁶ As the rate of Fe(III) photoreduction generally increases with decreasing pH,^{71,74} Fe(III) photoreduction is an important Fe(II) source in acidic rivers and lakes. Due to slower abiotic Fe(II) oxidation rates by O₂ at low pH,¹⁴⁴ higher dissolved Fe(II) concentrations can build up in these waters compared to waters with circumneutral pH, where abiotic Fe(II) oxidation to Fe(III) by O₂ and quick precipitation as Fe(III) (oxyhydr)oxides lead to a removal of Fe from the water column.^{52,76,145} Waters influenced by acid mine drainage often have low concentrations of DOM,^{146,147} which lead to low photochemical production of superoxide and H₂O₂.^{146,148} This would imply that direct LCMT reactions are the more important photochemical Fe(III) reduction pathway in acidic waters. Due to low pH and low DOM concentrations, photoreduction of dissolved inorganic Fe(III) species and photoreductive dissolution of particulate Fe(III) species or Fe(III) (oxyhydr)oxides play a relatively larger role in these environments^{73,76,147} than in circumneutral waters. At low pH, the dominant dissolved inorganic Fe(III) species is Fe(III)OH₂⁺^{75,148} and a light-induced LMCT induced by UV-light generates Fe(II) and hydroxyl radicals.^{62,147} During photoreductive mineral dissolution, formerly adsorbed phosphate or trace metals such as Cu, Zn, As or Pb^{145,146,149,150} are released into the water and can impact the activity of aquatic biota⁷⁶ on a relatively short time scale. With increasing pH, *e.g.* in rivers with a downstream pH gradient, dissolved Fe_{aq}²⁺ is oxidized to Fe(III) and usually precipitates as Fe(III) (oxyhydr)oxides, resulting in the scavenging of trace metals due to sorption processes.^{145,150} Fe(II) concentrations in acidic rivers and lakes also follow diel cycles^{75,151–153} correlated with light intensity^{146,152,154} with maximum concentrations at midday and minimum concentrations at night. The amounts of Fe(II) photochemically produced in acidic waters can be sufficient to serve as substrate for populations of Fe(II)-oxidizing bacteria¹⁵⁴ as slow abiotic Fe(II) oxidation kinetics leads to longer residence times of Fe(II) in the water. If no other external sources of Fe(II) exist, *e.g.* supplied by inflow of anoxic groundwater or oxidation of pyrite,^{154,155} Fe(III) photoreduction represents an important and also renewable Fe(II) source in acidic surface waters.¹⁵⁴ Dominant photochemical processes involving Fe(III) and the fate of produced Fe_{aq}²⁺ in a river with a downstream pH gradient are illustrated in Fig. 4.

Sedimentary Fe(III) photoreduction

Only recently, Fe_{aq}²⁺ formed by Fe(III) photoreduction in the porewater of freshwater and marine sediments was quantified.^{156,157} In sediments, Fe concentrations usually are in the

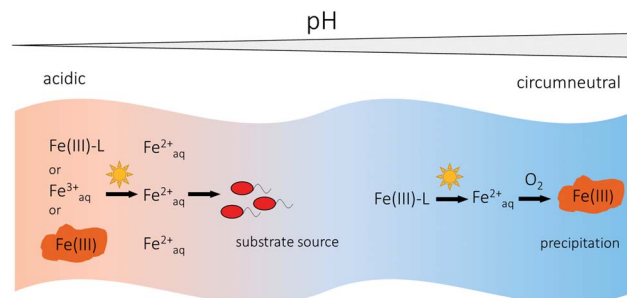


Fig. 4 River with downstream pH gradient showing dominant Fe processes in waters with acidic or circumneutral pH. At acidic pH, dissolved organically complexed (Fe(III)–L), dissolved inorganic Fe(III) species (Fe_{aq}³⁺) or Fe(III) (oxyhydr)oxides can photochemically be reduced to Fe_{aq}²⁺, which can, due to high concentrations, be used as substrate for Fe(II)-oxidizing bacteria. At circumneutral pH, dissolved Fe(III) occurs organically complexed and photoproduced Fe_{aq}²⁺ is mostly re-oxidized, *e.g.* by O₂, and predominantly precipitates as Fe(III) (oxyhydr)oxides.

