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The Role of Iron as a Limiting Nutrient for Marine Plankton Processes

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Our understanding of elemental cycling in the ocean, its mechanisms and implications for ecology and climate, has undergone revolutionary change since the previous SCOPE volume was published in 1983 (Bolin and Cook 1983). The most notable of the advances in ocean biogeochemistry concern the role of the oceans in the global carbon cycle (Hanson, Ducklow, and Field 2000) and recognition of iron as a key nutrient limiting ocean photosynthesis, carbon storage, and glacial-interglacial variations in atmospheric carbon dioxide concentrations. De Baar (1994) elegantly and comprehensively reviewed iron limitation up to the advent of the *in situ* iron fertilization studies of the past decade (see below). In this chapter we outline biological control of the ocean carbon cycle, focusing on the role of iron and its interactions with carbon, nitrogen, and phosphorus.

The Ocean Carbon Cycle, the Biological Pump, and Iron Limitation

Atmospheric CO_2 exchanges with the surface ocean by thermodynamic processes, as modulated by ocean circulation and biological cycling (Wallace 2001; Takahashi et al. 2002). Variations in temperature, wind, regional to basin-scale circulation, and ocean ecology result in a characteristic geographical distribution of the partial pressure of CO_2 (pCO_2) in the ocean surface layer, with strong atmospheric sources in the equatorial zone and strong sinks (areas of net ocean uptake) at higher latitudes, particularly in the North Atlantic and Southern Oceans (Takahashi et al. 2002). Primary productivity in the sea is dominated by unicellular phytoplankton including species less than one micron in diameter (picoplankton; Chisholm et al. 1988; Karl 1999). These autotrophs convert CO_2 into reduced organic matter, contributing about half the total global photosynthesis of 105 petagrams C (10^{15} gC; PgC) per year (Field et al. 1998) and drawing down pCO_2 below the atmospheric equilibrium. Carbon fixed in organic tissues is either respired in the surface layer or else transported to depth. Only about 0.1 percent of the organic carbon exported from the surface layer is buried in deep ocean sediments; most is oxidized back to CO_2 by bacteria in the water column. The net transport of organic carbon into the deep sea and its remineralization there are the result of complex interactions between trophodynamic processes, including ingestion by zooplankton, excretion of dissolved organic compounds and oxidation by bacteria, particle aggregation, gravitational settling, and advection. These processes combine to pump atmospheric CO_2 into the deep ocean (Volk and Hoffert 1985; Longhurst and Harrison 1989). This biological pump is responsible for maintaining about 80–90 percent of the vertical gradient in dissolved inorganic carbon (DIC) between the ocean surface and deep water, with the rest being due to physical solubility and circulation (Gruber and Sarmiento 2002).

The ecological process most responsible for regulating the biological pump is new production, or that fraction of the marine primary production supported by inputs of "new" or externally supplied limiting nutrients. Over sufficiently large time and space scales, the new production balances losses, or export of organic matter from the euphotic zone into the deep sea (Eppley and Peterson 1979; Ducklow 1995), and is about 10 percent of the total oceanic production. Traditionally, the most common limiting nutrient for marine productivity was assumed to be nitrogen, supplied as nitrate from deep water (Dugdale and Goering 1967). This traditional view is accurate for the oligotrophic gyres and the highly seasonal North Atlantic, where N and P are depleted in the surface layer by phytoplankton utilization, either seasonally or persistently. But in vast expanses of the Southern Ocean and the equatorial and subarctic North Pacific, these macronutrients remain at high concentrations and are never fully utilized by plant growth (Ruud 1930; McAllister, Parsons, and Strickland 1960). Moreover, and paradoxically, chlorophyll *a* remains persistently low in these regions of nutrient plenitude (Miller et al. 1991). These puzzling regimes are termed "high-nutrient–low-chlorophyll" (HNLC) systems (Colorplate 4). In these regions some other factor besides N or P must be limiting phytoplankton growth. Gran (1931) first hypothesized iron limitation in place of N or P. John Martin recast the modern debate over the maintenance of the HNLC condition by hypothesizing that iron limits primary production in the HNLC regimes (Martin and Fitzwater 1988).

