



## The Biogeochemical Cycles of Trace Metals in the Oceans

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## REVIEW

# The Biogeochemical Cycles of Trace Metals in the Oceans

F. M. M. Morel<sup>1</sup>\* and N. M. Price<sup>2</sup>

Planktonic uptake of some essential metals results in extraordinarily low concentrations in surface seawater. To sequester or take up these micronutrients, various microorganisms apparently release strong complexing agents and catalyze redox reactions that modify the bioavailability of trace metals and promote their rapid cycling in the upper water column. In turn, the low availability of some metals controls the rate of photosynthesis in parts of the oceans and the transformation and uptake of major nutrients such as nitrogen. The extremely low concentrations of several essential metals are both the cause and the result of ultraefficient uptake systems in the plankton and of widespread replacement of metals by one another for various biochemical functions.

The phytoplankton of the oceans are responsible for about half the photosynthetic fixation of carbon (primary production) on Earth (1). In contrast to most land plants, which grow relatively slowly and contribute only a small percentage of their biomass to the terrestrial food chain on any given day, marine phytoplankton divide every day or every

week to keep up with zooplankton grazers. To do this, they must take up from seawater—along with carbon, nitrogen, phosphorus, and silicon (for diatoms)—a suite of essential micronutrients that are present at trace concentrations (<0.1 μM). To make matters worse, these organisms impoverish their own milieu because the elements they require for growth are continuously exported out of the sunlit surface as settling organic biomass. In comparison, terrestrial plants, which can acquire nutrients from soil and recycled litter, have a bountiful life. With regard to essential micronutrients, the ocean,

particularly far from land, is the most extreme environment for life on Earth.

How does this system work? How do planktonic organisms acquire micronutrients and control their availability? To what extent does the low availability of these nutrients control the rate of enzymatic reactions, the productivity of the oceans, and the biogeochemical cycles of elements such as carbon and nitrogen? These are questions that oceanographers can now pose as testable hypotheses and can begin to answer.

## Low Surface Concentrations of Essential Metals

A dozen or so elements with atomic mass above 50 are known to have a biological role, often as cofactors or part of cofactors in enzymes and as structural elements in proteins. Of those, the trace metals—Mn, Fe, Co, Ni, Cu, Zn, and Cd—have been best studied by oceanographers (2) and are the focus of our discussion. They are present in the plankton biomass at concentrations ranging from about 50 μmol/mol C (~1000 μM) for Fe, which is used in a number

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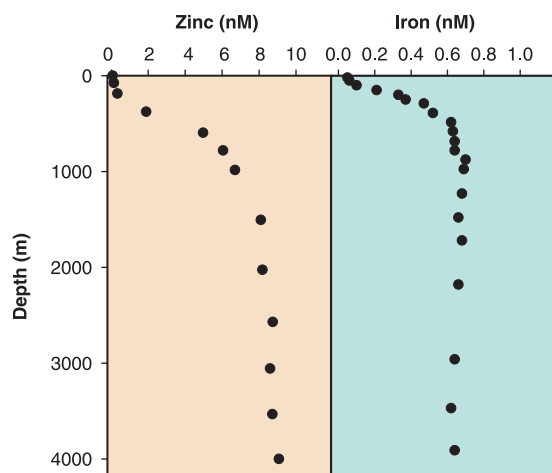


Fig. 1. Vertical profiles of dissolved zinc (43) and iron (44) concentrations in the north Pacific Ocean.

of the electron transfer intermediates and a host of enzymes, down to  $2 \mu\text{mol/mol C}$  ( $\sim 30 \mu\text{M}$ ) for Co, whose biochemical functions in planktonic organisms are not yet completely understood (3).

Although enriched in rocks and soil, the concentrations of these metals are kept low in the sea by virtue of their limited solubilities and effective removal from the water column, particularly in estuaries. As a result, their concentrations fall precipitously within short distances of the coastline (4). Long-range atmospheric transport through aeolian dust represents an important source only for Fe, Mn, and possibly Co, which are relatively enriched in crustal material (5).

