Iron & Manganese Cycle

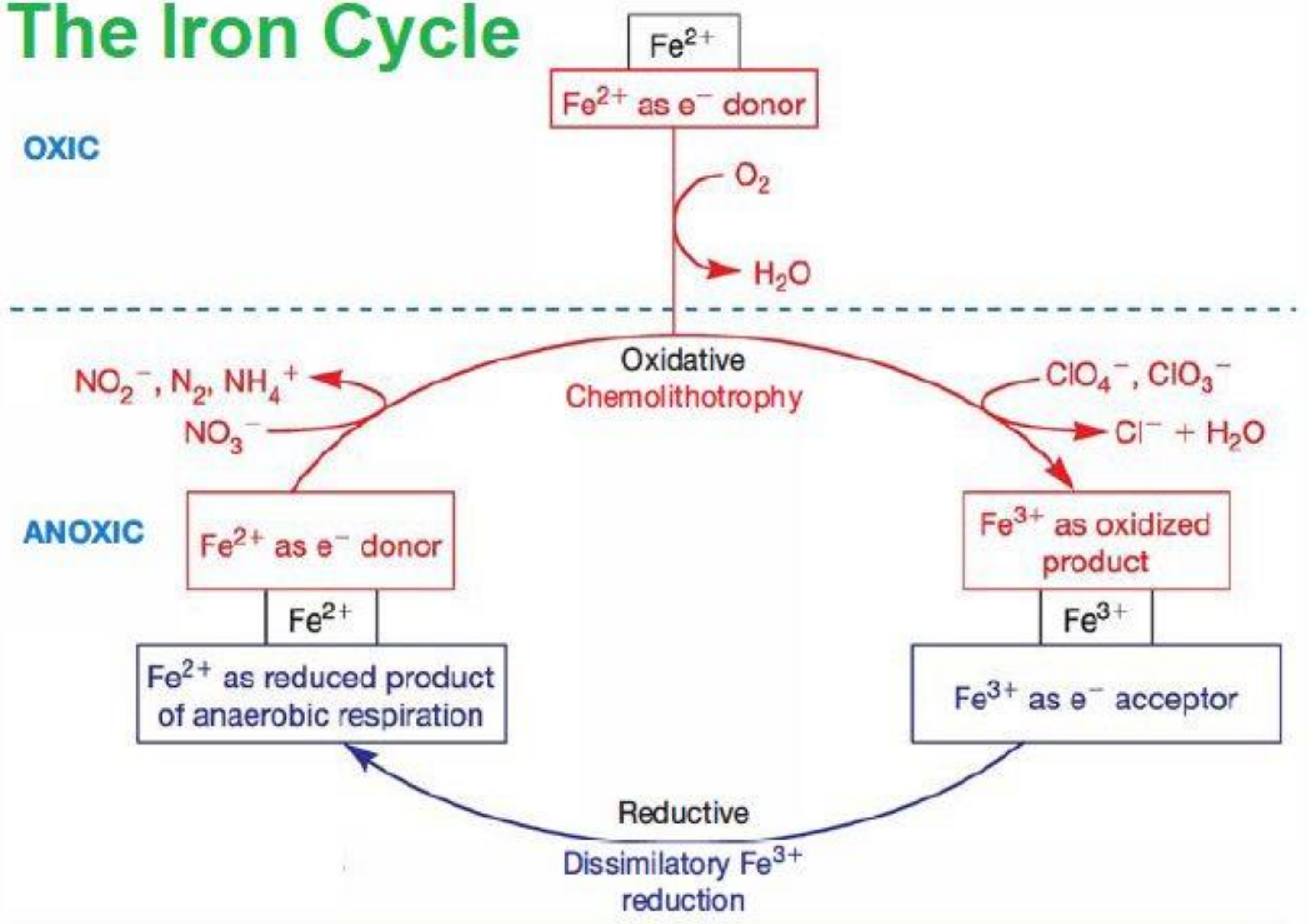
- Iron is an important limiting nutrient for plants, which use it to produce chlorophyll. Photosynthesis depends on adequate iron supply. Plants assimilate iron from the soil into their roots.
- Animals consume plants and use the iron to produce hemoglobin, the oxygen transports protein found in red blood cells. When animals die, decomposing bacteria return iron to the soil.
- The marine iron cycle is very similar to the terrestrial iron cycle, except that phytoplankton and cyanobacteria assimilate iron.
- Iron is typically released into the soil or into the ocean through the weathering of rocks or through volcanic eruptions.
- The iron cycle features the interchange of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}).
- The iron cycle (Fe),also known as the Ferrous Wheel, is the biogeochemical cycle of iron through the atmosphere, hydrosphere, biosphere and lithosphere.