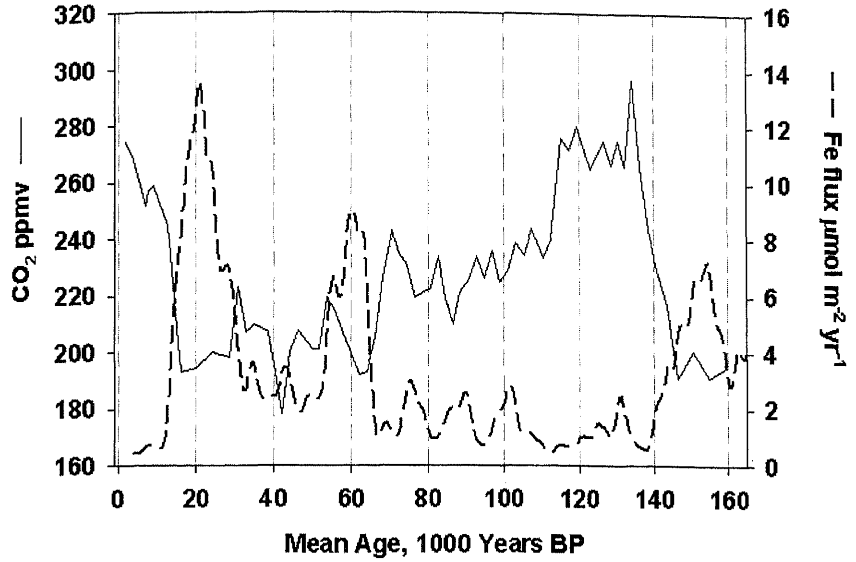

Figure 16.1. The Iron Hypothesis. Mean CO$_2$ concentrations from air entrapped in the Vostok ice core (Barnola et al. 1987) and mean iron flux in atmospheric dust (after Petit et. al. 1990). The data are from http://www.ngdc.noaa.gov/paleo/icecore/antarctica/vostok/. Iron flux was calculated from Petit's dust flux using a crustal iron abundance of 5.63 × 10^4 mg kg^{-1}. Graph revised from Martin (1990).

Solving the puzzle of HNLC systems is a key to a deeper understanding of climate variation. Three seminal papers (Knox and McElroy 1984; Sarmiento and Toggweiler 1984; Siegenthaler and Wenk 1984) linked the ocean carbon cycle to glacial-interglacial variations in atmospheric CO$_2$ and focused new attention on ocean biogeochemistry as a key driver of global climate. In the persistently nutrient-rich oceans DIC is not drawn down to the levels it would be if the deepwater macronutrients were fully utilized. In other words, the biological pump is not working at full efficiency in HNLC regions. If it were, atmospheric CO$_2$ would be 165 parts per million (ppm) in the absence of anthropogenic forcing, compared with the preindustrial value of 280 or the current, anthropogenically forced level of 370 ppm. Martin showed a striking correlation between glacial-interglacial iron supply rates to the ocean and atmospheric CO$_2$ (Figure 16.1) and boldly claimed that variations in iron regulated global ocean productivity and the efficiency of the biological pump, thus controlling the atmospheric CO$_2$ (Martin 1990). This is the Iron Hypothesis.

Iron is the fourth most abundant element in the Earth's crust and thus plentiful in windborne dust blown over the oceans (Colorplate 5), but it exists in dissolved (biologically available) form in only vanishingly low concentrations in the ocean. The mean concentration in the upper 200 meters is just 0.07 nanomoles per kilogram of seawater (nmol kg^{-1}) (Johnson, Gordon, and Cole 1997), a level comparable to the half-saturation coefficient for iron uptake by phytoplankton (Coale et al. 1996a). Iron concentration is kept low in surface waters by biological uptake and the ultralow solubility of Fe(III), the principal form in oxygenated solution. The rest stays in the particulate phase and is rapidly removed by sedimentation. Atmospheric deposition is the principal source of support for iron-based new production (Duce and Tindale 1991), supplying 96×10^9 mol per year to the open sea (Fung et al. 2000) away from continental margins, where river outflow, sediments, and upwelling are additional sources. This flux is well in excess of the model-estimated phytoplankton assimilation rate (12×10^9 mol yr^{-1} [Fung et al. 2000]), but only 1–10 percent of the iron is soluble. Thus the transport of dust in the atmosphere is a vector ultimately linking together ocean productivity and climate with the terrestrial biosphere.

