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Ronald Benner

*University of South Carolina - Columbia*, benner@mailbox.sc.edu



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# Loose ligands and available iron in the ocean

**Ronald Benner**[1]

*Department of Biological Sciences and Marine Science Program, University of South Carolina, Columbia, SC 29208*

The ocean covers ≈70% of the Earth's surface and plays a major role in regulating global climate and sequestering carbon dioxide from the atmosphere. Diverse populations of phytoplankton, namely photosynthetic microalgae and cyanobacteria, abound in sunlit surface waters of the ocean and account for half of global primary production. Phytoplankton require a variety of essential nutrients, including iron, to fix carbon dioxide and fuel ocean food webs, but the oxidized form of iron, Fe(III), that prevails in the ocean is only sparingly soluble in oxygenated seawater. The solubility of iron is enhanced through chelation with organic ligands, and nearly all of the dissolved iron in seawater is bound to natural ligands (1). The molecular identity and reactivity of seawater ligands has largely eluded discovery by the iron workers, leaving a gaping hole in our understanding of the availability of iron to phytoplankton. This has ramifications for the global C cycle, because phytoplankton productivity is limited by iron availability in vast regions of the surface ocean that have an ample supply of other critical nutrients, such as N and P (2). In PNAS, Hassler et al. (3) provide experimental evidence indicating saccharide-enhanced iron utilization by phytoplankton cultures and natural planktonic communities in surface seawater. Apparently, saccharides chelate iron in a bioavailable form, an observation that is likely to transform current thinking about iron cycling in the ocean. Saccharides (also known as carbohydrates) are abundant, bioreactive components of dissolved organic matter (DOM) that are produced by phytoplankton in the surface ocean (4, 5). It seems that saccharides play a critical role in sustaining ocean productivity through a positive feedback that links the C and Fe cycles (Fig. 1*A*).

The mix of natural organic ligands in seawater has been categorized into two classes, strong and weak, according to their binding affinities for iron (1). Much attention has been focused on the stronger binding ligands, particularly siderophores—a group of designer ligands biosynthesized by marine bacteria (6). Siderophores can grab iron from weaker ligands and lock iron in a complexed form that seems to be directly bioavailable only to bacteria. The recent discovery (7) that photolysis of a specific bacterial siderophore can be coupled with the uptake of released iron by marine phytoplankton provides a fascinating mechanism to make siderophore-bound iron available to marine microalgae, but it seems that siderophores supply a minor fraction of the iron requirements of the phytoplankton community (6). Common biochemicals, such as saccharides and amino acids, have functional groups that can form weak complexes with iron and other trace metals in seawater. Relatively little is known

