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Iron Biogeochemistry in Aquatic Systems: From Source to Bioavailability

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Abstract: Iron (Fe) is an essential trace element for several key metabolic processes in phytoplankton; however Fe is present in low concentration in many aquatic systems including vast oceanic regions and large lakes. In these systems, Fe can limit the growth of phytoplankton and atmospheric carbon dioxide biological fixation. Indeed Fe limitation exerts a global impact on the carbon cycle and the imprint of aquatic systems on our climate. In order to understand how aquatic systems function and increase our ability to predict their response to changing conditions, it is therefore paramount to understand when and how Fe controls operate. This review presents the complex relationship between Fe chemistry and the biology of surface waters to highlight the parameters defining the forms of Fe that are accessible for phytoplankton growth (or bioavailable). Particular attention is given to the identification of Fe sources and Fe organic complexation as these, in conjunction with biological recycling and remineralisation, mostly control Fe residence time, chemistry and bioavailability.

Keywords: Carbon · Iron · Lake · Limitation · Ocean · Phytoplankton

The Importance of Iron in Aquatic Systems

Phytoplankton are sensitive to environmental conditions and have a short life span, making them an ideal sentinel to track changes in aquatic systems. Phytoplankton plays a major role in aquatic systems as its biological functioning affects the biogeochemical cycles of carbon (C) and Fe (Fig. 1) as well as a number of other key elements (*i.e.* nitrogen (N), silicon (Si), sulphur (S), *etc.*). By the process of photosynthesis phytoplankton is responsible for up to 40% of atmospheric carbon dioxide (CO_2) biological fixation (referred as primary productivity), transforming inorganic carbon into organic forms that sustain the aquatic food web.[1,2] Phytoplankton therefore affects global carbon cycling and plays an important role in the regulation of Earth's climate. However, whereas the oceans are known to be a net sink for atmospheric CO_2, the carbon budget for lakes is less clear.[3]

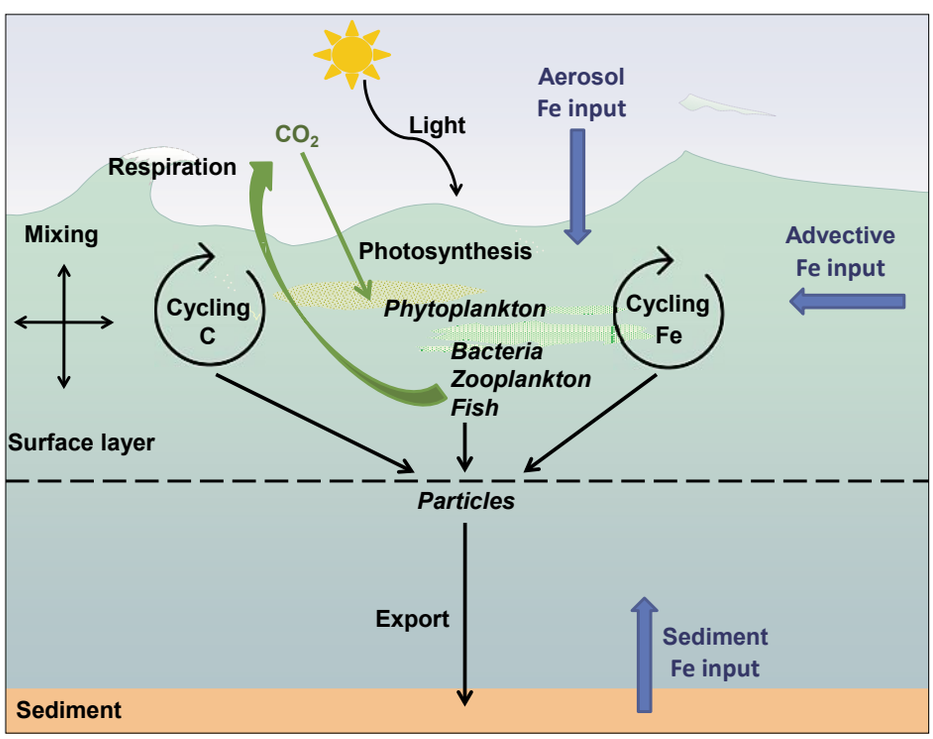

Fig. 1. Schematic of the links between iron (Fe) and carbon (C) cycling. Fe enters the oceans *via* a number of sources, *i.e.* aerosol input (dust, ash), advective processes (horizontal transport of coastal water masses, upwelling of sediments). Iron is a vital micronutrient for phytoplankton, which is involved in the process of photosynthesis. During photosynthesis phytoplankton fix atmospheric carbon dioxide (CO_2) into organic molecules. Thereby, transforming inorganic carbon into organic forms which are transferred through the entire marine food web. Some of the organic carbon is respired by phytoplankton and bacteria, recycled through the food web, and exported to the sediments. During these processes Fe will be recycled and exported. Processes are shown in bold black, Fe inputs in blue, carbon processes in green, and biological interactions in italics. Connections between the Fe and other elements (*e.g.* S, N, Si) cycling is not shown here for simplicity.

