Biogeochemical Cycling of Iron in Natural Waters

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Iron is one of the most important redox active trace metals present in aquatic systems. The redox cycling of iron is closely associated with the biogeochemical cycling of oxygen, dissolved organic carbon (DOC), and other trace metals. The redox chemistry of iron also affects the production and depletion of reactive oxygen species (partially reduced forms of oxygen).[1, 2] In spite of being the fourth most abundant element in the earth's crust (approximately 5% by weight), the dissolved iron concentration in oxygenated circumneutral natural waters is very small due to the rapid oxidation of Fe(II) to Fe(III).[3] The kinetics of the redox cycling of iron strongly depends on the chemistry of its two common oxidation states, the reduced ferrous iron (Fe(II)) and the oxidized ferric iron (Fe(III)).

The redox potentials of Fe(II)/Fe(III), and dissolved oxygen favor Fe(III) as the thermodynamically stable form of iron in circumneutral aqueous solutions. In spite of its stability, Fe(III) rapidly hydrolyzes to produce amorphous ferric oxide.[4] The exact nature of the iron oxides produced by the aging of amorphous ferric oxides generally depends on several environmental factors, including pH, ionic strength, presence of organic, and inorganic ligands, and temperature.[5] The solubility of Fe(III) significantly increases in the presence of organic ligands and approximately 99% of the total dissolved iron present in some aquatic systems is organically complexed. On the other hand, Fe(II) is thermodynamically unstable in oxygenated, circumneutral waters and oxidizes to Fe(III). Iron(II) is produced by a number of processes, including both photochemical and biological production, but then it is re-oxidized quickly by oxygen and other oxidants with a half-life of in the order of several minutes around pH 8.[4]

The redox cycling of iron can significantly affect the quality, transportation, bioavailability, and the decomposition of both naturally occurring and synthetic dissolved organic compounds.[1, 5, 6] Iron can significantly alter the chemistry of dissolved organic compounds by forming both strong and weak complexes with organic ligands. In addition, the reactive oxygen species ($O_2^{\cdot -}$, H_2O_2 and $HO^{\cdot}$) generated by the redox cycling of iron have been shown to accelerate the rate of decomposition of both naturally occurring and synthetic environmentally persistent organic matter such as humic substances, synthetic surfactants, herbicides, and insecticides.[5, 6] On the other hand, dissolved organic matter can significantly affect the biogeochemical cycling of iron. It has been reported that some natural, and synthetic organic ligands can dramatically increase the amount of Fe(II) produced by the photochemical reduction of Fe(III)-organo complexes, and amorphous ferric oxides.[7] Dissolved organic ligands have been reported to both decease and increase the rate of iron(II) oxidation.[8] Furthermore, the presence of organic ligands significantly increases the solubility of Fe(III), which in turn significantly enhances the microbial availability and the chemical reactivity of iron.

Formation of Fe(II)/Reduction of Fe(III) in Natural Waters

The concentration of Fe(II) observed at a given time is the balance between the production of Fe(II) by the reduction of Fe(III) compounds and the oxidation of Fe(II) back to Fe(III) to produce iron oxides. Therefore, a steady supply of electrons and energy are required to sustain a reasonable Fe(II) concentration in oxygenated aquatic systems.[9] All the Fe(III) reduction processes can be summarized into three major reactions: photochemical reduction, thermal reduction and microbial mediated reduction.

Photochemical Reduction

The production of Fe(II) by the photochemical reduction of both organic and inorganic complexes of Fe(III) and the photochemical reductive dissolution of amorphous ferric oxides is well documented.[1,7] Two major reaction pathways have been recognized in the literature to account for the majority of photochemical reduction processes: (i) reduction by photochemically induced ligand-to-metal-charge-transfer reactions (LMCT) and (ii) reduction by photochemically generated superoxide and organic radicals.[1,7]

Thermal Reduction

Some natural organic matter containing quinone-type functional groups can reduce Fe(III) to produce Fe(II) in natural waters.[1,7] The amount of Fe(II) produced by the thermal reduction of Fe(III) by Suwannee River fulvic acid (SRFA) generally decreases with increasing pH.[7] The reduction of Fe(III) by SRFA seems to occur via two steps: a rapid short initial reduction process followed by a long slow reduction process. It is assumed that SRFA contains at least two types of reducing sites: a limited number of fast-reducing sites and a relatively higher number of slow-reducing sites. Once the fast-reducing sites are consumed, the reduction process moves to slow-reducing sites.[7]

