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## Variation in iron(III) solubility and iron concentration in the northwestern North Pacific Ocean

**Abstract**—Vertical distributions of Fe(III) hydroxide solubilities ( $<0.025 \mu\text{m}$ ) and dissolved Fe ( $<0.2 \mu\text{m}$ ) concentrations at 0–250 m depth were studied inside (HP) and outside (LP) a high-production (phytoplankton spring bloom) patch area in the northwestern North Pacific Ocean during May 1999. In the surface mixed layer, the Fe(III) solubility values

at HP were much higher (2–4 nM) than those (0.3–0.9 nM) at LP and strongly correlated with chlorophyll *a* and nutrient concentrations. The high Fe(III) solubility observed in the surface mixed layer was probably due to a higher concentration or stronger affinity of natural organic Fe(III) chelators. In the surface waters, the dissolved Fe concentrations were generally

lower than the Fe(III) solubility values, resulting from the active biological removal of dissolved Fe and excess concentration of Fe-binding organic ligands. The Fe(III) solubility minima (0.2–0.4 nM) were present in a narrow depth range (40–125 m) below the surface mixed layer at all stations. The subsequent Fe(III) solubility levels appeared to increase up to 0.6–0.8 nM with depth at 100–250 m, in association with the increase in nutrient concentrations. The strong linear correlations between Fe(III) solubility values and nutrient concentrations in middepth waters suggest that the formation of organic Fe(III) chelators may be related to microbial decomposition of sinking biogenic organic matter. In middepth waters, the dissolved Fe concentrations were generally higher than the Fe(III) solubility values, which suggests that the small colloidal iron phases may be present in the dissolved Fe ( $<0.2 \mu\text{m}$ ) fraction.

Iron is one of the most important biogeochemical trace metals in the ocean. Recent studies of iron speciation and Fe(III) hydroxide solubility [Fe(III) solubility] in seawater have shown that iron complexation with organic ligands is prevalent in seawater (van den Berg 1995; Rue and Bruland 1995; Kuma et al. 1996, 1998, 2000a; Millero 1998; Nolting et al. 1998; Witter and Luther 1998; Liu and Millero 1999). It has been suggested that dissolved Fe concentrations in deep oceanic waters are controlled primarily by organic complexation and that the dissolved Fe source, like the source for major nutrients, is remineralization from sinking particulate organic matter (Johnson et al. 1997a,b; Kuma et al. 1998). Vertical distributions of ambient Fe(III) solubility in oceanic waters have several features in common. Fe(III) solubility is variable in the surface mixed layer, but it is generally higher in the chlorophyll *a* maximum. Solubility minima occur at 50–150 m depth, below the surface mixed layer. Finally, the subsequent solubility levels appear to increase with depth in association with the increase in nutrient concentrations (Kuma et al. 1996, 1998). The solubility profiles reveal the existence of natural organic Fe(III) chelators, which may be released by phytoplankton or bacteria through their metabolism in the surface mixed layer and by the oxidative decomposition and transformation of biogenic organic matter in middepth waters.

The low concentration of dissolved Fe present in oceanic surface water is generally associated with an excess of Fe-binding ligands (Rue and Bruland 1995, 1997; Kuma et al. 1996, 1998). Moreover, Rue and Bruland (1997) observed a rapid increase in Fe(III)-binding ligand concentrations, especially for the stronger ligand class ( $L_1$ ), after the initial iron infusion, in the equatorial Pacific Iron-Ex II study (Coale et al. 1996). In a recent iron fertilization experiment in the Southern Ocean (Boyd et al. 2000), Fe-binding ligand measurements revealed that the Fe-binding ligand concentrations increased inside a phytoplankton bloom patch in response to small additions of iron. In addition, Kuma et al. (1996, 1998) reported that Fe(III) solubility in the oceanic surface mixed layer is generally high and variable, with higher values sometimes corresponding with the depth of high Chl *a* concentrations. In coastal waters, high Fe(III) solubilities were found in the surface waters during and after the peak of the spring phytoplankton bloom (Kuma et al. 2000a). The high Fe(III) solubility in surface waters is prob-

ably due to a higher concentration or stronger affinity of natural organic Fe(III) chelators, which may be released by some phytoplankton or cyanobacteria (Trick et al. 1983a,b; Wilhelm 1994; Boye and van den Berg 2000; Witter et al. 2000).