Iron is one of the most important micronutrients required for the growth and survival of phytoplankton. It is a cofactor of metaloenzymes and proteins, which are vital to metabolic processes such as photosynthesis, respiration, electron transport, nitrate reduction, and the detoxification of reactive oxygen species.[1,4–7] However,

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Fe limitation is widespread, affecting up to 50% of the world oceans, thereby impacting phytoplankton growth, primary productivity, community structure and biodiversity, and on a larger scale, ecosystem functioning and CO_2 fixation.[6,8–10] In order to understand how aquatic systems function and increase our ability to predict the response of phytoplankton to changing conditions, it is therefore paramount to understand how Fe controls operate and where they are relevant. This review presents the complex relationship between Fe chemistry and the biology of surface waters to highlight the parameters defining the forms of Fe that are accessible for phytoplankton growth (or bioavailable).

Iron Limitation in Aquatic Systems

Numerous bottle incubations, as well as large-scale natural and artificial Fe fertilisation experiments, have confirmed John Martin's 'iron hypothesis'[11] and demonstrated that the limitation of accessible Fe to sustain phytoplankton growth is the primary factor leading to low phytoplankton biomass in high nutrient, low chlorophyll (HNLC) regions.[8,12,13] These include high latitude areas as well as important upwelling regions (*e.g.* ref. [14]). Fe limitation is not restricted to HNLC regions; areas of the Atlantic Ocean and the Coral Sea exhibit reduced primary productivity due to low nutrient concentrations, specifically nitrate (NO_3),[15,16] and are termed 'low nutrient, low chlorophyll (LNLC)' regions. Here Fe becomes a co-limiting factor due to its crucial role in nitrogen assimilation and N_2 fixation.[15] In these cases an input of Fe is unlikely to have the same effect as that seen in HNLC regions[17] as the concentrations of other vital nutrients are too low to initiate growth.

Studies based on natural lake waters highlighted Fe deficiencies and limitations.[18–21] It was demonstrated that Fe additions, using bioassay approaches, can stimulate phytoplankton growth and photosynthetic efficiency.[20] A recent study conducted in Lake Geneva, showed similar results, with an increase of *in vivo* chlorophyll *a* content in Fe-enriched treatments.[22] These results suggest that the phytoplankton communities of these lakes are at least Fe stressed, or even, Fe limited.[20,21]

Iron Distribution in Aquatic Systems

As it is the fourth most abundant element[23] one would expect that Fe concentrations in aquatic systems would reflect this. However, the solubility of Fe is extremely low in contemporary well-oxygenated water with pH >7[24–27] resulting in low Fe concentrations in many natural waters.

The ubiquity of Fe in the environment makes accurate determination of this element in aquatic systems extremely difficult, particularly in open ocean samples. It is likely that sample contamination led to some inconsistencies in early measurements (pre 1970s) (see ref. [28] for a review). However, the development of 'clean' techniques for sampling, sample handling, and analysis has alleviated this issue somewhat.[21,28,29] The advancement of analysis techniques and improved sensitivity have also improved the accuracy of Fe measurements.

Since the 1990s numerous studies have measured dissolved iron (dFe) in the ocean. In fact, large international efforts in the framework of the GEOTRACES program resulted in the release of 3D dFe distributions of most ocean basins (eGEOTRACES, *www.egeotraces.org*).

In large areas of the oceans dFe concentrations in surface waters are extremely low, often <1 nM.[30–33] Since the introduction of clean techniques data for lakes are still limited,[34] recent studies highlighted that Fe concentrations are much lower than previously perceived.[20,35] For the lakes studied (Laurentian Great Lakes, Lake Geneva and Lake Kinneret) dFe is reported to be present in concentrations ranging from 0.5 to 312 nM (Table 1).[20,35–39]

The vertical and spatial distributions of dFe have similar patterns in large lakes and in the ocean. Vertical distributions are nutrient-like with low concentrations at the surface, as a result of biological uptake, and increasing concentrations with depth due to remineralisation, aggregation and settling, and sediment resuspension.[22,42–44] In the global ocean, average dFe concentrations vary from 0.07 nmol at the surface to 0.76 nmol at depth (Table 2).[44] Fe seasonal variability exhibits a net decrease of dFe concentrations at the level of the deep layer chlorophyll *a* maximum during spring to summer months and an increase due to winter mixing. This indicates that biological activities and mixing processes are important for Fe distribution. A spatial gradient of dFe in the epilimnion of lakes has been observed, from nearshore (dFe mean: 31.7 nM) to isolated areas (dFe mean: 1.5 nM), showing a strong increase of dFe concentration along the coastline as a result of lake-edge sources.[20,35,41] Elevated Fe concentrations are indeed generally found in near-shore waters,[64] often in the range of 100–1000 times higher than that found in the open ocean.[6] Despite a relatively high concentration of Fe in rivers,[64] very little riverine Fe reaches the open ocean as most of it is removed by precipitation, coagulation, and sedimentary processes favoured by the increase of salinity in estuaries.[64]