As a result of the uptake by plankton, most essential trace metals (with the notable exception of Mn) are depleted at the surface, as exemplified by the concentration profiles of Fe and Zn in the water column of the north Pacific Ocean (Fig. 1) (6, 7). Such concentration profiles are characteristic of many algal nutrients and result from the steady downward flux of settling biomass originating chiefly from the larger phytoplankton, such as diatoms and coccolithophorids, often packaged in the feces of zooplankton. This downward flux is balanced by a slow upward advective/diffusive flux of dissolved elements remineralized at depth by heterotrophic bacteria. Much of the organic matter, including most of what is produced by the picoplankton ( $<2 \mu\text{m}$  diameter), is remineralized at the surface. Essential elements are thus recycled rapidly through the biota at the surface and more slowly during vertical transport in the water column. The surface depletion in dissolved metal concentrations is so intense in most areas of the oceans that the surface concentrations are only a small fraction of those in the deep: Most are present at concentrations between picomolar and nanomolar, about one-millionth of the cellular concentrations in the plankton itself.

### Metal Chelation

How do phytoplankton manage to accumulate necessary metals despite such low concentrations? To answer this question, we need to know the chemical forms of the metals—their speciation—in surface seawater and the mechanisms of uptake by organisms. Measuring the extraordinarily low concentrations of trace metals at the surface of the ocean is a challenge for chemical oceanographers working from rusty ships. But the elucidation of the chemical speciation of these metals poses a much more formidable analytical problem and is yet unsolved. Nonetheless, some field measurements and laboratory culture studies are beginning to provide a coherent picture. By pushing electrochemical methods to

the limit, a few fastidious folks have demonstrated that the bulk of the dissolved concentrations of several metals—Fe, Co, Cu, Zn, and Cd—are present in nonreactive forms at the ocean surface (6, 8, 9). This absence of reactivity is *prima facie* evidence that the metals are bound to some strong unknown ligands. A fraction of the metal that is measured as dissolved ( $<0.4 \mu\text{m}$  filter) may be colloidal (10, 11).

There is good reason to believe that strong metal chelators may be present in surface seawater, because cultured marine microorganisms release such chelators in their growth medium (Fig. 2A). The best documented case is the production of siderophores by marine bacteria. Some of these siderophores have been characterized and found to contain the usual hydroxamate and catechol functionalities (12). Some siderophores have fatty acid tails of variable length and a head group that contains one  $\alpha$ -hydroxy acid in addition to hydroxamates (13). The hydrophobic nature of these siderophores

gives a tantalizing clue about their likely mode of action in the oceans. Further, the cleavage of both the hydrophobic tail and the  $\alpha$ -hydroxy acid group upon illumination may be important in enhancing the diurnal redox cycle of Fe in surface seawater (14). Hydroxamate and catechol functionalities have indeed been identified in the dissolved organic matter in seawater (15). Further, the rapid loss of reactivity of the Fe added to some ocean ecosystems argues strongly for a microbial source of Fe chelators (16).

Both prokaryotic and eukaryotic phytoplankton species also release strong Cu and Cd complexing agents in cultures when exposed to high concentrations of these metals. These agents presumably serve to detoxify the metals, for it appears that the complexes are exported from the cells: Cd phytochelatin complexes [chiefly  $(\gamma\text{-Glu-Cys})_2\text{-Gly-Cd}$ ] from diatoms (17); novel peptide complexes of Cu [Gln-Cys-Cu(I) and Arg-Cys-Cu(I)] from coccolithophores (18); and unknown Cu-complexing agents from the cyanobacterium *Synechococcus* (19). So far, no ligand specialized in the uptake rather than the detoxification of metals other than Fe has been characterized. Cyanobacteria appear to re-