range of micromolar concentrations^{158–160} and therefore Fe is generally not considered to be a limiting nutrient. However, gradients of Fe(II) establish at a millimeter to centimeter scale with increasing concentrations downwards due to chemical redox processes and microbially catalyzed reactions, including Fe(III) reduction in deeper, anoxic as well as abiotic Fe(II) oxidation by O₂ in shallow, oxic sediment layers.^{156,157,160} Fe-metabolizing bacteria that use Fe for gaining electrons and energy, need Fe concentrations above the trace element level for growth. In the upper millimeters of light-influenced, oxic sediment layers, Fe(III) photoreduction produces substantial amounts (micromolar range) of Fe_{aq}²⁺, where it is usually limited as substrate for growth.¹⁵⁶ The produced Fe_{aq}²⁺ persists even in the presence of O₂, probably due to stabilization by organic matter, which can slow down Fe(II) oxidation rates.^{85,147,161} By this, Fe(III) photoreduction has a strong impact on Fe(II) gradients in sediments and presumably has consequences for the inhabiting microbial community of Fe-metabolizing bacteria, which cannot only oxidize free, dissolved Fe_{aq}²⁺ but also Fe(II)–organic complexes.^{162–164} Also in sediments, the extent of Fe(III) photoreduction is determined by the DOM concentration of the sediment porewater.¹⁵⁶ So far, the relative contribution of direct LMCT and reduction of Fe(III) *via* photochemically produced superoxide to the overall photochemical Fe(II) production in sediments was not determined yet. However, photochemical production of superoxide and ROS in sediments can be expected by photolysis of dissolved DOM of the porewater, especially in organic rich sediments. While in water columns, photochemical reduction of Fe(III) mainly controls primary production by delivering bioavailable Fe_{aq}²⁺ as a nutrient, it substantially produces Fe_{aq}²⁺ as additional Fe_{aq}²⁺ source serving as substrate for growth for Fe(II)-oxidizing bacteria besides Fe_{aq}²⁺ originating from the Fe(III) reduction zone. Thereby, Fe(III) photoreduction changes Fe_{aq}²⁺ gradients and fluxes in sediments.¹⁵⁶ Fig. 5 summarizes sources and fate of Fe(II) in ocean and sediments.

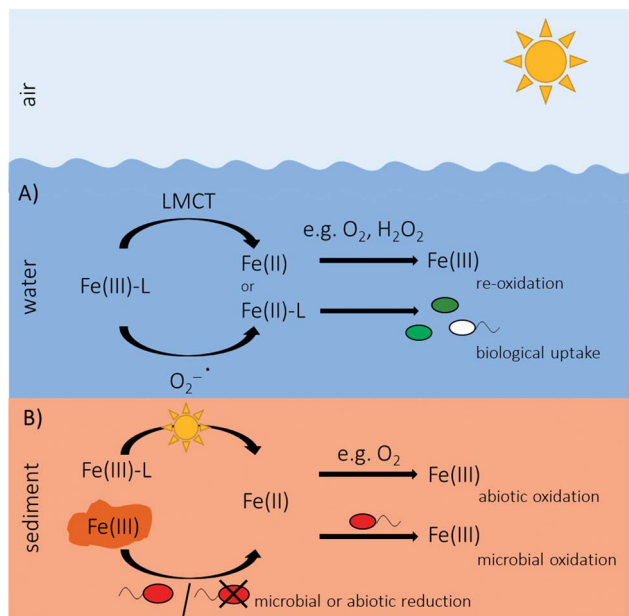


Fig. 5 (A) Illustration of photoreduction in the water column of organically complexed Fe(III) (Fe(III)-L) via ligand-to-metal-charge transfer (LMCT) reaction or via superoxide ($\text{O}_2^{\cdot -}$) forming Fe(II), which either gets re-oxidized by e.g. O_2 or H_2O_2 to Fe(III) or is taken up by phytoplankton. (B) Sketch of Fe(II) production in sediments by either Fe(III) photoreduction or by biotic or abiotic Fe(III) reduction. Fe(II) either gets abiotically re-oxidized, e.g. by O_2 or serves as substrate for microaerophilic, phototrophic or nitrate-reducing Fe(II)-oxidizing bacteria.