In general, the presence in surface seawater of natural organic Fe(III) chelators with a strong affinity for Fe(III) reduces the bioavailable inorganic Fe(III) species (Hutchins et al. 1999a; Wells 1999). It has been recently reported that the natural organic ligands complexed with Fe(III) play an important role in biological availability of iron in seawater via a cell-surface reduction process, photochemical cycling, and thermal and microbial decomposition of organic ligands complexed with Fe(III) (Wells and Mayer 1991; Hutchins et al. 1999b; Kuma et al. 1999, 2000b; Maldonado and Price 1999, 2000).

In the present study, we demonstrate the vertical changes of Fe(III) solubility and dissolved Fe ( $<0.2 \mu\text{m}$ ) at 0–250 m depth collected inside and outside a high-production (spring phytoplankton bloom during May 1999) patch area in the northwestern North Pacific Ocean (Fig. 1). The aim of this study is to examine the Fe(III) solubility in seawater during bloom and nonbloom conditions and to infer from these measurements the role of biological production of Fe(III) chelators.

*Materials and methods*—Seawater samples were collected at 0–250 m depth inside (HP) and outside (LP) the high-production (phytoplankton spring bloom) area within the range of 44.0°N–44.8°N and 154.8°E–156.3°E in the northwestern North Pacific Ocean (Fig. 1) in May 1999 by use of acid-cleaned, Teflon-coated, 12-liter Niskin X sampling bottles (General Oceanics) attached to a CTD-RMS (Rosette Multi Sampler). Sample filtration (that used acid-cleaned 0.2- $\mu\text{m}$  Nuclepore polycarbonate filters) for analyses of Fe(III) solubility and dissolved Fe ( $<0.2 \mu\text{m}$ ) concentration took place in a class 100 laminar flow cabinet on board as soon as the samples were collected. The filtrates (100 ml) used for Fe(III) solubility analysis were immediately frozen in precleaned bottles to  $-20^\circ\text{C}$  in the dark until measurement in the laboratory. The filtrates (100 ml) used for dissolved Fe concentration analysis were buffered at pH 3.2 with a 10 M formic acid–2.4 M ammonium formate buffer solution (0.5 ml per 100-ml sample solution) and then kept in a refrigerator ( $4^\circ\text{C}$ ) until analysis in the laboratory.

The frozen samples for analysis of Fe(III) solubility were thawed and warmed to room temperature in the dark just before the start of the experiment. The Fe(III) solubility (at  $20^\circ\text{C}$ ) in the defrosted filtered seawater sample at each depth was determined by a simple filtration (0.025- $\mu\text{m}$  Millipore cellulosic membrane filter) that involved a  $\gamma$ -activity measurement of  $^{59}\text{Fe(III)}$  after the addition of radioactive  $^{59}\text{Fe(III)}$  into the seawater sample, as reported in studies elsewhere (Kuma et al. 1996, 1998, 2000a). In brief, a small amount of radioactive  $^{59}\text{Fe(III)}$  solution was added to 40 ml of the defrosted 0.2- $\mu\text{m}$ -filtered seawater samples ( $20^\circ\text{C}$ ) in acid-cleaned 125-ml polypropylene bottles to make a final iron concentration of  $\sim 100$  nM. The addition of dissolved Fe(III) to seawater results in hydrolytic precipitation of metastable Fe(III) hydroxide, which slowly transforms to