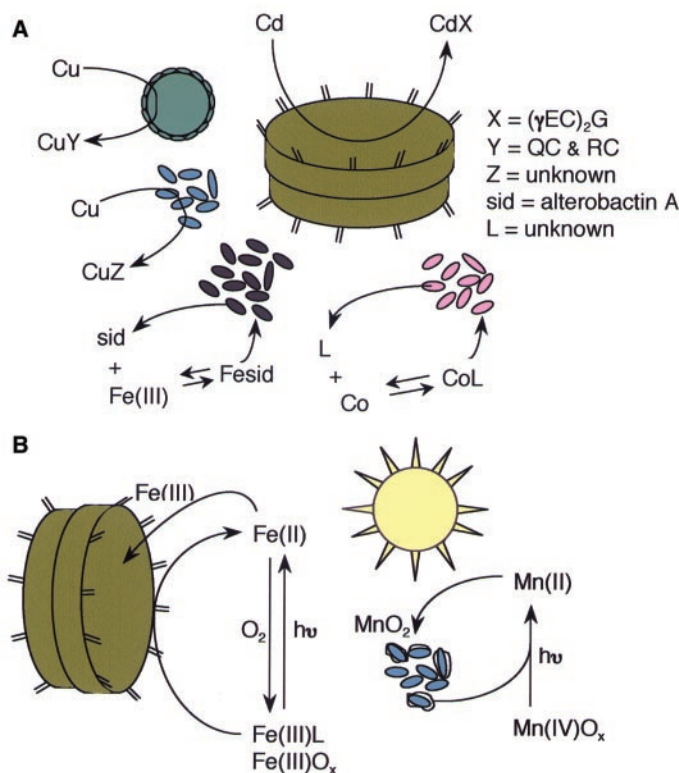


Fig. 2. (A) Examples of release of complexing agents and metal ligand complexes from marine plankton: CdX, phytochelatin-Cd complex released by diatoms (25); CuY, peptide complexes of Cu released by coccolithophorids (26); CuZ, unidentified Cu ligand complex released by *Synechococcus* (27, 28); sid, siderophore released by heterotrophic bacteria and cyanobacteria (17); L, unidentified Co complexing agent released by *Prochlorococcus* (29); C, Cys; E, Glu; G, Gly; Q, Gln; and R, Arg. (B) Redox cycling of Fe and Mn via photochemical and biochemical processes. Diatoms extracellularly reduce Fe(III) ligand complexes during Fe uptake (33, 34); heterotrophic marine bacteria oxidize Mn(II), forming a  $\text{MnO}_2$  casing around the cell (38, 39).



lease a “cobalophore,” whose function in Co uptake and sequestration is similar to that of siderophores for Fe (20).

There are biogenic sources for the putative seawater chelators of Fe, Cu, Cd, and Co, even if some of these have only been observed to be produced at relatively high metal concentrations in cultures (Fig. 2A). Notably absent so far is any laboratory evidence for the production of chelators of Zn, one of the most tightly bound trace metals in surface seawater according to electrochemical data. Nonetheless, a reasonably prudent working hypothesis is that the dissolved Fe, Cu, Zn, Cd, and Co in seawater is dominated by organic complexes—some with low molecular mass ligands produced specifically for metal transport, sequestration, or detoxification; some in high molecular mass compounds (presumably, proteinaceous material in the process of decomposition)—which may exchange the metals more or less readily and may be separable as colloidal material.

### Redox Cycle of Metals

In addition to being the object of competitive binding by biogenic ligands, the trace metals that can attain more than one oxidation state in seawater—Fe, Mn, Cu, and Co—are also subjected to a dynamic redox cycle (Fig. 2B). This cycle is directly or indirectly powered in part by photochemistry. Absorption of light in the high visible–low ultraviolet range promotes charge-transfer reactions in many complexes of Fe(III)

(21) and Cu(II) (22), including those at the surfaces of solids. Often the reduced metal is then released from the oxidized ligand. Metals can also be subjected to reduction (and oxidation) by  $O_2^-$  derived from photolysis of organic matter. The photochemical reduction of Mn(IV) oxides to soluble Mn(II) results in the atypical maximum in dissolved Mn concentration observed at the surface (23).