Sources of Iron

Iron sources are numerous, and their relative importance to the observed Fe concentration varies regionally and seasonally. Fe reaches marine waters *via* atmospheric aerosols,[24,65–67] riverine input, melting of sea ice,[68,69] icebergs,[69] glacial ice,[70,71] continental margins,[72–74] transport of hydrothermal Fe residuals,[75] anoxic sediments, and recycling by organisms from viruses to whales.[43,76–84]

Four Fe sources dominate in lakes: (i) river inputs (*e.g.* fluvial influx and wastewaters), (ii) atmospheric inputs (*e.g.* precipitation and dust), (iii) sediment resus-

Table 1. Range of measured dissolved and particulate Fe(III) in different lakes.

	Dissolved Fe [nM]	Particulate Fe [nM]	
Lake Waters			
Lake Erie	2.2–90	na	[35]
	3–34	na	[20]
	2.7–312	na	[36]
	1.2–5.7	45.5–3643	[40]
Lake Ontario	2.6–73	na	[35]
	0.5–26	na	[35]
Lake Superior	1.6–8.7	39.4–75.4	[38]
	0.6–27	na	[35]
	15	na	[39]
	1.3–75.8	na	[41]
Lake Kinneret	31–37	86–379	[37]
Lake Geneva	2–30[a]	na	

[a]Moisset *et al.,* unpublished data[22]

Table 2. Range of measured dissolved and particulate Fe(III), Fe-binding organic ligand concentration, and measured stability constants with inorganic Fe (log $K'_{Fe'-L}$) in different ocean basins.

	Dissolved Fe [nM]	Particulate Fe [nM]	[Ligand] [nM]	log $K'_{Fe'-L}$	
Sea Waters					
Arctic	1.0–3.2	na	na	na	[45]
Subarctic Pacific	0.02–0.1	na	na	na	[46]
	0.6–0.8	na	na	na	[47]
	0.02	>1.0	0.5	11.3–12.5	[48]
North pacific	na	0.1–0.2	na	na	[49]
	na	0.1–0.3	na	na	[50]
	0.2	na	na	na	[51]
	0.7–0.8	na	**L1:** 0.4 **L2:** 1.5	**L1:** 13.1 **L2:** 11.5	[51]
Equatorial Pacific	≤0.05	na	na	na	[52]
	0.05	na	na	na	[53]
	0.02–0.04	0.1–0.5	**L1:** 3.1 **L2:** 1.9	**L1:** 12.6 **L2:** 11.8	[54]
Arabian Sea	0.5–2.4	na	na	na	[55]
	1.3–2.6	na	0.2–3.8	na	[56]
North Atlantic	1.8	na	na	na	[57]
	0.2	na	3.5–4.8	18.8–19.7	[58]
	0.4–0.7	na	0.5–0.6	na	[59]
	0.4±0.05	na	**L1:** 1.1 ± 0.09 **L2:** 2.1 ± 0.002	**L1:** 13 **L2:** 11.6	[59]
South Atlantic	0.05–0.3	na	na	na	[33]
Southern Ocean	0.08±0.03	na	Na	na	[60]
	0.05–0.5	na	0.2–1.4	na	[32]
	0.3±0.2	na	0.7±0.2	na	[32]
	0.06–0.09	na	0.6–0.8	na	[61]
	na	0.5–0.9	na	na	[62]
Southern Ocean	0.2–0.4	na	0.8±0.20	11.5±0.2	[63]

pension and (iv) reductive remobilization of Fe from the sediment. Those sources are mainly balanced with outflow and sedimentation processes.[37,85] To date, only a few studies have measured Fe budgets in freshwater lakes. Measurement of high dFe concentration in river influx of Lake Kasumigaura (686–2910 nM) compared to lakewater (35–254 nM), suggest that riverine Fe was the major source in this lake.[86] Similar observations were made in Lake Kinneret where the Jordan River appears to be the main source of dFe (6–13 μM[37]). The high contribution of fluvial inputs to dFe concentrations can be explained by the lakes' large watershed area.[37] Indeed, Fe comes from the products of weathered rocks and soil around watersheds.[85]

Globally the largest input into the oceans comes from atmospheric dust deposition,[67] although exceptions to this may be upwelling areas or coastal regions with large river inputs.[52] It is estimated that ~3 times more dFe enters the oceans *via* atmospheric deposition than *via* rivers.[67]