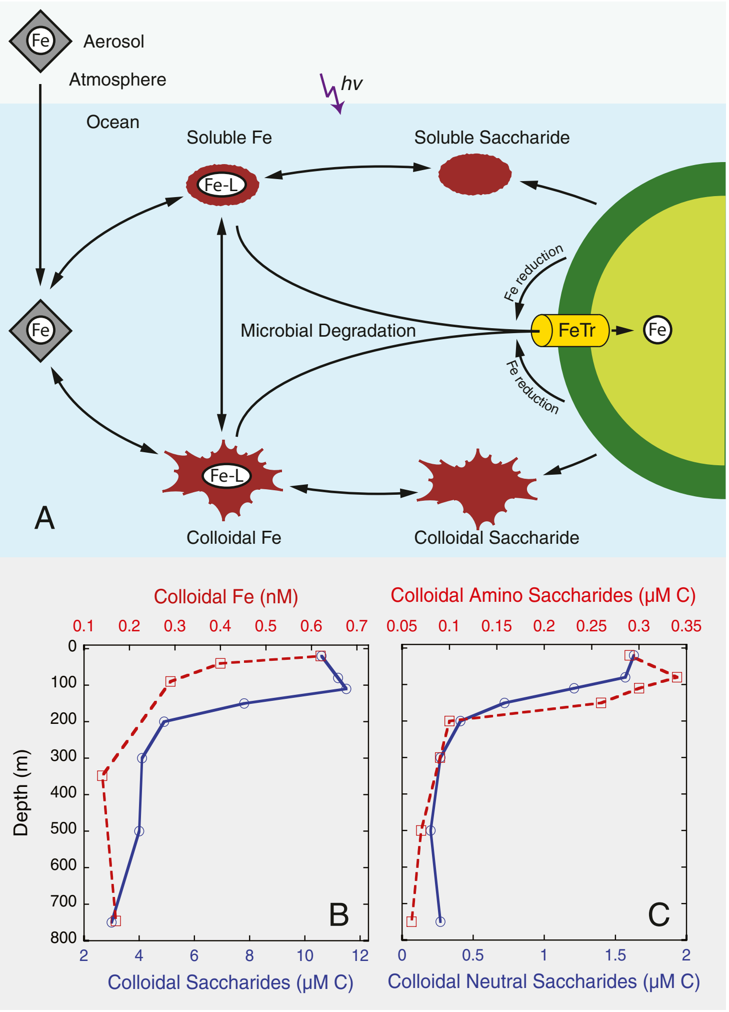


**Fig. 1.** Simplified schematic of iron and saccharide sources, interactions, and utilization in the surface ocean. (*A*) Aerosol iron rapidly dissolves in the surface ocean and complexes with soluble and colloidal ligands (8), shown as saccharides as described in PNAS by Hassler et al. (3). Saccharides are released from phytoplankton and play an important role in supplying available iron to phytoplankton in a dynamic feedback cycle that enhances biological productivity. Photochemical and biological processes drive the speciation of iron and the production and degradation of colloidal and soluble carbon. Iron is reduced to Fe(II) on the cell surface by phytoplankton before uptake (9). (*B*) Concentrations of colloidal iron (15) and saccharides (17) in the upper water column of the NPSG. Phytoplankton production maintains high concentrations of colloidal saccharides in surface waters and biological utilization rapidly consumes saccharides in the upper 300 m of the water column. Colloidal iron concentrations follow a similar depth distribution, indicating linkages between the cycling of colloidal iron and organic carbon. (*C*) Colloidal amino and neutral saccharides, specific components of the total saccharide pool, are also largely produced in the surface ocean and consumed in deeper waters of the NPSG (17, 18). These saccharides show varying dynamics in the upper 200 m, indicating that the cycling of colloidal saccharides varies with composition and is likely to influence the cycling of complexed iron.

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[1]E-mail: BENNER@mailbox.sc.edu.

about the bioavailability of iron complexed with these ligands, but weak ligands are abundant throughout the ocean water column (1, 8). The bioavailability of iron is influenced by the chemical nature of organic ligands. Weak ligands, such as saccharides, could facilitate phytoplankton access to iron by more readily disassociating and releasing unchelated Fe(III) to the surface of a phytoplankton cell, where it can be rapidly reduced to Fe(II) and transported into the cell (9). Microbial degradation of iron–saccharide complexes could also increase the pool size of unchelated Fe(III) available to phytoplankton (Fig. 1*A*).

Saccharides are the most abundant class of biomolecules identified in surface ocean DOM (4, 10). Extracellular release from phytoplankton, zooplankton grazing, and viral lysis are the primary mechanisms contributing saccharides to the DOM reservoir (11). Mono-, oligo-, and polysaccharides occur in seawater, as well as saccharides combined with other biochemicals, such as amino acids, lipids, and nucleobases (12). Saccharides are a diverse class of biochemicals that incorporate a variety of heteroatoms, such as N, P, and S, which, in addition to hydroxyl and carboxyl functional groups, can bind iron. Saccharide concentrations are $\approx 10^3$ to $10^5$ times higher than iron concentrations on a molar basis in surface seawater and are likely to complex a major fraction of dissolved iron even in the presence of strong ligands, such as siderophores. Saccharides are abundant on cell surfaces, where they also could complex iron and other trace metals. The chemical composition of extracellular saccharides released from phytoplankton is quite different from the intracellular composition of saccharides, indicating functional differences that could be related to metal-chelating characteristics of extracellular saccharides. Do phytoplankton release saccharides that bind iron and other trace metals by design, or are these metal-binding saccharides released by chance?

**It seems colloidal iron in the surface ocean is more bioavailable than previously thought.**

DOM exists in a continuum of size ($10^{-10}$to $10^{-6}$ m) in seawater and includes colloids and high–molecular-weight macromolecules ($10^{-9}$ to $10^{-6}$ m), which account for ≈30% of the dissolved organic carbon in the surface ocean (12). Saccharides are the dominant components in the colloidal size fraction, constituting more than half of all of the carbon (4). Microorganisms rapidly use plankton-derived colloidal organic matter in seawater (13, 14). Most dissolved iron in the surface ocean is also found in the colloidal size fraction (15, 16). Depth profiles of the concentrations of colloidal saccharides and iron in the upper water column of the North Pacific Subtropical Gyre (NPSG; Fig. 1*B*) indicate colloidal saccharides and iron decline by ≈75% in the upper 300 m of the water column (17, 18). Likewise, the concentrations of colloidal amino and neutral saccharides decline by ≈75% in the upper 300 m (Fig. 1*C*). Colloidal iron concentrations decline more rapidly than saccharide concentrations in the upper 100 m. Colloidal iron could be bound to specific saccharides of greater bioavailability than bulk saccharides, which are several orders of magnitude more abundant than iron. Differences in the profiles of amino and neutral saccharides are also apparent in the upper 100 m (Fig. 1*C*). The rapid decline in colloidal saccharide concentrations in the upper ocean is primarily due to biological utilization (11, 13). Is the rapid decline in concentrations of colloidal iron in the upper ocean also indicative of biological utilization? Total dissolved iron concentrations are minimal (0.09 nM) in the lower euphotic zone (110 m) of the NPSG near the deep chlorophyll maximum (19), which is consistent with biological utilization of the colloidal and soluble fractions of dissolved iron. It seems colloidal iron in the surface ocean is more bioavailable than previously thought, owing in large part to its association with saccharides.

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