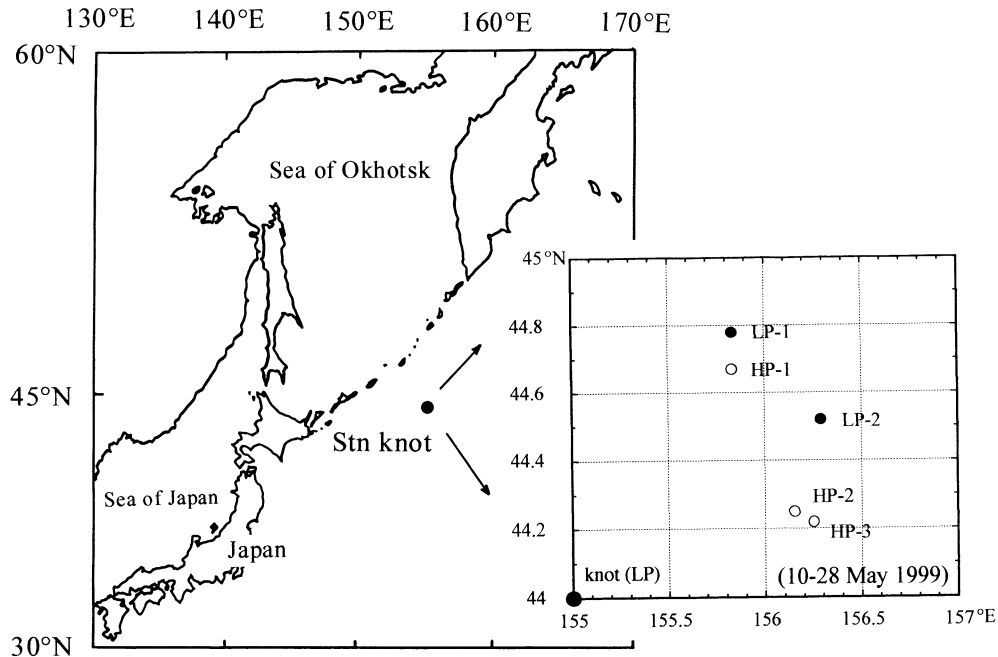


Fig. 1. Sampling locations inside (HP-1, HP-2, and HP-3) and outside (LP-1, LP-2, knot [LP]) the high-production patch area around station knot (44°N–45°N, 155°E–157°E) in the northwestern North Pacific Ocean during May 1999 (Table 1).

more stable solid phases. The bottles that contained seawater solution were kept at  $20^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$  in a dark incubator. After standing in the dark for 2–3 weeks at  $20^{\circ}\text{C}$ , each 7.5-ml sample aliquot was filtered through an acid-cleaned  $0.025\text{-}\mu\text{m}$  filter and acidified by addition of  $10\ \mu\text{l}$  of concentrated HCl, to prevent the adsorption of filtered Fe(III) on the wall of the collecting vials. In a study elsewhere (Kuma et al. 1996), the solubility values of Fe(III) hydroxide in seawater ( $20^{\circ}\text{C}$ ) were almost constant during aging for 1–5 weeks, presumably being in saturation equilibrium. The  $\gamma$  activity of the 2.5-ml acidified sample filtrates was measured in 5-ml counting vials with a gamma counter (Aloka ARC-301 B). The  $0.025\text{-}\mu\text{m}$ -filtered iron concentrations [Fe(III) solubility] were calculated from the counts (cpm corrected with an average counting efficiency for  $^{59}\text{Fe}$  of the scintillation counter), the volume of solution in the vial, and the amount of Fe per count. The pH values of the seawater samples measured after the solubility measurement were within a range of 8.0–8.2.

The Fe concentration in each buffered sample was determined by an automated Fe analyzer (Kimoto Electric) by use of a combination of chelating resin concentration and luminol-hydrogen peroxide chemiluminescence (CL) detection in a closed flow-through system (Obata et al. 1993, 1997; Nishioka et al. 2001). Briefly, Fe in a buffered sample solution (9 ml) was selectively collected on 8-quinolinol-immobilized chelating resin and then eluted with dilute 0.3 N HCl. The eluent was mixed with luminol solution, 0.6 N aqueous ammonia, and 0.7 M  $\text{H}_2\text{O}_2$  solution successively, and then the mixture was introduced into the CL cell. Finally, the Fe concentration was determined from the CL intensity.

Major nutrient concentrations were determined by use of

a Technicon autoanalyzer. Chl *a* concentrations were determined by the fluorometric method of Suzuki and Ishimaru (1990). Phytoplankton composition and cell density ( $10\text{-}\mu\text{m}$  cell size) were measured within a depth range of 0–50 m every 10 m at stations knot (LP) and HP-1. At each depth, 1 or 2 liters of seawater was fixed with neutral formalin (1% v/v). Each sample was subsequently concentrated by settling prior to microscopic examination. Hydrographic data (salinity, temperature, and depth) were obtained by use of a conductivity-temperature-depth instrument.