In HNLC regions and oligotrophic waters, the flux of upwelled Fe has been found to be significant, and in some cases, the dominant source.[64] For example, it is estimated that the upward Fe flux is ~10 times and >5 times higher than that of the atmospheric contribution in the equatorial Pacific[52] and in the Southern Ocean,[74] respectively. As such, upwelled Fe represents the primary source of this element in Antarctic waters.[87] In the subarctic Pacific however, atmospheric sources appear to be dominant (~10 times greater than upwelled Fe).[64,87]

The Southern Ocean is the largest HNLC area where the lack of Fe limits the growth of phytoplankton.[88] In Antarctic sea ice Fe can accumulate in concentrations one or two orders of magnitude higher than that of the underlying seawater (sea ice 2.6–26 nM[89]). Lannuzel *et al.*[68] showed that, over a 10-day period, 70% of the accumulated Fe could be released to surface waters through brine drainage during sea ice melting, suggesting that sea ice may promote the onset of a spring phytoplankton bloom, or at the very least sustain an existing bloom in Polar waters. Similarly, localised enhanced chlorophyll *a* has been observed in the vicinity of free drifting icebergs.[71,90]

The effect of Fe input on aquatic phytoplankton depends on the time-set of input, rate and duration, the phytoplankton community present and its Fe nutritive status.[91] Therefore, variability of Fe input may cause corresponding variations in atmospheric/ocean CO_2 exchange fluxes, the C, N, and Si budgets,[92] depending on the dominant phytoplankton species present.

If future climatic variations alter dust seasonal transport and deposition processes, we are likely to see corresponding changes in the atmospheric deposition.[65] For example, predictions of a dryer Australia with increased storm events may lead to increased dust deposition in the Tasman Sea and Southern Ocean, a possible increase in bioavailable Fe,[93] and changes in phytoplankton community structure. Due to increased industrial and human activities, atmospheric dusts are becoming richer in essential elements such as N and toxic elements such as Pb (*e.g.*, ref. [14]), leading to complex effects on phytoplankton dynamics in natural systems.

Several tracers can be used to identify Fe sources. For example, the primary source of aluminium (Al) is from atmospheric dust; therefore, the Fe/Al ratio is an ideal measurement to identify atmospheric input versus continental margin inputs.[94,95] Additionally, radium isotopes (Ra) can be used to identify sedimentary inputs and dispersal rates.[96] Fe isotopic signature is another promising technique sensitive to Fe redox and biological reactions.[97]

This method has been used successfully in palaeo-reconstructions of marine environments[98] and studies of contemporary ocean waters reveal that many Fe sources have unique Fe isotopic signatures (*e.g.* desert soils δ^{56} total Fe (Fe_T) 0.04 to 0.08‰, soluble Fe ~0.13‰,[99] hydrothermal inputs –0.11 to –0.77‰,[100,101] continental shelf sediments –3.4 to –2.7‰.[102] Therefore additional effort should be made to characterise these signatures in order to efficiently track Fe sources.

Iron Chemistry in Aquatic Systems

Iron is present in a variety of size fractions, operationally defined as dissolved and particulate.[64] A significant fraction of dFe is in fact colloidal, likely both inorganic and organic colloids.[103–106] The dissolved phase is therefore further split into soluble and colloidal. To complicate matters further the speciation of Fe is controlled by the redox state (Fe(II) or Fe(III)), and complexation with a variety of organic ligands (Fig. 2).[40,83,107,108]

Iron chemical speciation has been studied using Competitive Ligand Exchange-Adsorptive Cathodic Stripping Voltammetry (CLE-ACSV) since 1994.[51,57] The results indicate that >99.9% of the dFe in seawater is bound to organic ligands.[109] The ambient Fe-binding ligands determined by this technique are typically described as ligand 'classes' which are operationally defined by the associated conditional stability constant K_{FeLi}^{cond} measured. Ligand classes are denoted as L_i, where i = 1 for stronger ligand classes and i = 2, 3, *etc.*, for progressively weaker ligand classes. Generally, speciation of Fe(III) is dominated by L_1 ($K_{FeL1} > 10^{22}$ M^{-1}) in the mixed layer and L_2 ($K_{FeL2} \approx 10^{21-22}$ M^{-1}) in the deep ocean.[51] Several Fe binding organic ligands have been identified in seawater. These include bacterially produced siderophores (L_1),[107,110,111] exopolymeric substances (EPS), which are released by most microorganisms (L_1 or L_2),[112,113] porphyrin and saccharides, released *via* cell lysis and grazing (L_2),[108,114,115] and humic substances (HS, L_2).[116,117] The role of these organic ligands has been recently reviewed elsewhere.[109,118,119]

Humic substances (HS) can make up a substantial percentage of the dissolved organic matter (DOM) pool in aquatic environments, with estimates ranging between 40 and 80% in freshwater,[120,121] and between 10 and 50% in estuaries and coastal waters.[122] HS are less abundant in marine systems but can account for 5–25% of the DOM pool even in remote ocean regions.[120] Several studies conducted in coastal oceans,[116] estuaries[123] and rivers[86,124] have demonstrated that the HS (fulvic acid, and to a lesser extent, humic acid) can account for the majority of the total ligand pool. To date, only one study has investigated the organic Fe speciation in lakes.[86] Their results revealed that most of the dFe is largely organic and is primarily bound to fulvic acid.

