Soluble and Colloidal Iron in the Oligotrophic North Atlantic and North Pacific

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In the oligotrophic North Atlantic and North Pacific, ultrafiltration studies show that concentrations of soluble iron and soluble iron-binding organic ligands are much lower than previously presumed "dissolved" concentrations, which were operationally defined as that passing through a 0.4-micrometer pore filter. Our studies indicate that substantial portions of the previously presumed "dissolved" iron (and probably also iron-binding ligands) are present in colloidal size range. The soluble iron and iron-binding organic ligands are depleted at the surface and enriched at depth, similar to distributions of major nutrients. By contrast, colloidal iron shows a maximum at a surface and a minimum in the upper nutricline. Our results suggest that "dissolved" iron may be less biologically available to phytoplankton than previously thought and that iron removal through colloidal aggregation and settling should be considered in models of the oceanic iron cycle.

Phytoplankton growth (1, 2) and nitrogen fixation (3) in the ocean are strongly influenced by Fe availability, which in turn is determined by the physicochemical speciation of dissolved Fe (4). Electrochemical measurements (5–7) have shown that more than 99% of the operationally defined "dissolved" Fe (Fe that passes through a 0.4-μm filter) is strongly bound by organic ligands. It is widely assumed that these organic Fe chelates are of low molecular weight, are relatively long-lived in deep ocean waters, and do not readily adsorb on particle surfaces. Consequently, the presence of Fe chelates should retard the removal of Fe from seawater through adsorption on settling particles (8, 9) and facilitate Fe availability to marine phytoplankton (4). However, current estimates of available Fe fluxes to the oceanic euphotic zone (10, 11) are based on measurements of operationally defined "dissolved" Fe, which necessarily includes both small soluble Fe species and larger colloidal Fe forms. The occurrence of Fe in colloidal particles may decrease Fe bioavailability (12, 13) and increase Fe removal through colloid aggregation into larger particles, which then settle from the water column (14). Investigators have been unable to distinguish between these two forms of Fe because of analytical difficulties. We used a new procedure combining microfiltration and a microanalytical method (15) to determine vertical profiles of soluble Fe (with a molecular diameter of <0.02 μm) and colloidal Fe (0.02 to 0.4 μm) in oligotrophic waters of the eastern and western North Atlantic and central North Pacific.

Soluble Fe and colloidal Fe exhibit distinct vertical distributions (Fig. 1). Soluble Fe shows similar vertical profiles in all three regions. It is depleted to a concentration of ~0.1 nM at the surface and increases to a maximum of 0.3 to 0.4 nM at ~1000 m, resembling profiles of classic nutrients such as phosphate and nitrate (Fig. 1A). In contrast, colloidal Fe shows maximum concentrations in the surface and minimum concentrations in the upper nutricline (~120 to 500 m) (Fig. 1B). These data indicate that a substantial portion of the Fe, which had previously been referred to as "dissolved Fe," is actually present in the colloidal size range (80 to 90% in near-surface waters and 30 to 70% in deep waters, Fig. 1).

Soluble Fe concentrations (0.1 to 0.4 nM, Fig. 1A) are above the solubility limit for inorganic Fe(III) hydrolysis species in seawater (~0.08 ± 0.03 nM) (16) and are well above concentrations of soluble Fe hydrolysis species measured in ambient seawater by electrochemical methods (~<2 pm) (3). Thus, the soluble Fe must exist as complexes with organic ligands. These organic ligands would not only have to be soluble themselves but would also have to form sufficiently stable chelates to prevent Fe hydroxide precipitation. Using a new ultrafiltration method (17), we determined concentrations of organic ligands that are capable of forming soluble complexes (~<0.02 μm) with added Fe(III) in our seawater samples. In the eastern North Atlantic and the North Pacific, these soluble organic ligands are depleted within the surface mixed layer (~0.1 nM) and enriched at depth (0.7 to 0.8 nM for the eastern North Atlantic and 1.0 to 1.3 nM for the North Pacific). The shapes of these profiles are similar to those of soluble Fe and major nutrients nitrogen and phosphorus, suggesting that all of these constituents (including soluble ferric chelates) are released together from microbial degradation of settling biogenic particles (e.g., fecal pellets) (Fig. 2) (18). These ligand concentrations are much lower than those of operationally defined "dissolved" (<0.4 μm) Fe-binding ligands (1 to 3 nM) reported for the western North Atlantic and central North Pacific (5, 7, 19), implying that a substantial portion of the organic ligands previously referred to as "dissolved" ligands may be colloidal in nature (20). Therefore, the colloidal Fe we observed in our seawater samples may be bound to these colloidal ligands.