Microbial Mediated Reduction

Microbial mediated reduction of both poorly and well-crystallized iron oxides, iron containing clay (phyllosilicates), and dissolved Fe(III) compounds are important sources of Fe(II) in anoxic and micro-oxic environments.[10] Many microorganisms can reduce Fe(III) using a variety of substrates as electron donors, including hydrogen gas (H2) and fixed carbon. Microbial mediated reduction is favorable in acidic and anoxic/microoxic environments because of the higher solubility of Fe(III) in these environments.[10] The microbial mediated reduction of insoluble iron oxides may occur via several possible pathways. *Geobactor* species directly attach to the iron oxide surface and transfer electrons to surface bound Fe(III) via flagella or pili as conductive cellular nanowires. Some other iron reducing bacteria (e.g. *Geothrix* species) use exogenously and endogenously produced external electron shuttles to reduce iron oxides without establishing a direct contact between the microorganism and the iron oxide surface. Some of these electron shuttles have been identified as redox-active organic compounds such as humic acids, plant exudates, and antibodies.[11] *Acidiphilium* species appear to produce extracellular compounds to accelerate the dissolution of crystalline iron oxides. Microbial mediated reduction of iron containing phyllosilicates may or may not be a significant source of Fe(II) because most of the redox-sensitive iron may undergo many redox cycles inside the lattice without moving or mobilizing into the aqueous phase.

Oxidation of Fe(II)/Formation of Fe(III) in Natural Waters

The oxidation of Fe(II) in natural waters occurs via two major reaction pathways: chemical (abiotic), and microbial mediated oxidation. The chemical oxidation of Fe(II) is a rapid process in oxygenated natural waters especially at higher pH. The microbial oxidation of Fe(II) is important only in acidic and/or anoxic environments because of the very slow rate of chemical oxidation of Fe(II) in these environments.

Chemical (abiotic) oxidation of Fe(II)

The chemical oxidation of Fe(II) has been studied for several decades under a wide variety of experimental conditions that are relevant to freshwaters[3, 4] and also to brines.[12] The rate of the chemical oxidation of Fe(II) strongly depends on pH, temperature, dissolved H_2O_2/O_2 concentrations, ionic composition, ionic strength and the presence of both organic, and inorganic ligands. The kinetics of Fe(II) oxidation was initially investigated using micromolar concentrations of Fe(II); however, the first systematic study using nanomolar concentrations of Fe(II) was done fairly recently in 1995 by King and coworkers.[13]

The homogeneous oxidation of Fe(II) in the absence of organic ligands is generally explained according to the Haber-Weiss mechanism,

$$\mathrm{Fe(II)} + O_2 \rightleftharpoons \mathrm{Fe(III)} + O_2^{\cdot -} \qquad \log(k) = -13.77 + 2.0\,(\mathrm{pH}) \quad ^{*(i)}$$

$$\mathrm{Fe(II)} + O_2^{\cdot -} + 2H^+ \rightleftharpoons \mathrm{Fe(III)} + H_2O_2 \qquad k = 1.0 \times 10^7 \quad ^{*}$$

$$\mathrm{Fe(II)} + H_2O_2 \rightleftharpoons \mathrm{Fe(III)} + OH^- + HO^{\cdot} \qquad \log(k) = -2.45 + 0.97\,(\mathrm{pH}) \quad ^{*(ii)}$$

$$\mathrm{Fe(II)} + OH^{\cdot} \rightleftharpoons \mathrm{Fe(III)} + OH^- \qquad k = 5.0 \times 10^8 \quad ^{*}$$

* rate constants ($M^{-1}s^{-1}$) summarized in King *et al.* (1995)
(i) valid between pH 6.0 - 8.3
(ii) valid between pH 6.0 - 8.0

The overall reaction is:

$$4\ \mathrm{Fe(II)} + O_2 + 2H^+ \rightarrow 4\ \mathrm{Fe(III)} + 2OH^-$$

At micromolar concentrations of Fe(II), a 4:1 and a 2:1 stoichiometric ratio have been observed for the oxidation of Fe(II) by O_2 and H_2O_2, respectively. This observation suggests that superoxide ($HO_2^{\cdot}/O_2^{\cdot -}$) and hydroxyl ($HO^{\cdot}$) radicals can stoichiometrically oxidize micromolar concentrations of Fe(II).[13] However, it has been shown that even at micromolar concentrations of Fe(II), only about 1% of Fe(II) is directly oxidized by the hydroxyl radical and almost all of the hydroxyl radicals react with other reduced chemical species such as chloride and carbonate to produce other radicals. The newly generated radicals may effectively oxidize Fe(II), maintaining the 4:1 stoichiometric ratio between Fe(II) and O_2.

The rate of the homogeneous oxidation of Fe(II) in carbonate buffer solutions is generally expressed according to rate the law (M refers to mol L^{-1}),

$$\frac{-d[\mathrm{Fe(II)}]}{dt} = k[\mathrm{Fe(II)}][\mathrm{O_2}][\mathrm{OH^-}]^2$$

Millero and co-workers (1987)14 confirmed that the above rate law is valid in the pH range of 5 and 9, in ionic strengths between 0 to 6 m (molal) and temperatures from 5 °C to 45 °C. At a given pH, the rate law simplifies to:

$$\frac{-d[\mathrm{Fe(II)}]}{dt} = k_{app}[\mathrm{Fe(II)}][\mathrm{O_2}] \quad k_{app} = k[\mathrm{OH^-}]^2$$

The rate law can be further simplified if the oxidation is taking in solutions where $[O_2] >> [Fe(II)]$,

$$\frac{-d[\mathrm{Fe(II)}]}{dt} = k'[\mathrm{Fe(II)}]$$

$$[\mathrm{Fe(II)}] = [\mathrm{Fe(II)}]_0 e^{-k't} \qquad k' = k_{app}[\mathrm{O_2}]$$

The plot of ln[Fe(II)] vs time is linear with a slope of k'.

