

Iron as a limiting nutrient in the oceans

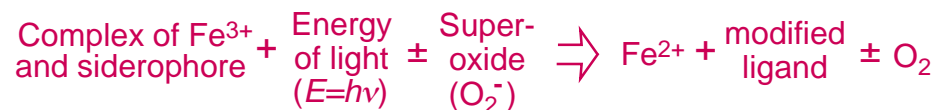
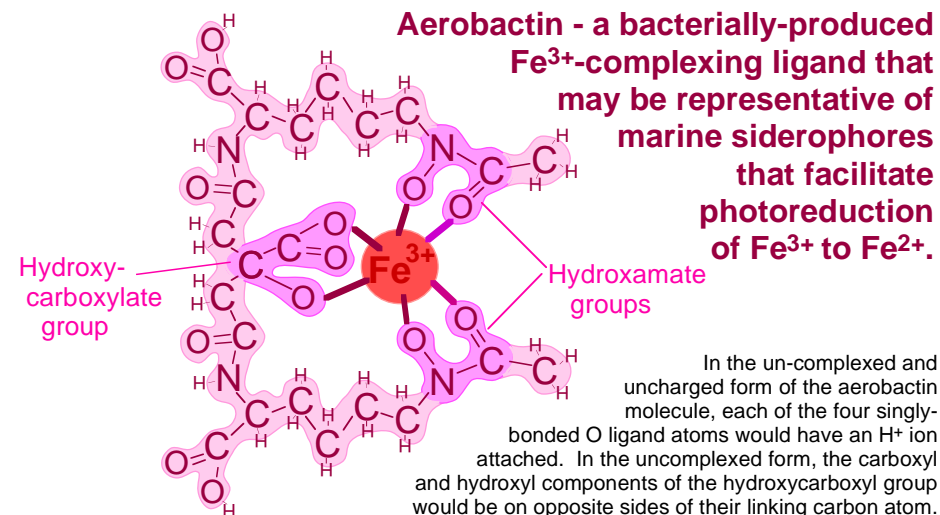
Previous pages in this series have focused on dissolved nitrate, phosphate, and silicate as limiting nutrients in the oceans. Those three nutrients have much in common: they are more abundant in deep water than in typical surface water, and more abundant in older deep water than in younger deep water, and so their availability as nutrients for photosynthesis has much to do with ocean circulation and upwelling. Another feature that they have in common is that they have long been recognized as limiting nutrients for marine photosynthesizers.

An entirely different sort of limiting nutrient in at least some regions of the ocean is iron. Iron is different in that its availability has little to do with ocean circulation, and much more to do with photochemical reactions, as discussed here. Another feature is that iron has only been recognized as an important limiting nutrient since the 1990s.

Iron is a scarce solute in seawater, and the abundance of dissolved O_2 in seawater means that what little iron is present in the ocean is typically oxidized iron, Fe^{3+} . This oxidized Fe forms inert iron oxides and hydroxides and is thus essentially not available to photosynthesizing organisms. On the other hand, Fe^{2+} , the reduced form of iron, is more soluble and thus more biological reactive – but rapid oxidation to Fe^{3+} would seemingly make existence of Fe^{2+} nearly impossible.

The key to availability of Fe^{2+} for photosynthesis is that some Fe^{3+} is complexed with organic ligands. These ligands are called "siderophores" (i.e., "iron-bearers"), and many of them are produced by marine bacteria. Many such ligands contain carboxyl ($-COOH$) groups, hydroxyl ($-OH$) groups, and combinations of the two as hydroxycarboxylate groups. The sketch at right illustrates one representative siderophoric ligand, aerobactin.

Ligands like the one shown seemingly promote the photochemical reduction of Fe^{3+} to Fe^{2+} . In that process, energy from sunlight drives the transfer of an electron to the iron atom and thus reduces that atom from its 3+ to 2+ state. The mechanism of this reaction is not clear, and the source of



the required electron may be the ligand itself, or it may be photochemically-produced oxygen-bearing radical species like superoxide (O_2^-). The ligands may also facilitate photochemical dissolution of Fe^{3+} -bearing hydroxides. Regardless, the result seems to be reactive reduced iron, Fe^{2+} , that may be used by photosynthesizers – or it may be oxidized back to Fe^{3+} .

To summarize, iron is a nutrient with a very different behavior than that of nitrate, phosphate, and silicate. Whereas nitrogen and phosphorous are converted from non-nutrient organic compounds to inorganic nutrient compounds by oxidation in the dark depths of the ocean and must be returned later to the sea surface by upwelling, iron undergoes reduction driven by the sun's energy at the sea surface to become a nutrient immediately, but briefly, available to photosynthesizers.

Sources: Barbeau, K., 2006, Photochemistry of organic iron(III) complexing ligands in oceanic systems: *Photochemistry and Photobiology*, v. 82, p. 1505–1516, and Harris, W.C. et al., 1979, Coordination chemistry of microbial iron transport compounds. 16. Isolation, characterization, and formation constants of ferric aerobactin: *Journal of the American Chemical Society*, v. 101, p. 2722-2727 – and many thanks to Dan Bulger for educating the author about this business.