The coexistence of Fe and organic ligands in both soluble and colloidal size ranges implies that vertical distributions of soluble and colloidal Fe may be controlled by a competition between soluble ligands and colloidal ligands for binding labile Fe introduced into ambient water. In ocean surface waters, free soluble ligands are not detectable, and any labile Fe introduced from elution deposition, a major source of Fe input, would bind to colloidal ligands. The complexation of eluctor Fe by colloidal ligands in the absence of soluble ligands in surface water could readily explain the surface water colloidal Fe maximum and soluble Fe minimum (Fig. 1, A and B). In deep ocean waters, the Fe that is released to ambient water from microbial decomposition of sinking organic particles will be complexed by these two classes of ligands. The ratio of the average stability constants for Fe bound by soluble ligands to that of Fe bound by colloidal ligands (KFe-Sol.L/KFe-Coll.L) (Fig. 2) can be calculated from the equation

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\frac{K_{Fe-Sol.L}}{K_{Fe-Coll.L}} = \frac{[Sol.L]}{[Coll.L]} \left( \frac{[Sol.Fe]}{[Coll.Fe]} \right)
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if a chemical equilibrium is assumed. On the basis of this equation, we estimate the ratio of KFe-Sol.L/KFe-Coll.L to be ~3 in deep waters of the North Pacific (21). These calculations suggest that soluble ligands have a higher average stability constant for binding Fe than do colloidal ligands. The formation of soluble Fe-ligand complexes tends to hold Fe in solution and decrease the rate of Fe loss from seawater through association with settling particles.

The presence of low concentrations (~0.1 nM) of soluble Fe in oligotrophic surface waters (Fig. 1A) has important implications for nitrogen fixation by oceanic cyanobacteria, such as Trichodesmium. On the basis of
the high Fe requirement for nitrogen fixation and low rates of eolian Fe input, it has been suggested that Fe availability limits the rate of nitrogen fixation in present-day oligotrophic oceans (3). It has been further suggested that increased eolian Fe inputs to the glacial ocean may have increased the rate of nitrogen fixation and enhanced sequestration of atmospheric CO₂ in the deep ocean by a stronger biological CO₂ pump (22). However, the “dissolved Fe” (<0.4 μm) concentration maximum frequently observed in stratified surface waters of oligotrophic ocean gyres (23) (Fig. 1C), where most nitrogen fixation occurs, would seem to argue against such limitation. Our observation that only a small fraction of this surface water “dissolved Fe” exists as more bioavailable soluble Fe-organic complexes (whereas most occurs as much less available colloidal Fe forms, Fig. 1) implies that Fe is less available than previously thought, arguing in favor of Fe limitation of nitrogen fixation in the present-day ocean.

There is evidence that marine phytoplankton can use low molecular weight organically complexed Fe, either by direct uptake, as in the case of Fe-siderophore complexes, or by reductive dissociation at the cell surface (4). Algal uptake models (24) indicate that the rate of Fe uptake can be limited by the rate of diffusion of Fe complexes to the surface of individual algal cells or colonies. Because the diffusion rate of Fe species to the surface of a phytoplankton cell is inversely related to the molecular radius of the diffusing Fe complex species (Stokes-Einstein equation), the diffusion rate of a ferric chelate of ~1 to 2 nm size (for a typical Fe-siderophore complex) (25) should be one to two orders of magnitude greater than that of the colloidal Fe species we measured, which have diameters of 20 to 400 nm. On this basis, colloidal Fe should be much less available than soluble Fe for algal uptake, provided the uptake is limited by Fe diffusion. Because diffusion limitation increases markedly with increasing size of algal cells or colonial cell aggregates, diffusion limitation may be particularly severe for Trichodesmium colonies, which have diameters of 1 to 3 mm, two to three orders of magnitude higher than most unicellular algae in oceanic waters.

The presence of a substantial portion of deep water “dissolved Fe” (<0.4 μm) in the colloidal size range (Fig. 1B) has important implications for Fe removal from the deep sea. The removal of “dissolved” Fe from the deep ocean by scavenging onto settling particles is a root cause for Fe limitation of algal growth in the present-day high-nutrient, low-chlorophyll Southern Ocean, an important region for air/sea exchange of CO₂ on glacial/interglacial time scales (2, 11, 26). Fe supply to productive surface waters comes from both eolian deposition and the upwelling of subsurface waters enriched in available Fe and macronutrients phosphorus and nitrogen. Because eolian deposition supplies Fe to the euphotic zone but supplies little phosphorus and nitrogen (27), it can only relieve but not cause Fe limitation. Therefore, Fe limitation must result from a depletion of Fe relative to macronutrients (nitrate and phosphate) in subsurface waters. Unlike macronutrients, regenerated Fe is lost from deep seawater by scavenging onto sinking particles (28), a process that is controlled by Fe speciation. The complexation of “dissolved” Fe by organic ligands in the deep sea (5, 6, 7, 19) is thought to restrict Fe adsorption onto settling particles and thereby minimize its loss from the water (8).