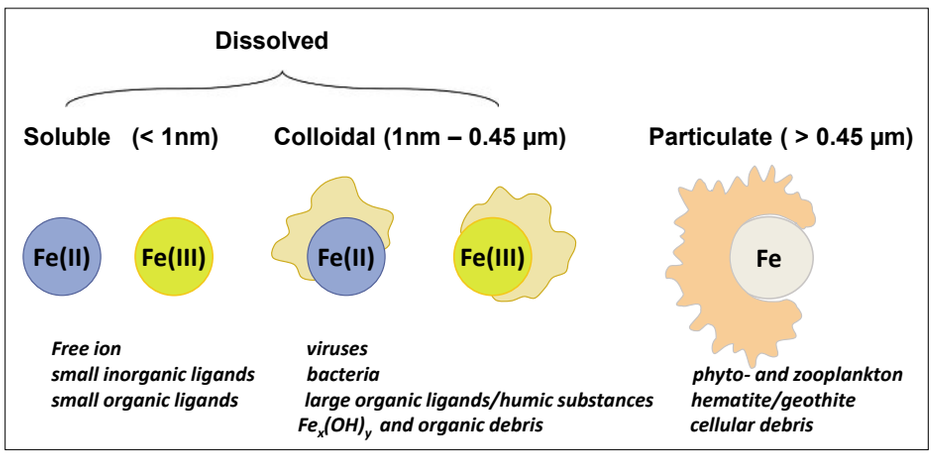

Fig. 2. The various size fractions, species, and associated biology and natural organic matter (NOM) of Fe that exist in marine waters. Iron size fractions are operationally defined as dissolved and particulate. The dissolved fraction is further split into soluble (< 1 nm) and colloidal (1 nm – 0.45 µm). Fe is present in the ocean as both Fe(III) and the reduced Fe(II) species, and occurs as free ions and, predominantly, associated with organic ligands and humic substances.

Recent data suggested that EPS could represent a significant portion of the HS present in the open ocean with important consequences for phytoplankton growth.[125,126] Carbohydrates are an important component of DOM as well as EPS. For example, the concentration of uronic acids are variable in both algal and bacterial EPS,[127,128] but can account for between 20–50% of the polysaccharides produced by some marine bacteria.[129] Saccharides can bind Fe, enhancing its reduction and solubility, and forming highly bioavailable Fe forms to marine phytoplankton.[112–114,119,130–132] Interestingly, high levels of dFe (0.2–14.4 nM) and EPS (2.8–2690 µg xanthan equivalent L^{-1}), were measured in Antarctic sea ice compared to underlying seawater.[133] However EPS contain many other metals (toxic and essential) and macronutrients as well as many functional binding groups, so the mechanisms by which it associates with Fe, as well as its impact on phytoplankton, is not yet resolved.[125,126]

Organic complexation is extremely important for maintaining solubility[25,134–136] and controlling the bioavailability of Fe to bacterio- and phytoplankton.[108,109,112,135,137–139] Soluble complexed Fe is not scavenged but remains accessible in surface waters for prolonged periods.[140] For example, in the presence of organic ligands the solubility Fe(III) is in the order of 0.2–0.6 nM in surface waters,[26,136] and reaches minimum values (0.15–0.2 nM) at depths between 50 and 200 m.[136] In the absence of organic complexation however, inorganic Fe(III) is highly insoluble[141] and will rapidly hydrolyse and form colloidal Fe oxyhydroxides[25,142] resulting in the continual removal of Fe oxides from the surface ocean *via* scavenging and adsorption onto sinking particles.[143]

Generally the predominant form of Fe in seawater is the more thermodynamically stable Fe(III).[144] Fe(II) generally undergoes rapid oxidation in well-oxygenated surface waters, exhibiting a half-life of minutes at the normal pH of seawater (~8).[144,145] However, factors such as low temperatures, and complexation with organic ligands have been shown to slow down the oxidation kinetics of Fe(II), and increase the half-life, in some cases to hours.[146–149] In lake systems, the ratio Fe(II)/Fe_T showed a day/night cycle with concentrations of Fe(II) below the detection limit during the night and up to 1nM near the surface during the day.[150] These low concentrations are associated with the rapid reoxidation of the Fe(III) species. An exception was observed in lake Kinneret[151] where concentrations of Fe(II) ranging from 0.05 µM to 0.15 µM were measured during the year. It has been proved that these high values are due to both phytoplankton driven reduction of Fe(III) and the stabilization of Fe(II).[37]