**Results**—The oceanographic regime in the surface did not change in the northwest Pacific between  $44^{\circ}\text{N}$  and  $44.8^{\circ}\text{N}$  and  $155^{\circ}\text{E}$  and  $156.5^{\circ}\text{E}$ , except at station knot (LP) (Fig. 1). Vertical profiles of temperature and salinity (Fig. 2) indicated either a subarctic water mass with low temperature, low salinity, and a high nutrient level (eutrophic water) or the transition zone between subarctic and subtropical water masses. Temperature and salinity in the surface mixed layer (0–50 m depth) were generally lower at HP ( $1.5^{\circ}\text{C}$ – $3^{\circ}\text{C}$ ,  $S = 32.90$ ) than at LP ( $2.7^{\circ}\text{C}$ – $5.2^{\circ}\text{C}$ ,  $S = 32.95$ – $33.1$ ). The surface waters at HP probably came from the northern coastal region along the Kamchatka Peninsula through the Western Subarctic Gyre (S. Saitoh pers. comm.).

Vertical profiles of Fe(III) solubility, Chl *a*, and nutrient concentrations are plotted in Figs. 3 and 4. Extremely high Fe(III) solubility values (2.2–4.4 nM) were observed in the surface mixed layer at HP that nearly corresponded with the depth of high Chl *a* concentrations (Fig. 3). However, the Fe(III) solubility at LP was low (0.3–0.9 nM). The maximum Fe(III) solubility values at HP coincided with depths that exhibited depletion of  $\text{NO}_3 + \text{NO}_2$  concentration in the surface mixed layer (Fig. 4). The dominant phytoplankton ( $\geq 10$

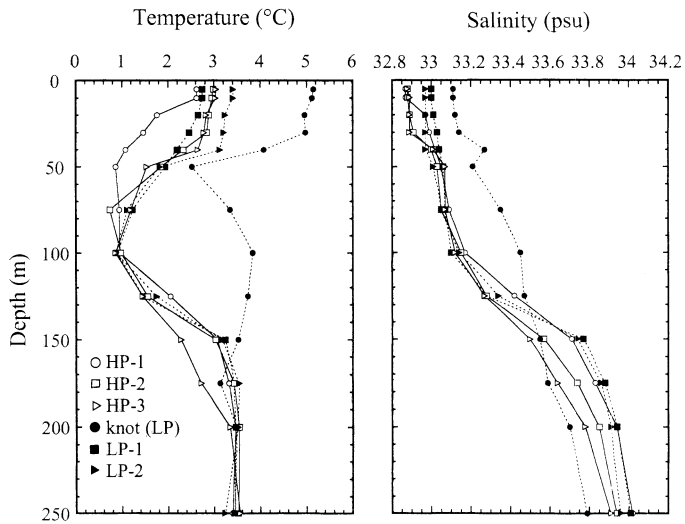


Fig. 2. Vertical profiles of temperature and salinity at 0–250 m depth inside (HP) and outside (LP) the high-production patch area.

$\mu\text{m}$  cell size) at stations knot (LP) and HP-1 were diatom species. The cell density of dominant marine diatom species at station knot (LP) was 5–6 times lower than that at station HP-1. Dominant diatom species at knot (LP) were *Chaetoceros concavicornis* (centric diatom), an oceanic species, and *Pseudonitzschia* spp. (pennate diatom), whereas those at HP-1 were *Thalassiosira nordenskiöldii* (centric) and *Fragilariopsis oceanica* (pennate). *T. nordenskiöldii* is a coastal marine diatom that expands its distribution into the open ocean during the spring bloom (Hasle 1976; Semina 1997). Just below the surface mixed layer, a Fe(III) solubility minimum (0.22–0.37 nM) was present in a narrow depth range (40–125 m) at all stations (Fig. 4). Fe(III) solubility minima have also been observed in the eastern Indian Ocean and the northwestern and northern North Pacific Ocean (Kuma et al. 1996, 1998). In middepth waters (100–250 m depth), the solubility levels increased to 0.6–0.8 nM with increasing depth in association with the increase in  $\text{NO}_3 + \text{NO}_2$  concentration (Fig. 4).