Our observation that a substantial portion of the “dissolved” Fe occurs in the colloidal size range (Fig. 1B), however, provides a new mechanism for “dissolved” Fe removal from the deep sea. The colloidal Fe species are too small to have appreciable settling rates, but they can aggregate and settle out from the deep water. This process may be a part of the overall aggregation of marine colloidal organic matter into large sinking particles (14, 18, 29). Colloidal aggregation has been considered to be responsible for removing “dissolved Fe” in low-salinity estuarine environments (30) and carbon and radionuclides (e.g., thorium) from oceanic surface waters (14, 31, 32). Our colloidal Fe observations suggest that Fe removal through colloidal aggregation needs to be considered in any future models of Fe cycling in the ocean.

Fig. 1. Vertical profiles of (A) soluble (<0.02 μm) Fe, (B) colloidal (0.02 to 0.4 μm) Fe, and (C) dissolved (<0.4 μm) Fe in the eastern North Atlantic (September 1999; 22.8°N, 36.8°W), in the western North Atlantic (July 1998; 34.8°N, 57.8°W), and in the North Pacific near Hawaii (April 2001; 22.8°N, 158.8°W).

Fig. 2. Vertical profiles of soluble (<0.02 μm) ligands in the eastern North Atlantic (September 1999; 22.8°N, 36.8°W) and in the North Pacific near Hawaii (April 2001; 23.8°N, 158.8°W). Squares, eastern North Atlantic; circles, North Pacific near Hawaii.
The observations presented here provide an initial step in assessing the role of colloidal coagulation in controlling Fe removal from seawater and therefore its role in controlling Fe budgets and Fe limitation of carbon fixation in the ocean.

References and Notes
15. Sampling and analytical methods: Seawater samples were collected on cruises Endeavor 328 (September 1999, 22°N, 36°W), Oceanus 326 (July–August 1998, 34°N, 57°W), and Wecoma MP2 (April 2001; 23°N, 158°W). High density Polyethylene (HDPE) bottles (50 ml volume), acid leached with 1 M HCl, were mounted on a MITESS sampler (23) suspended below standard hydrosail. The sealed bottles were open at depth, allowing for the replacement of distilled water by seawater, and then closed again before returning to the surface. Filtration was performed on board in class 100 high efficiency particle accumulator filtered flow benches. Sample replicates were processed with three different microfiltration methods: (i) HDPE syringes were used to pressure-filter samples through 25-mm-diameter 0.02-μm pore size Anotop Al-oxide filter discs, a 0.15-bar vacuum was used, and then through 74-mm-diameter 0.025-μm pore size Millipore mixed cellulose ester membranes mounted on 47-mm-diameter Teflon filter holders, and (iii) a 0.5-bar vacuum was used to draw 25-mm-diameter 0.025-μm Nuclepore polycarbonate filters mounted on 47-mm-diameter Teflon filter holders. The soluble Fe in seawater samples is considered to be that passing through 0.02-μm Anotop and 0.025-μm Millipore filters. The difference between the soluble Fe and the Fe passing through 0.4-μm Nuclepore filters is considered to be colloidal Fe. Before final collection of filtrates, the filtering devices and sample bottles were cleaned by rinsing with 0.1 M HCl, distilled water, and sample water. Filtrates were acidified to pH 2.5 by the addition of distilled water to seawater at pH 8.1. The solubility of the Fe(OH)3, in its age on its age with higher values for freshly formed amorphous Fe(OH)3 (0.08 nM as determined above as the Fe passing through a 0.02-μm pore Anotop syringe filter) does not reach its solubility limit at pH 1.5 followed by an equilibration (1:1 stoichiometry) for Fe-ligand complexes: [FeL]/[Fe3+]. This can be readily computed from [FeL]/[Fe3+] = K[Fe3+] for [Fe3+] of 0.08 nM and, thus, should be substantially detected by our method, again, provided that the ligands are soluble. The concentrations for solubility binding ligands that we measured in the subtropical North Pacific range from 0.1 to 0.5 nM in near-surface waters to 1.0 to 2.0 nM at depths of 1000 m. By contrast, total ligand concentrations measured by CSV in the same region (15) are 1.3 nM in the upper 100 m and 2.6 ± 0.2 at depths of 500 to 2000 m. The higher concentrations determined by CSV analysis suggest that a substantial fraction of the ligands detected by this method present Fe-ligand complexes and is bound to Fe. We would not be detected by our method.
21. In this calculation, [Coll.] is taken as the difference between the excess <0.4 μM ligand concentration (=[Fe3+]) and the weak Fe-ligand concentration (0.75 nM) [Fig. 2]. [Coll.] is 0.2 ± 0.1 nM [Fig. 1A]. [Coll.] is 0.2 ± 0.1 nM [Fig. 1B].
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