Light as driver of microbial Fe cycling

Besides the purely chemical process of Fe(III) photoreduction, light can also serve as energy source for the metabolism of anoxygenic phototrophic Fe(II)-oxidizing bacteria present in freshwater or marine sediments^{159,165} or in water columns^{166,167} which thereby couple the oxidation of Fe(II) to CO_2 fixation.²² Anoxygenic photosynthesis was suggested to be an important metabolism in ancient environments of the Archean Ocean where O_2 was absent and reduced species such as Fe(II) dominated in the water column.^{168,169} It probably accounted for most of the primary production in sunlit waters.¹⁷⁰ With the evolution of oxygenic photosynthesis, today's mostly oxic aquatic environments formed and anoxygenic phototrophs were displaced to anoxic, sunlit niches. However, they are still present as primary producers in many environments today and are part of the biogeochemical cycling of Fe.²⁵ The production of O_2 by oxygenic photosynthesis also has consequences for other Fe-metabolizing bacteria that either have anaerobic metabolisms or need to compete with the fast abiotic Fe(II) oxidation kinetics with O_2 at circumneutral pH. In contrast, the oxidation kinetics of Fe(II) by O_2 in acidic conditions is much slower¹⁴⁴ and in acidic waters, Fe(III) photoreduction produces significant amounts of Fe(II) and can thus control the presence and distribution of Fe(II)-oxidizing acidophilic bacteria¹⁴⁶ due to longer half-life times of Fe(II) at acidic pH.¹⁴⁴ The discovery of Fe(III) photoreduction in freshwater and marine sediments adds

another Fe(II) source, besides biotic and abiotic Fe(III) reduction, to the sedimentary biogeochemical Fe cycle.¹⁵⁶ By supplying light-influenced sediments with Fe(II) concentrations in the micromolar range, microaerophilic Fe(II)-oxidizing bacteria can grow in oxic sediment layers, in which rapid abiotic Fe(II) oxidation by O_2 would otherwise dominate due to the rapid oxidation kinetics at circumneutral pH.¹⁷¹ Light is therefore driving the biogeochemical cycling of Fe in modern aquatic environments and sediments by not only serving as energy source for phototrophic Fe(II)-oxidizers but also providing substantial amounts of Fe(II) for other Fe(II)-oxidizing bacteria.

ROS related processes in the dark

Sunlight is directly or indirectly driving many chemical and biological reactions in natural waters and sediments. However, most of our ecosystems on Earth are never reached by light and only exist in darkness – the deep biosphere.¹⁷² However, even in the dark, there are parallel processes compared to photochemical mechanisms that involve, among others, the formation and consumption of ROS species.

Due to their high temperatures, hydrothermal vents emit light into the dark of the ocean, mainly as thermal radiation in the IR wavelength region (>700 nm), but temporally also in small intensity in the VIS wavelength region.^{173,174} The energy of this radiation can potentially be used by photosynthetic bacteria such as green sulphur bacteria, which are potentially able to oxidize Fe(II), for the fixation of CO_2 to organic carbon (Fig. 6).¹⁷⁵ Apart from being used for photosynthesis, IR presumably does not deliver sufficient energy for the formation of ROS in the environment as photolysis of DOM and concomitant ROS production usually occurs by absorption of UV and VIS light.^{16,26,176}

The aeration of anoxic water containing Fe(II) leads to the formation of hydroxyl radicals by Fenton reactions (eqn (5)),^{177,178} as the oxidation of Fe(II) by O_2 also proceeds in darkness producing H_2O_2 and further hydroxyl radicals (eqn (4) and