Confirming Iron Limitation of Phytoplankton Growth

Using trace-metal clean sampling techniques, Martin and Fitzwater (1988) added trace amounts of iron (<2.5 nanomolar) to bottles containing natural phytoplankton assemblages and found marked increases in biomass through time. Because bottles do not contain copepod grazers and because microzooplankton often suffer declines under containment, the applicability of these results to *in situ* processes was questioned (Banse 1994). At the same time it became possible to add an inert tracer to the ocean in extremely low quantities (sulfur hexaflouride; SF_6) to follow a patch of the ocean through time. By adding iron and SF_6 simultaneously, it was possible to investigate the effects of trace metal additions to natural plankton communities without enclosures. Thus, oceanographers were able to manipulate the ocean on a scale never before possible and to follow the effects of the perturbation unambiguously.

The first iron addition experiment (IronEx-I) added iron and SF_6 once at the start of the experiment off the Galapagos. Kolber et al. (1994) convincingly showed a dramatic increase in photochemical efficiency upon iron addition for all components and sizes of phytoplankton, suggesting that photosynthesis was indeed limited by iron concentrations. Lindley and Barber (1998) also found that the quantum yield (a measure of photochemical efficiency) increased within twenty-four hours of iron addition and remained elevated for at least seven days. Although photochemical and physiological enhancements of phytoplankton photosynthesis were noted, no nutrient or CO_2 reduction was observed (Watson et al. 1994). Banse (1994) argued that this was because grazing and removal processes

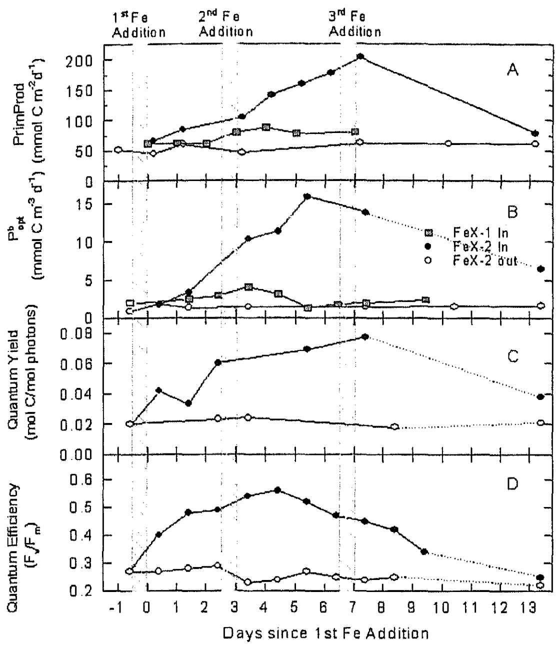

Figure 16.2. Response of phytoplankton to *in situ* iron enrichment in the IronEx-II iron fertilization experiment in the eastern Pacific (see Table 16.2 for details). The responses include increases in primary productivity (A), the maximum rate of photosynthesis within the water column (P^b_{opt}) (B), quantum yield (C), and photosynthetic efficiency (D).

balanced CO_2 uptake, but it also was suggested that the water mass was subducted to depth and that the iron was rapidly lost from the surface layer (Coale et al. 1996b).

A second experiment (IronEx-II) was conducted in 1995, and the revised experimental strategy included refertilizing the same patch with iron approximately every three days. In this experiment a clear and unambiguous response to iron enrichment was noted (Coale et al. 1996b): nutrients and CO_2 were removed, phytoplankton biomass increased, and primary productivity was stimulated (Figure 16.2 and Colorplate 6). All components of the phytoplankton responded, but diatom biomass responded most markedly (an eighty-five-fold increase over non-enriched waters). Photochemical efficiency again increased (Behrenfeld et al. 1996). Picoplankton doubled, but their increase was largely balanced by increased losses due to microzooplankton grazing. Mesozooplankton ingestion of larger phytoplankton was insignificant, suggesting a minor role for larger zooplankton on the time scales of the induced bloom. Hence, the iron hypothesis was proven, albeit slightly modified. The iron paradigm thus became that iron limits the growth of diatoms, whereas smaller forms, while iron-stressed, were limited by their removal by microzooplankton (Landry et al. 1997).