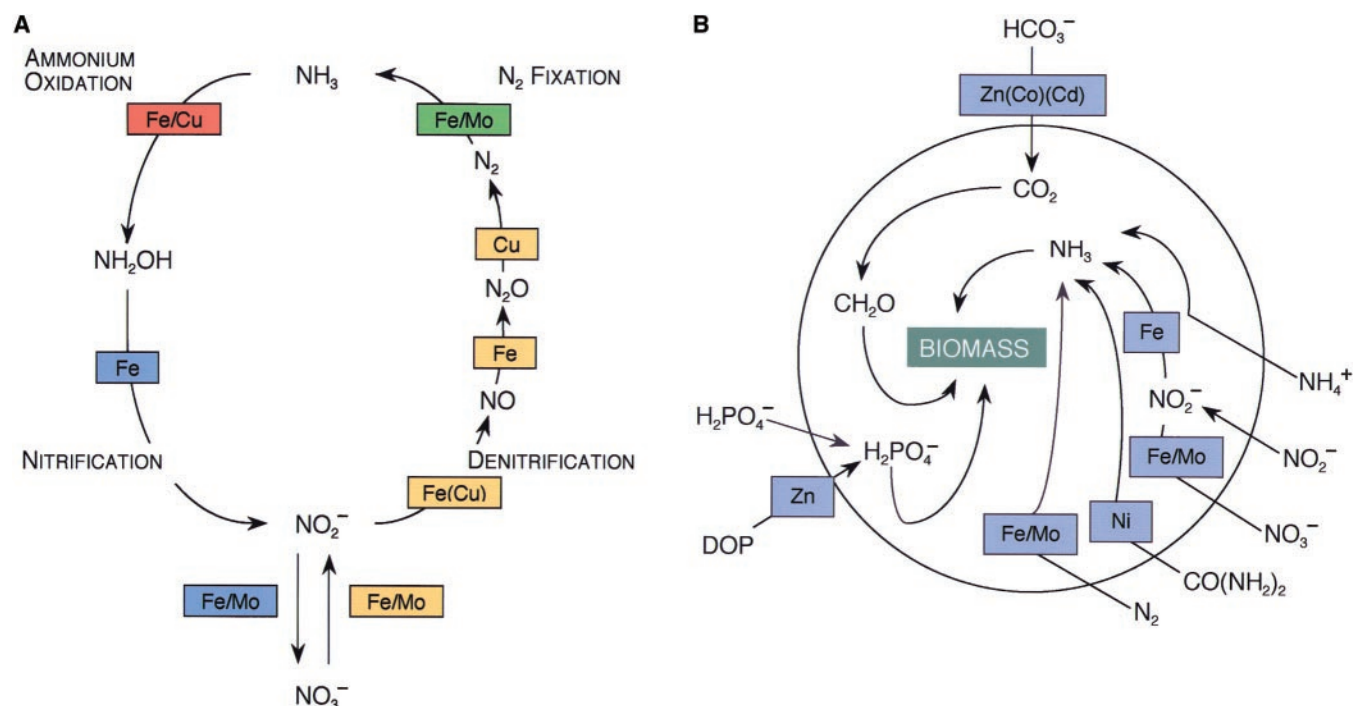
The planktonic biota is also active in promoting redox transformations of metals. Diatoms are known to reduce Fe(III) extracellularly from complexes such as siderophores through an uncharacterized and possibly indirect enzymatic pathway (24). This reduction allows the organisms to access a pool of Fe that would otherwise be unavailable. Fe(II) uptake involves reoxidation by a Cu-dependent oxidase at the cell surface (25). Manganese presents the best documented case of microbially mediated redox transformation in seawater. Mn(II) is oxidized by a number of bacteria and bacterial spores via an extracellular multicopper oxidase (26). The function of this oxidation, which results in the formation of a solid Mn oxide casing around the organism, is unknown, although it has been speculated that it might be a way to bring oxidative power into reducing sediments upon settling of the resting cells or spores (27).

The picture that emerges is one of an extremely dynamic trafficking in essential trace metals in surface seawater. Some organisms are taking up metals, some are sequestering them for their own use, and some are binding them in nontoxic forms. Some organ-

isms are chelating metals; others are prying them loose from chelators. Some organisms are reducing metals; others are oxidizing them. All this activity suggests that these trace metals matter greatly to the plankton in the sea, which raises the question of what role they play in the growth of microorganisms and their cycling of major nutrients.

### Limitation by Trace Metals

Historically, the question of what limits the productivity of the oceans has been debated among N and P partisans with respect to the areas of the oceans affected and the temporal and spatial scales involved. But over the past dozen years, Fe has also become recognized as a prime limiting element (28, 29). In experiments of various scales and durations, addition of N, P, or Fe has been shown to increase the rate of photosynthesis in samples of surface waters from various parts of the world. But this is perhaps too simplistic a view: These additions do not accelerate equally the growth of all phytoplankton taxa, and the acquisition of major nutrients is not independent of the availability of trace metals that catalyze their transformations. For example, the dearth of Fe that has been shown to limit primary production in the Equatorial Pacific inhibits diatom growth most effectively (30). By virtue of their large size, these phytoplankton have more difficulty than smaller ones in acquiring nutrients fast enough to maintain rapid growth. Unlike picoplankton, they cannot grow on the low ambient  $NH_4^+$  concentration and



must instead rely on  $\text{NO}_3^-$ , whose reduction to  $\text{NH}_4^+$  before assimilation requires Fe both as a cofactor in the reductases and for photosynthetic production of reductants (31). Diatoms thus need relatively more Fe and are less able to take it up. In an environment characterized by very low concentrations of trace metals, the acquisition and transformation of major nutrients may often be limited at both cellular and ecosystem levels by the activity of key metalloenzymes.