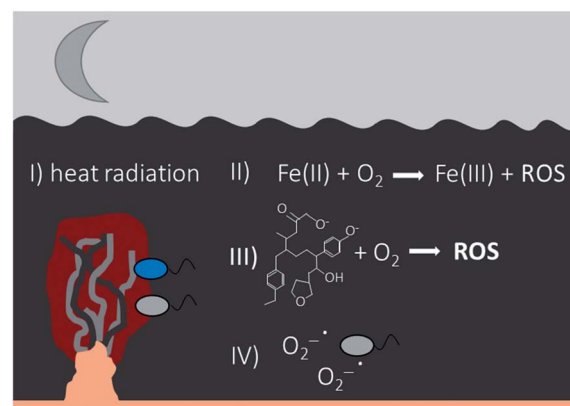


Fig. 6 Illustration of reactions proceeding in darkness (I) IR light emission at hydrothermal vents, which may be used for anoxygenic photosynthesis, (II) Fenton reaction forming ROS, (III) ROS formation by oxidation of reduced organic molecules, (IV) extracellularly production of superoxide by bacteria or phytoplankton.

(5)). In general, biotic reductive processes (e.g. Fe(III)-reducing bacteria such as *Shewanella oneidensis*) or abiotic reductants (e.g. sulphide) that are able to reduce Fe(III) to Fe(II), enhance the formation of ROS, as was observed in natural waters or marsh sediments.^{179–182} The formed Fe(II) further reacts as described in eqn (3)–(6) with O₂ forming ROS (Fig. 6). These reactions involving O₂ are important e.g. at oxic–anoxic interfaces or anoxic soils or sediments that are flushed with oxygenated water.¹⁸³ During abiotic or biotic Fe(III) reduction, the reducing equivalents are not photons, but they are produced in chemical and biological reactions, which have a similar impact on ROS production as photochemical sources.¹⁷⁹ Besides the Fenton-like reactions yielding ROS, the abiotic oxidation of reduced DOC or humic acids by O₂ forms ROS as well (Fig. 6).^{177,183} Superoxide is also extracellularly produced by several microorganisms such as different heterotrophic bacteria or phytoplankton (Fig. 6).^{80,82,83,184,185} This light-independent biological production of superoxide in marine and freshwater systems is a significant source of ROS concentrations as measured in sunlit waters.¹⁸⁶ Those reactions also proceeding in darkness are similar important drivers of biogeochemical cycles as photochemically-induced processes.

Conclusions

Photochemical reduction of Fe(III) by either direct LMCT reactions or by photochemically produced superoxide plays a major role in the Fe cycle of aquatic environments. It is the main source for the production of Fe_{aq}²⁺ in water bodies such as the ocean and thus strongly influences the primary productivity of marine systems by supplying Fe_{aq}²⁺. Besides biological uptake, rapid chemical oxidation of photochemically formed Fe(II), mainly by O₂ or H₂O₂,^{84,136} closes this photochemically driven diel Fe cycle in the oceans.^{55,131,187} Fe(III) photoreduction also is a major source of ROS (eqn (1)–(6)), which are key oxidants in natural waters^{71,188} playing an important role in the biogeochemical cycling of trace metals and carbon.^{189,190} In acidic waters or sediments, Fe(III) photoreduction can even provide micromolar concentrations of Fe_{aq}²⁺ and influence the presence and abundance of different Fe(II)-oxidizing bacteria. Photochemical effects generally decrease with water or sediment depth as light is attenuated depending on the wavelength.⁵⁶ Especially light in the UV region, which is not only very efficient for Fe(III) photoreduction but also for the photochemical production of radicals,^{43,44} is strongly attenuated in both, water and sediments. Photochemical processes thus strongly impact and control the biological life and biotic processes in natural waters of different pH and in sediments, mainly by supplying bioavailable Fe(II) as nutrient or substrate for growth to the inhabiting organisms. Without those light-induced chemical processes, other element cycles such as the carbon cycle would lack an important driver.

Conflicts of interest

There are no conflicts to declare.

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