Since the IronEx-II experiment additional trace-metal fertilizations have been

Table 16.1. Mesoscale iron enrichment experiments conducted in the open sea

Study	*Dates*	*Location*	*Result*
Iron-Ex I[a]	October 1993	Equatorial Pacific Galapagos Islands, 5°S; 93°W	Chl 3× increase, photochemical response, small pCO_2 decrease, 80% increase in DMSP
Iron-Ex II[b]	May–June 1995	Equatorial Pacific Galapagos Islands, 6°S; 108°W	Chl 20×; diatoms 80×, NO_3 and DIC utilization, and pCO_2 drawdown
SOIREE[c]	February 1999	Southern Ocean, 61°S; 140°E	Chl 5×, NO_3, $Si(OH)_4$ decrease, pCO_2 drawdown, DMS increase, no increase in particle export, long-lived bloom
EISENEX[d]	November 2000	Southern Ocean, 48°S; 21°E	Chl ≥4× increase, NO_3 down 10%, $Si(OH)_4$ down 30%, pCO_2 drawdown, storms and mixing obscured results
SOFEX	February 2002	Southern Ocean, 56°S; 172°W and 66°S; 171°W	2 experiments in areas with differing NO_3:Si ratios, N and S of Polar Front; Chl increases and diatom growth in both areas

[a]Martin et al. (1994). [b]Coale et al. (1996b). [c]Boyd et al. (2000). [d]Smetacek (2001).

conducted in the Southern Ocean (Table 16.1), since that region is the largest reservoir of unutilized nutrients in the ocean, and the region which potentially could have the largest impact on the marine carbon cycle (Sarmiento et al. 1998). The locations of the cruises were quite different, however. SOIREE (Boyd et al. 2000) was conducted in February at 62°S in a region with about 20 micromolar μM nitrate and 5 μM silicate, whereas EISENEX was conducted in November at about 55°S (initial nitrate ≈ 30 μM, initial silicate ≈ 60 μM). SOFEX, conducted in January-February, fertilized two regions, one at about 65°S (initial nitrate ≈ 28 μM, initial silicate ≈ 60 μM) and one at approximately 57°S, where nitrate and silicic acid were about 5 and 1 μM at the experiment's start, respectively. All of these experiments showed similar responses (large phytoplankton are selectively stimulated, with a concomitant increase in photosynthetic efficiency, biomass, and

Table 16.2. Inorganic nutrient limitation of phytoplankton functional groups by various elements

Group	*Limiting elements*
Diatoms	Si, Fe, N
Diazotrophs (N fixers)	Fe, P
Other groups (Coccolithophorids, dinoflagellates, cyanobacteria, etc.)	Fe, N, P

Note: The most commonly limiting element is listed first. Other likely limiting nutrients listed subsequently. Importance varies regionally and seasonally.

productivity, paralleled by a reduction in CO_2 and macronutrients), although variations in some details have been noted (e.g., the surprising increase in Fe^{+2} in SOIREE; Boyd et al. 2000). None of the experiments conclusively demonstrated that iron enrichment stimulated organic matter export below 300 meters, but the duration of the experiments was limited and the fate of the increased organic matter load was difficult to quantify. On the other hand, there is no example anywhere in the ocean where diatoms have been stimulated to bloom (by any nutrient) and biogenic matter has *not* been exported to depth. Regardless of the relationship of flux and iron-stimulated growth, the paramount role of iron to the ocean's plankton processes and in maintaining HNLC regions is now firmly established. Research has turned to defining the inputs of iron, clarifying the cycling of trace metals in surface waters, and understanding the controls of iron on plankton community composition.

Iron, Elemental, and Organic Matter Interactions

Phytoplankton may be limited by one or more inorganic nutrients (Table 16.2). Iron not only influences the different phytoplankton taxa differentially, but it also modifies the biogeochemistry of other elements during phytoplankton growth. Silicic acid (a component of diatom cell walls) uptake is greatly enhanced relative to carbon or nitrogen when iron is limiting (Hutchins and Bruland 1998; Takeda 1998), so that the Si:N ratio increased from about 1 (iron replete growth) to ratios of 5 and more under severe iron limitation. Carbon:nitrogen ratios appear to be unaffected by iron concentrations. Hence, diatoms that grow under iron limitation are highly enriched with silica, and the relative fluxes of carbon, nitrogen and silica to depth are also altered. Such an alteration might explain the highly siliceous (and relatively carbon depauperate) deposits that are found in the Polar Front region in the Antarctic.