The reduction and oxidation of Fe can occur through a number of processes whether present as Fe(III) prime (Fe(III)') or Fe(II) prime (Fe(II)') (which are inorganic species), or as Fe(III) or (II)-ligand complexes (Fig. 3). These processes include direct mediation through the photochemical reduction of colloidal Fe[152] or

Fe(III)-organic ligand complexes,[107,153] or direct biological reduction *via* biological ferrireductase. Indirect reduction pathways come from the production of the reductant superoxide *via* the photodegradation of natural organic matter (NOM)[154–156] or from microbial excretion products.[157] Work by Garg *et al.*[154] using the red tide algae *Chattonella marina* indicates that the production of superoxide plays a much larger role in Fe uptake when the Fe is bound to weak ligands than when it is bound to strong ligands. Light can influence not only the Fe but also the organic ligands themselves. Chromophores contained in HS are highly susceptible to photodegradation,[153] however this is not the case for all organic ligands. Siderophores containing hydroxamate groups are photochemically stable whether free or bound to Fe. The siderophores containing catecholate groups photo-oxidise when free but are stable when bound to Fe. However, for those siderophores containing α-hydroxy carboxylate groups the opposite is true.[153] Fe redox processes are influenced by the Fe species and organic ligands present, and the chemical environment of the surrounding waters, with Fe(II) complexes often being weaker than Fe(III) complexes.[141]

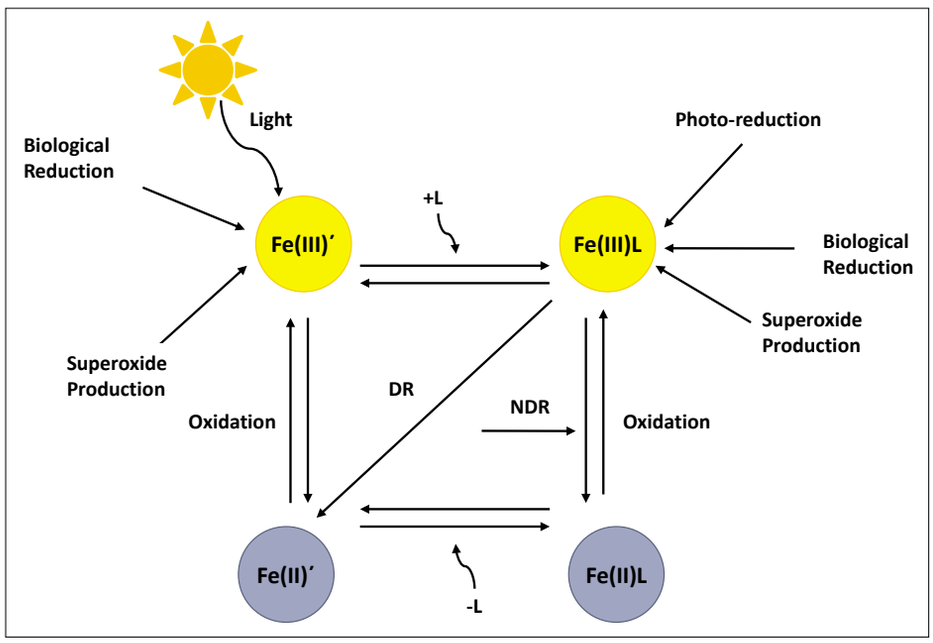

Fig. 3. Representation of the Fe redox cycle. Fe exists in the ocean mainly as Fe(III), either as inorganic Fe(III)', or bound to organic ligands (Fe(III)L). Organically bound Fe(III) is the predominant form (>99%). Both Fe(III)' and Fe(III)L can be reduced by the action of sunlight (photo-reduction, production of superoxide by NOM), or by biological activity (biological reduction, *i.e.* ferrireductase, and biological production of superoxide). Fe reduction can induce the dissociation of Fe(III)L (*e.g.* dissociative reduction, DR), or generate Fe(II)L (*e.g.* non-dissociative reduction, NDR). The Fe(II)L complexes are generally weaker than Fe(III)L complexes and will easily dissociate to Fe(II)'. In oxygenated water the Fe(II)' is then rapidly reoxidised by O_2 to Fe(III)'.