The most pervasive effect of low trace metal concentrations on the productivity and ecology of the oceans is probably the Fe limitation of  $\text{N}_2$  fixation, which requires the metal in nitrogenase and additional energy and reducing power (32). Although firm experimental evidence showing limitation of nitrogenase activity in the field is lacking, laboratory data show that *Trichodesmium*—a major  $\text{N}_2$  fixer—requires five times as much Fe per C when grown on  $\text{N}_2$  than when grown on  $\text{NH}_4^+$  (33). Such data, coupled with models of the iron budget of the world oceans, predict widespread Fe limitation of  $\text{N}_2$  fixation (34).

Because all nitrogen transformations involve metalloenzymes (Fig. 3A), it is possible that low metal availability also limits other critical steps in the nitrogen cycle. For example, low Cu availability in oxygen minimum zones has been hypothesized to be responsible for the release of  $\text{N}_2\text{O}$  to the atmosphere as a result of low nitrous oxide reductase activity (35). Low Fe may also inhibit nitrate and nitrite reductase activities both in the assimilatory pathway of phytoplankton (as mentioned above for diatoms) and in the dissimilatory pathway of denitrifiers. Low concentrations of Ni, a cofactor in urease, may limit the ability of plankton to assimilate urea, a quantitatively important source of nitrogen (36).

In addition to influencing the carbon cycle indirectly through their effects on the nitrogen cycle, trace metals have a direct effect on photosynthesis and respiration at the cellular and ecosystem levels. The low productivity in Fe-depleted regions of the oceans is primarily due to the low efficiency of the light reaction of photosynthesis, which requires a host of Fe-containing electron transfer intermediates. Electron transfer in respiration also becomes inefficient at low Fe, and heterotrophic bacteria then convert less of the C they consume into biomass (37). By itself, the dark reaction of photosynthesis (the Calvin cycle) does not require trace metals, but the acquisition of inorganic carbon does. Because of the low affinity ( $K_s = 20$  to  $100\ \mu\text{M}$ ) of the enzyme ribulose-1,5-bisphosphate carboxylase-oxygenase (RuBisCO) for  $\text{CO}_2$  (and the competition by  $\text{O}_2$ ), the  $\text{CO}_2$  concentration at the site of fixation must be increased above its concentration in seawater ( $\sim 10\ \mu\text{M}$ ). In all marine phytoplankton, the carbon-concentrating mechanism (CCM) involves the Zn metalloenzyme carbonic anhydrase, which catalyzes the equilibrium be-

tween  $\text{HCO}_3^-$  and  $\text{CO}_2$ . In some taxa, carbonic anhydrase can function with Co or Cd as a metal center (38). Thus, the acquisition of  $\text{CO}_2$  depends in part on the availability of Zn, Co, and Cd, particularly under conditions of low  $p\text{CO}_2$  (Fig. 3B). This new understanding, along with fundamental questions regarding the mechanisms of the CCM in various taxa, is resulting in a resurgence of interest in the role of  $\text{CO}_2$  availability in controlling the growth of marine phytoplankton and the assemblage of phytoplankton species in the sea (39).

The replacement of one essential element by another may be a common occurrence in marine plankton, as suggested in some growth experiments. For example, the replacement of Zn by Cd and Co observed in carbonic anhydrase may also occur in other Zn metalloenzymes such as alkaline phosphatase, which allows phytoplankton to acquire P from organic compounds. Metal substitution may explain some low metal requirement observed in open-ocean species (40). For example, oceanic diatoms that have extremely low Fe requirements are easily limited by Cu and may have replaced Fe with Cu in some critical biochemical functions. In contrast, ambient Cu concentrations are toxic to some cyanobacteria (41), perhaps as a result of nonfunctional Cu substitution for essential metals. Hence, the growth of cyanobacteria depends on the presence of sufficient Cu-chelating agents, and the modulation of Cu chelation by various microorganisms may represent a continual battle between those that need to acquire copper and those that need to repress its toxicity.

Although planktonic microorganisms control the chemistry and cycling of biologically important trace metals in the sea, the metals control in part the growth of the organisms and their cycling of major nutrients such as C and N. This mutual interaction results from the complex coevolution of planktonic life and ocean chemistry. The paradoxical result is a maintenance of biological productivity in an environment impoverished in essential elements. The concentrations of some trace metals in surface seawater are so low that the kinetics of metal uptake by phytoplankton in the sea are reaching the limits posed by diffusion and by the kinetics of binding to transport ligands at the surfaces of cells (42). It also seems that the metalloenzymes of marine microorganisms often have unusual metal centers: Any metal that can be used in a particular biological function may actually be used that way by some marine organism. The biogeochemical cycle of trace metals in the oceans may thus have reached the limit of what is physically, chemically, and biochemically possible.

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