Nitrogen-fixing cyanobacteria apparently have elevated iron demands that are approximately tenfold greater than those of non-N_2-fixing phytoplankton (iron replete cultures have Fe:C molar ratios of about 50×10^{-6}; Berman-Frank et al. 2001). Indeed, the Fe:C ratios of pelagic plankton are highly variable and can range over an order of magnitude (from 5×10^{-6} to 0.2×10^{-6}); furthermore, they appear to respond dramatically to reduced iron concentrations and allow phytoplankton to maintain cellular processes at an optimal rate.

Models are now being run that include significantly more detail in the biological processes than were previously available. For example, Moore et al. (2001) simulated the growth of three functional components of phytoplankton (diatoms, small phytoplankton, and diazotrophs) in a global circulation model and predicted the areas where iron limitation would occur. In general, mid-ocean gyres are nitrogen-limited for diatoms and small phytoplankton, whereas the subarctic and equatorial Pacific and the Southern Ocean are iron-limited. Other regions (equatorial waters of the Indian and Atlantic Oceans) and the North Atlantic also become iron-limited during summer months, largely because of reduced atmospheric inputs during this time.

Within the past decade oceanographers have recognized the significance of microbial transformations of organic matter as a dominant process in ocean biogeochemistry (Colorplate 7; Azam 1998). This dominance extends to controlling the concentrations and availability of iron in low-iron waters. Apart from marine viruses (Fuhrman 1999), heterotrophic bacteria (Whitman, Coleman, and Wiebe 1998), autotrophic bacteria (Chisholm et al. 1988; Beja et al. 2002), and *Archaea* (Karner, DeLong, and Karl 2001) are the numerically dominant organisms in the ocean. Their biomass can equal or exceed that of phytoplankton (Ducklow 1999), and no other member of the plankton community exerts as much influence on the fate of elements in the ocean (Williams 2000; Carlson 2002). The principal ecological role of heterotrophic bacteria in the plankton foodweb is remineralizing nitrogen-, phosphorus-, and iron-containing organic matter (Pomeroy 1974; Cotner and Biddanda 2002).

Dissolved organic matter (DOM) is the largest pool of organic carbon in the ocean (685 Pg C) and its export is a component of the biological pump (Hansell and Carlson 1998a,b; Williams 2000; Carlson 2002). The majority of the removal of DOM is through consumption of carbon by heterotrophic bacteria. Consumption is a variable process as DOM has a wide range of composition and lability, which is determined by the production process and the biogeochemical transformations occurring within the ocean foodweb. Much of the DOM is refractory owing to extensive microbial transformation (Carlson 2002), allowing it to serve as a carbon reservoir on the time scale of the ocean circulation (Hansell and Carlson 1998b). Heterotrophic bacteria are major remineralizers not only of the carbon in DOM, but also of its phosphorus (Clark, Ingall, and Benner 1998), nitrogen (Zehr and Ward 2002), and biogenic silica (Bidle and Azam 1999).

Concurrent with heterotrophic growth and remineralization of DOM are the uptake and recycling of inorganic nutrients (N and P) and trace elements such as iron. Bacteria possess the ability to compete effectively with phytoplankton for these nutrients, particularly in the regions of the global ocean that are most influential in the carbon cycle (HNLC regions) where iron is the probable limiting nutrient. Low atmospheric flux of iron to HNLC waters and its low solubility in seawater are initial constraints on phytoplankton and possibly heterotrophic bacterial growth. The numerous small-scale and mesoscale iron enrichment experiments have confirmed this for phytoplankton but not for heterotrophic bacteria. This is surprising given the fact that heterotrophic bacteria have a higher per cell iron demand than phytoplankton (Tortell, Maldonado, and Price 1996). The bacterial response within the fertilized patches during IronEx II (Cochlan 2001) and SOIREE (Hall and Safi 2001) was modest with little to no accumulation of biomass and threefold increases in bacterial production in both experiments. Direct stimulation of bacterial growth by iron could not be discounted entirely in either experiment, but multiple lines of evidence point toward growth enhancement by phytoplankton-derived DOM (Church, Hutchins, and Ducklow 2000; Kirchman et al. 2000). Scenarios may exist where iron can directly stimulate growth (Pakulski et al. 1996); however, the sum of the evidence suggests that iron in HNLC waters is rarely in low enough concentration to limit heterotrophic bacterial growth.