Iron Bioavailability

Bioavailable Fe is the part of this element pool present in an aquatic system which is biologically accessible to microorganisms and can sustain their growth. Therefore, in Fe limited regions, bioavailability controls phytoplankton biomass and the species composition of the phytoplankton assemblage, which in turn influences the community food web.[112,158] The complex and dynamic behaviour of Fe in surface waters, its speciation, and redox chemistry means that the parameters which control Fe bioavailability are still poorly understood.

The bioavailability of Fe, is dependent on physical (diffusion[159]), biological (transport across cell membranes or uptake[141,160]), and chemical factors (dissociation kinetics of metal complexes and the various chemical forms of Fe[141,158,160]) both within the cell and in the environment immediately adjacent to the cell.[160] The rate of any of the steps (diffusion, uptake, or kinetic flux) has the potential to limit the efficiency of Fe assimilation. The importance of Fe kinetics in seawater was recently reviewed in Croot and Heller.[161] The rate of uptake is defined by a microorganism's Fe requirement, Fe transporters, and the concentration of free Fe and labile Fe.[141,160] The diffusive flux of Fe to the cell surface is determined by the size fraction of the Fe present (*i.e.* dissolved, colloidal, particulate[160,162]), the shape and size of the organism, and their motility.[163,164] If the uptake rate is faster than the rate at which the Fe diffuses at the cell surface then diffusion limitation will occur.[140] The kinetic flux to the cell surface is determined by the stability and binding affinity of Fe complexes and the rate at which dissociation of these complexes occurs.[141,160] Again, the strength of the Fe complex and therefore the rate of its dissociation can limit uptake rate.[141]

Iron solubility measurements have often been used to infer bioavailability; but the two terms are not interchangeable. Typically it is assumed that dissolved Fe(III)' and Fe(II)', and some dissolved organically complexed Fe(III) are bioavailable.[108,165–167] However, the Fe requirement and uptake strategies of planktonic communities differ considerably[6,166] so a pool of Fe that is bioavailable to one species will not necessarily be available to another.[113] For example, dFe(II) is not always bioavailable to diatom species[167–169] and organically complexed Fe is not universally available to both bacterioplankton and eukaryotic phytoplankton.[108,110]

Iron biological requirement for growth defines the control that Fe bioavailability exerts on the structure of the phytoplankton community, and the threshold of the bioavailable Fe concentration under which phytoplankton induce high affinity transporters to increase Fe uptake rates.[170] The different Fe biological transporters used by phytoplankton were recently reviewed in Morrissey and Bowler.[171] Coastal phytoplankton usually have a higher Fe requirement for growth than oceanic species.[6] In addition, the Fe requirement seems to be related to the phytoplankton aspect ratio (ratio of cellular volume to surface).[114,172] Elemental stoichiometric ratio can also be used to infer biological requirement for growth or Fe limitation.[119,173] To date, little is known on freshwater eukaryotic phytoplankton Fe requirement.

In some regions of the world ocean the concentration of inorganic Fe is sufficient to sustain phytoplankton growth. However, in other areas, such as HNLC regions, the reported inorganic Fe concentrations (<2 pM) are not. In these regions the production of Fe binding organic ligands and the rate of the kinetic flux (*i.e.* mediated by photoreactions or biological transformation) will be important factors in determining the bioavailable Fe pool,[137,160] particularly to phytoplankton with high biological Fe requirement.

Concentration of bioavailable Fe in seawater and freshwater samples can be inferred using different methodologies. One is by using bioassays based on whole-cell Fe-dependent cyanobacterial bioreporters. The bioreporter BMB04 is a genetically modified strain of *Synechococcus* sp. (strain PCC 7002) constructed by introduction of the Fe-responsive gene *isi*AB fused

to the *lux*AB genes that produce luminescence in response to environmental Fe availability in seawater.[174] Cellular bioluminiscence increases with Fe limitation and it needs to be carefully calibrated in artificial seawater with varying dFe concentrations and a constant concentration of an appropriate Fe binding organic ligand.[175] Other cyanobacterial bioreporters have been optimised to sense Fe bioavailability[176] and other macronutrients (nitrate and phosphate) in freshwater environments.[177,178] Because bioreporters' signal is based on gene expression, it includes metabolic uptake and homeostasis costs.[119]

The other method typically used to infer Fe bioavailability is based on bioaccumulation experiments to calculate Fe uptake rate. Bioaccumulation experiments measure intracellular Fe concentrations after incubation of the microorganisms of interest in the medium enriched with the radioisotope ^{55}Fe or ^{59}Fe.[179] This methodology offers the advantage that it can be used with monoclonal cultures or natural phytoplankton communities typical to the study area and incubated under *in situ* environmental conditions. Because cyanobacterial bioreporters rely on a different uptake pathway than eukaryotic phytoplankton,[180] both methodologies should be used in combination in order to strengthen determination of Fe bioavailability to natural phytoplankton.[119]