- On our planet, iron Is ubiquitous in the hydrosphere,lithosphere,biosphere and atmosphere, either as particulate ferric [Fe(III)] or ferrous [Fe(II)] iron-bearing minerals or as dissolved ions.
- Redox transformations of iron, as well as dissolution and precipitation and thus mobilization and redistribution, are caused by chemical and to--a significant extent by microbial processes.
- Ferrous iron is a soluble form of iron that is stable at extremely low pH or under anaerobic conditions.
- Under aerobic, moderate pH conditions ferrous iron is oxidized spontaneously to the ferric (Fe^{3+}) form and is hydrolyzed abiotically to insoluble ferric hydroxide [$Fe(OH)_3$].
- Microbially influenced transformations of iron are orten much faster than the respective chemical reactions.They take place in most soils and sediments, both in fresh water and marine environments, -and play an important role in other (bio)geochemical cycles, in particular in the carbon cycle.
- Iron exists in a range of oxidation tates from -2 to +7; however, on Earth it is predominantly in its +2 or +3 redox state and is a primary redox-active metal on Earth.
- The cycling of iron between its +2 and +3 oxidation states is referred to as the iron cycle.
- This process can be entirely abiotic or facilitated by microorganisms, especially iron-oxidizing bacteria.
- The abiotic processes include the rusting of iron-bearing metals, where Fe2+ is abiotically oxidized to Fe3+ in the presence of oxygen, and the reduction of Fe3+ to Fe2+ by iron-sulphide minerals.
- The biological cycling of Fe2+ is done by iron oxidizing andreducing microbes.

- Its assimilation presents two challenges for most aerobic microorganisms.
- First, while iron is an essential element, free iron is usually present in very small quantities. Second, Fe^{3+} dominates in oxic environments, but microbes generally incorporate Fe^{2+} into biomolecules.
- The use of siderophores solves both problems. Siderophores are low molecular weight organic molecules that bind Fe^{3+}, facilitating its transport into the cell, where it is reduced to Fe^{2+}.
- Dissimilatory reduction occurs when ferric iron serves as a terminal electron acceptor during anaerobic respiration. In most environments, Fe^{3+} is found chiefly in a crystalline phase (e.g., hematite and magnetite) and as a component of sediment clays.
- A wide range of bacteria and archaea are capable of dissimilatory Fe^{3+} reduction. This includes genera from Euryarchaeota and Crenarchaeota, all five classes of *Proteobacteria*, *Firmicutes*, *Deferribacteraceae*, *Acidobacteria*, *Thermotoga*, and *Thermus*.
- In addition to ferric iron (Fe^{3+}) as a terminal electron acceptor, some magnetotactic bacteria such as *Aquaspirillum magnetotacticum* transform extracellular iron to the mixed valence iron oxide mineral magnetite (Fe_3O_4) and construc
- Furthermore, some dissimilatory iron-reducing bacteria accumulate magnetite as an extracellular product.

- Ferrous iron can also be oxidized under anoxic conditions with nitrate as the electron acceptor.
- One interesting anaerobic microbe is *Dechlorosoma suillum*, which oxidizes Fe^{2+} using perchlorate (ClO_4^-) and chlorate (ClO_3^-) as electron acceptors.
- Because perchlorate is a major component of explosives and rocket propellants, it is a frequent contaminant at retired munitions facilities and military bases.
- Thus *D. suillum* may be used in the bioremediation (biological cleanup) of such sites.
- This process also occurs in aquatic sediments with depressed levels of oxygen and may be another route by which large zones of oxidized iron have accumulated in environments with lower oxygen levels.