Siderophores: A Competitive Edge

Low atmospheric flux of iron coupled with low solubility in seawater explains the paradox of the HNLC condition. The findings that DOM primarily limits heterotrophic bacterial growth rather than iron suggests an additional mechanism that might allow the HNLC condition to persist. Such a mechanism might be mediated through the extracellular release of iron-binding ligands called siderophores. Siderophores are low molecular weight organic molecules (500–1,000 Daltons) secreted by heterotrophic and autotrophic bacteria generally under conditions of low dissolved iron concentrations (Reid et al. 1993; Wilhelm and Trick 1994; Wilhelm, Maxwell, and Trick 1996). They have an extremely high affinity for ferric (Fe^{3+}) iron (stability constant, $K = 10^{49\text{-}53}$; Reid et al. 1993), as well as other trace elements (Butler 1998). Once the siderophore binds iron, the siderophore-iron complex is acquired by the cell through cell-surface receptors and internalized where the iron is reduced and catabolized (Raymond, Muller, and Matzanke

1984). The strategy of siderophore production has enabled marine bacteria to be highly competitive and influential in the biogeochemical cycling of iron (Tortell et al. 1999). This biochemical strategy, however, has been usurped by some siderophore-producing and non-siderophore-producing organisms (cyanobacteria and phytoplankton), which have employed their own strategies to utilize siderophore-iron complexes as a source of iron (Trick 1989; Granger and Price 1999; Hutchins et al. 1999; Maldonado and Price 1999). Utilization of siderophores as a carbon source has been demonstrated for terrestrial bacteria (Warren and Neilands 1964; DeAngelis, Forsyth, and Castignetti 1993) but not for any marine organism. The interactions between iron, siderophores, and the plankton community are fundamentally important because the majority of the dissolved inorganic iron in the oceans (more than 99 percent) is complexed to low-molecular-weight organic ligands. These ligands appear to be ubiquitous; however, they vary slightly in their concentrations and their affinity for iron. In the North Pacific these ligands fall into two classes (L1 and L2) based on their conditional stability constants for inorganic ferric iron (Rue and Bruland 1995). Organic ligands have also been found in the northwest Atlantic Ocean (Wu and Luther 1995), South and equatorial Atlantic Ocean (Powell and Donat 2001), and the Southern Ocean (Nolting et al. 1998). Rue and Bruland (1997) observed the production of these iron-binding ligands during IronEx II but stopped short of calling them siderophores. Presently, the chemical composition of these organic ligands is unknown. Identifying the origin of siderophores and other organic ligands within the milieu of DOM, characterizing their composition, and understanding their role in iron-plankton dynamics represents a formidable challenge to biological and chemical oceanographers (Colorplate 7).

Geoengineering with Iron

The postulated link between iron limitation, increased iron supply during glacial periods, and atmospheric CO_2 raised the possibility of slowing the increase in anthropogenic CO_2 accumulation in the atmosphere and ameliorating global warming by stimulating carbon export to depth through large-scale iron fertilization (Chisholm and Morel 1991; Chisholm 1995). Modeling studies suggest the practical effect on atmospheric CO_2 would be small even with prolonged, intensive fertilization (Sarmiento and Orr 1991), as well as practically impossible to document for carbon accounting purposes. The same studies also suggest other effects on the ocean might be profound and far reaching. For example, increased organic matter production will stimulate respiration, leading to hypoxia in some areas (Sarmiento and Orr 1991) and increased nitrous oxide production (Fuhrman and Capone 1991). Unintended consequences like release of N_2O and methane, powerful greenhouse gases, suggest the complexity of such interventions in global biogeochemical cycles. Although the issue remains controversial a decade after it was first raised (Chisholm, Falkowski, and Cullen 2001; Johnson and Karl 2002), several patents have been applied for, and various commercial efforts aimed at global trading of carbon credits gained through iron fertilization seem likely (see, e.g., http://www.planktos.com/eco-solutions.htm).

The manifold and pervasive roles of iron in ocean ecology and biogeochemistry have only begun to be understood. Differential responses to iron additions by diatoms modulate element ratios in the nearshore and deep ocean. Bacterial production of and interactions with organic ligands regulate iron availability for primary producers. Terrestrial soil fungi as well as ultraviolet radiation may also mobilize iron in airborne dust (Saydam and Senyuva 2002). Although our focus on iron has been its role as a limiting nutrient in the sea, a wider focus on its role as a critical linking mechanism in the Earth system (Falkowski 1997) seems justified.

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