It is estimated that ~80% of the Fe present in phytoplankton cells is involved in the photosynthetic machinery.[181] Under Fe deficient conditions, phytoplankton modify their photosynthetic machinery by reducing the concentration of Fe-rich cellular components[182,183] and modifying the light-harvesting systems.[184] These changes cause a decrease of the photochemical efficiency in phytoplankton photosynthesis and growth rate.[185] For instance, the growth of cyanobacteria *Synechococcus* sp. (strain PCC 7002) was characterized in artificial seawater under different concentrations of *p*Fe (equivalent to $-\log_{10}$ [Fe(III)]). The concentration of Fe required to achieve a growth rate half of maximal (K_m) was 22.7±0.6 *p*Fe (Michaelis-Menten fit $R^2 = 0.9$; $P < 0.0001$). In line with this, the Fv/Fm (quantum yield of fluorescence) decreased from 0.4±0.014 at 19.7 *p*Fe to 0.2±0.02 at 22.7 *p*Fe, which also highlights the limited ability of this microorganism to maintain growth under low Fe conditions. Therefore, the assessment of photosynthetic parameters also constitutes a meaningful tool to investigate the nutritional *status* of marine and freshwater natural phytoplankton communities,[186–188] including Fe limitation in high nutrient low chlorophyll areas.

Looking Towards the Future

Despite numerous studies, a picture of the complex and dynamic relationship between Fe chemistry and the biology of surface waters is only just emerging. Determining what controls the bioavailability of Fe to phytoplankton is one of the main challenges in understanding how Fe limits oceanic primary productivity and biodiversity. Fe cycling is influenced by both its chemistry and biology; it is a balance between input, biological uptake and recycling, and Fe sedimentation (Fig. 1). Despite the knowledge that >99.9% of dFe is bound to organic ligands,[109] these compounds have been poorly characterised and literature regarding their environmental role on Fe cycling, and the role of aquatic microorganisms and viruses in the production and recycling of Fe binding organic ligands, is scarce.[119,189]

Through the production of organic material, such as siderophores, EPS and cell lysis material (*e.g.* heme), the microorganisms themselves are clearly exerting a feedback effect on Fe chemistry,[108,190] although currently the role of the mixture of these products in Fe biogeochemistry is not fully resolved. Recent progress has been made on the identification of siderophores and hemes in natural waters.[109] It is likely that the organic complexation of Fe to a yet poorly defined range of ligands exerts the largest influence on Fe bioavailability. However, progress needs to be made on their composition and identification in order to establish their relative importance in each aquatic region. This will move towards a better understanding of how Fe chemistry affects Fe limitation and co-limitation observed in both HNLC and LNLC regions. Similarly, the nature of organic ligands present in lakes needs further attention.

Due to differences in Fe biological requirements and uptake pathways, it is then expected that for a given Fe chemistry, the pool of bioavailable Fe will differ between species.[118,173,191] As such further process studies complemented by large scale mapping exercises are required to better understand how Fe chemistry constrains phytoplankton biodiversity and productivity in different aquatic systems and regions. The measure of Fe bioavailability is currently suffering from a lack of standardisation, and tools that are able to rapidly measure Fe bioavailability are urgently needed. Such an approach is required to allow inter-laboratory efforts to map, in a quantitatively comparable manner, the extent of Fe limitation in aquatic systems. Possibly due to our limited understanding of the complex causality of the numerous Fe subcellular responses, it is still unclear whether a direct measurement (*e.g.* bioreporter, marker gene) or an indirect measurement (yet undefined chemical proxy, photobiology) of bioavailability is to be preferred.

Identification of the main regional Fe source is also critical to understanding its relationship to bioavailability, as this affects the retention time and chemical reactivity of Fe in the euphotic zone. Different sources may be more bioavailable than others but this will also be dependent on Fe speciation (and therefore its stability), the size fraction, and mode of supply to the upper ocean. Efforts in measuring their impact for aquatic chemistry and biology as well as the development of chemical tracers need to be maintained.

One of the most noticeable changes predicted in water chemistry is acidification. The fate of Fe limitation in acidifying oceans and lakes still remains unclear as Fe will become more soluble at lowered pH, but will be more strongly bound to organic ligands.[192] How a changing environment will alter the nature of biologically produced organic ligands, the rate of production and complexation, and essentially the bioavailability of Fe are largely unknown. Whether these alterations will be positive or negative, they will certainly affect phytoplankton productivity and biodiversity. Changes in the composition of phytoplankton communities have the potential to alter ecological interactions and functioning, thereby creating indirect effects throughout entire marine food webs. Only by improving our knowledge of these parameters will we be able to (i) understand the dynamic of Fe limited aquatic regions, (ii) improve existing biogeochemical models to accurately predict carbon fixation; and (iii) develop sustainable strategies for ocean resources.

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