The vertical profiles of Fe(III) solubility and dissolved Fe ( $<0.2 \mu\text{m}$ ) concentration are plotted in Fig. 5. At all stations, the dissolved Fe concentration was higher at 0-m depth than at 10-m depth. The dissolved Fe was generally depleted (0.16–0.40 nM) in the surface waters (10–75 m depth) and then increased with depth up to 1–1.5 nM at 250-m depth. Fe(III) solubility was generally higher than the dissolved Fe concentrations in surface waters and lower than the dissolved Fe concentrations in middepth waters (100–250 m depth).

**Discussion**—The higher Fe(III) solubility in the surface waters at HP was probably due to a higher concentration or stronger affinity of natural organic Fe(III) chelators, which may be released by dominant phytoplankton or bacteria species during the spring bloom. There are significant correlations between the Fe(III) solubility values, Chl *a*, and nutrient ( $\text{NO}_3 + \text{NO}_2$ ) concentrations at 0–50 m depth (Fig. 6). The correlation coefficients ( $r$ ) between Fe(III) solubility

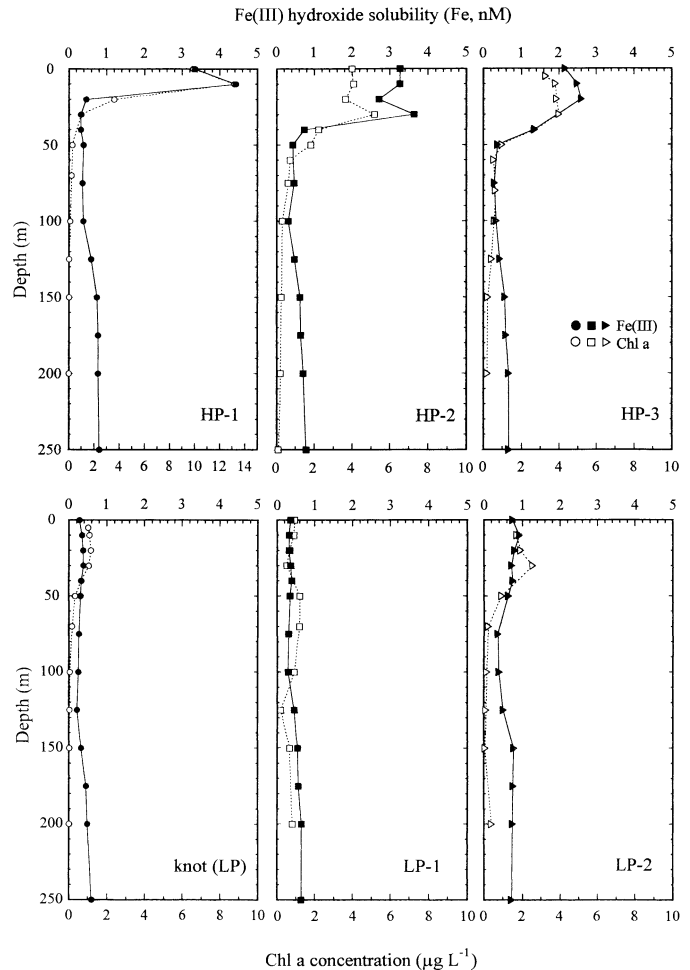


Fig. 3. Vertical distributions of Fe(III) solubility and Chl *a* concentrations inside and outside the high-production patch area.