According to the above equation , at a given pH and in the presence of excess dissolved O_2, the rate of oxidation of Fe(II) by O_2 is a pseudo first order reaction. Almost all the kinetic studies using micromolar concentrations of Fe(II)[8] and a few studies using nanomolar concentrations of Fe(II)[15] have confirmed the validity of the rate law given in equation . However, most of the kinetic studies using nanomolar concentrations of Fe(II)[4, 13] and a few studies using micromolar concentrations of Fe(II)[16] have reported that the rate of oxidation of Fe(II) can deviate from a pseudo first order reaction especially, towards the end of the oxidation process.

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Anabolic Androgenic Steroid Doping: Facts, Effects and Health Risks

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Introduction

Anabolic androgenic steroids (AAS) are a group of hormones consisting of the male sex hormone testosterone and its synthetic derivatives. AAS were initially developed in the 1930s as a drug to promote the growth of skeletal muscle and to develop male sexual characteristics, and have been used as a medication to treat conditions such as reproductive system dysfunction, breast cancer, and anaemia. In the 1950s, competitive athletes started using AAS as an ergogenic aid with the intention of promoting the growth of skeletal muscle mass. Furthermore, in the 1980s, non-athletes started using AAS for cosmetic purposes. The most common pattern followed by AAS users is “Stacking” (combining two or more oral and injectable AAS) accompanied with “Cycling” (taking multiple doses for a period of time, stopping, then restarting), which lasts for 4-12 weeks.[1,2]

World Anti-Doping Agency (WADA), which was formed as a subsidiary of the International Olympics Committee (IOC), is responsible for conducting scrutiny of doping in sports at present. Anabolic steroids were first identified as a banned class by the Medical Commission of the (IOC) in 1974. In the 1990s, the name was changed to “Anabolic Agents”, so that Clenbuterol and other β_2-agonists which possess anabolic activity could also be included in the group. The anabolic agents have been reported as the most frequently detected doping substance in sports. According to WADA’s Anti-Doping Administration and Management System (ADAMS) reports in 2017, 44% of the substances identified as adverse analytical findings were anabolic agents.[3,4]

Types of Anabolic Androgenic Steroids

The androgens naturally produced in the body are C19 steroids. Testosterone, the primary male hormone, is produced by Leydig cells in the testes of eugonadal men. In addition to testosterone, several other androgens are also present in the body. Testosterone and 5 α-dihydrotestosterone (DHT) are characterized by a 17-β hydroxyl and 3-oxo groups. DHT is produced by the action of the cytoplasmic action of 5-α-reductase. The oxidation of testosterone produces androstenedione, dehydroepiandrosterone (DHEA) and androsterone. Epitestosterone is an epimer of testosterone with a 17-α hydroxyl group. Testosterone and DHT are the most active forms of the androgens, and all other natural androgens show a weak androgenic activity compared to testosterone.[2,5]

The chemical structures of principal natural androgens are shown in Figure 1.

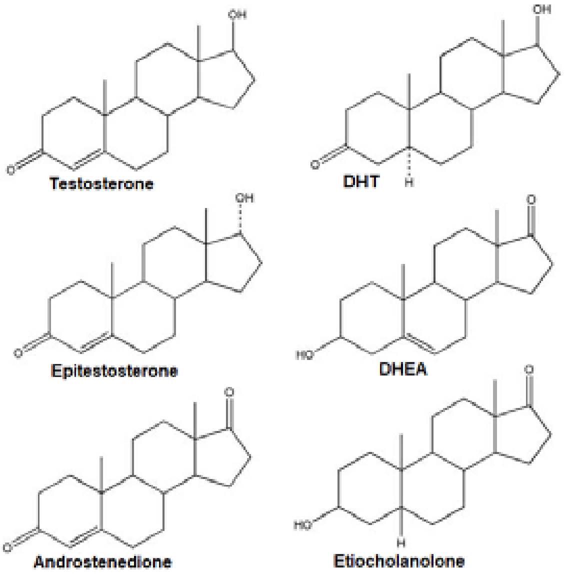

Figure 1: Principal natural androgens

Testosterone was first isolated and synthesized in 1935. Testosterone has been used as the template molecule to synthesize anabolic steroids by incorporating several structural modifications. Structural optimization of testosterone was done to minimize androgenic effects and to maximize anabolic effects while increasing its stability. Figure 2 summarizes the structural modifications to testosterone that affect its androgenic and anabolic activities. Examples of some commonly used AAS are given in Figure 3.[5,6]
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