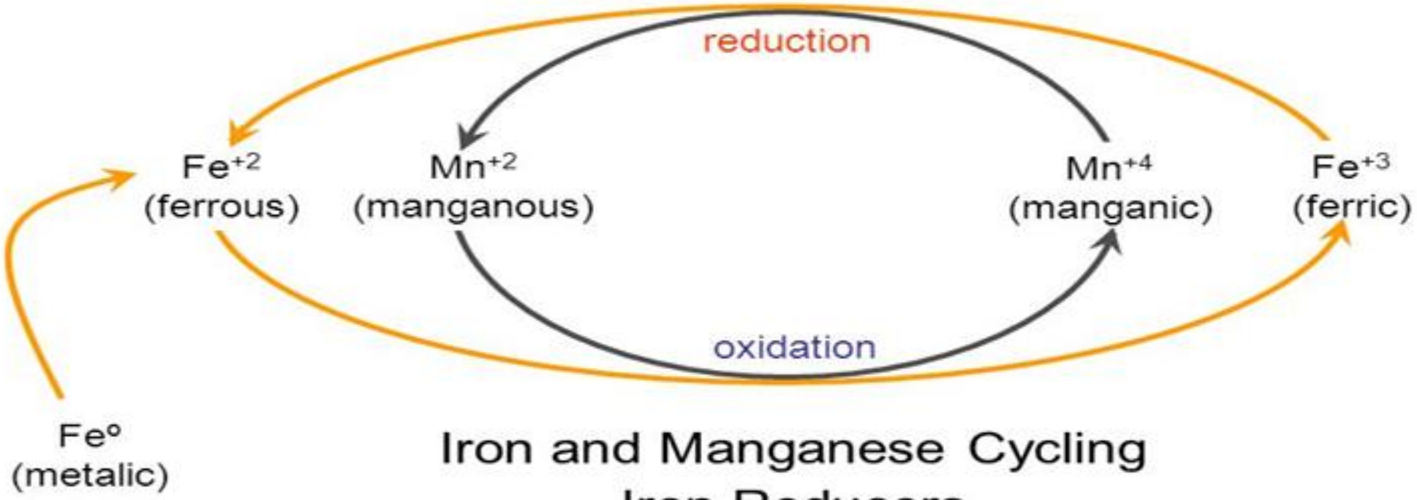
The Iron Cycle



Manganese Cycle

- Microorganisms have long been known to mediate manganese(Mn) oxidation in a variety of nvironments, including caves.
- Chemolithoautotrophic Mn oxidation is highly unlikely to be carried out with the enzymes currently known, although indirect oxidation of Mn during heterotrophic growth or reproduction has been observed In both bacteria and fungi.
- Mn can precipitate at high pH, lowering Mn availability so deficiencies are most likely to occur in high pH soils (calcareous soils or over-limed soils).
- Manganeseis most available at soil pH levels of 5 to 6.5.
- The transformations of iron and manganese in nature and the relationship between the cycling of these and other biologically active elements occurs.
- Both the oxidation and the reduction of iron and manganese in natural environments is, to a large extent, promoted by microbial catalysis, but abiotic transformations are also important and may compete with the biological processes.
- In the Earth's crust, iron and manganese are mainly found as minor components of rock-forming silicate minerals such solivine, pyroxenes, and amphiboles.
- Iron has a high abundance of4.3% by mass in the continental crust. At a 50-fold lower crustal abundance than iron, manganese is the second most abundant redox-active metal.
- There are many similarities between iron and manganese in terms of both geochemistry and microbiology.
- Microbes play an important role in the oxidation of reduced iron and manganese.
- Dissimilatory iron and manganese-reducing microorganisms catalyze the reduction of Fe (III) to Fe (II), and of Mn (III)or Mn (IV) to Mn(II).
- The microbial manganese and iron reduction also occur in aquatic environments.

Metals Cycling



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Iron Reducers
Iron Oxidizers
Acid Mine Drainage
Manganese Nodules