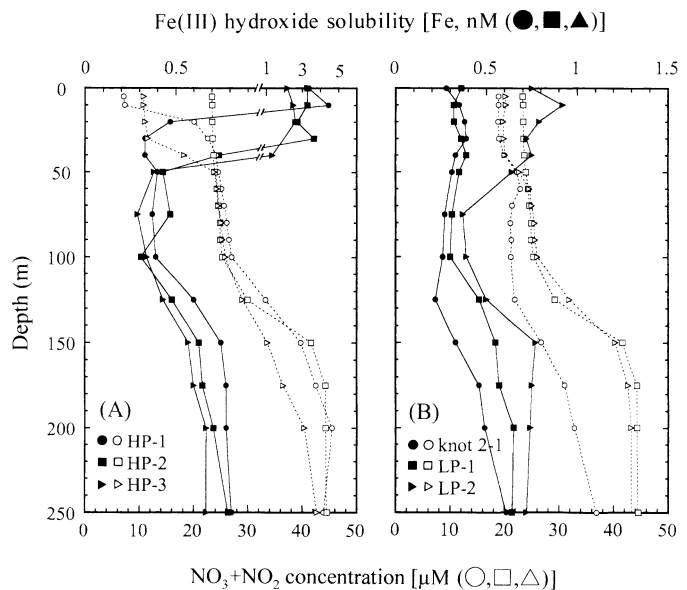


Fig. 4. Vertical distributions of Fe(III) solubility and  $\text{NO}_3 + \text{NO}_2$  concentrations inside (A) and outside (B) the high-production patch area.

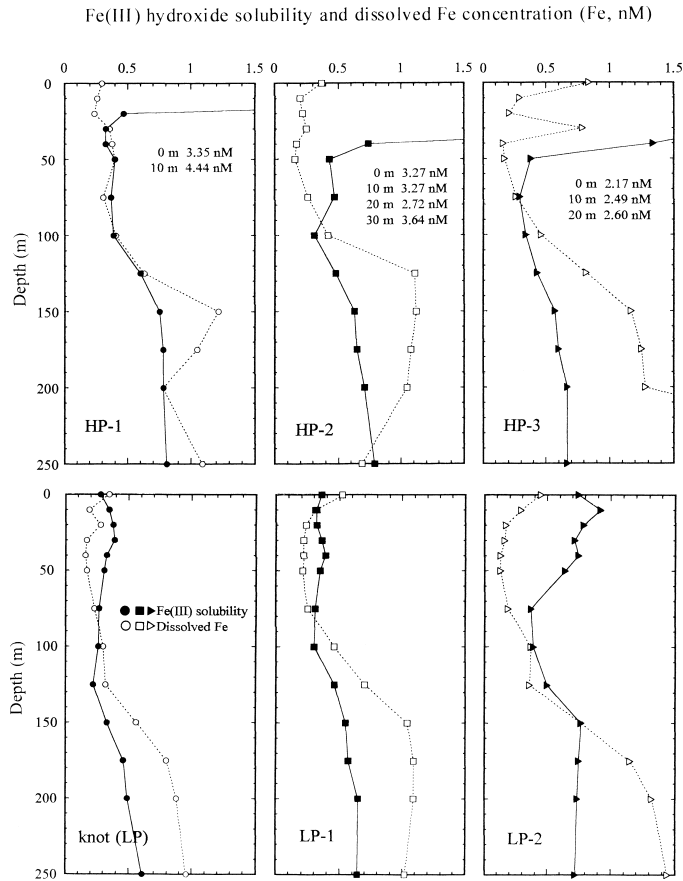


Fig. 5. Vertical distributions of Fe(III) solubility and dissolved Fe ( $<0.2 \mu\text{m}$ ) concentration inside (A) and outside (B) the high-production patch area. Fe(III) solubilities over 1.5 nM are off the x-axis scale and are given as numerical values.

values and Chl *a* concentrations at both HP and LP (all stations) and between Fe(III) solubility values and  $\text{NO}_3 + \text{NO}_2$  concentrations at only HP are 0.859 ( $n = 41$ ) and 0.953 ( $n = 15$ ), respectively (Fig. 6A,B). In addition, we calculated the standing stocks of Fe(III) solubility, Chl *a*, and consumed  $\text{NO}_3 + \text{NO}_2$  at the 0–50 m depth interval for each HP and LP station (Table 1). The consumed  $\text{NO}_3 + \text{NO}_2$  at each depth was calculated by subtracting the  $\text{NO}_3 + \text{NO}_2$  concentration at each depth from that at 100 m depth (Fig. 4). The correlation coefficients ( $r$ ) between the standing stocks of Fe(III) solubility and Chl *a* and between those of Fe(III) solubility and consumed  $\text{NO}_3 + \text{NO}_2$  are 0.821 ( $n = 6$ ) and 0.983 ( $n = 6$ ), respectively (Fig. 6C). In the previous studies, there were no significant correlations between the Fe(III) solubility values and the Chl *a* concentrations in the surface mixed layer along latitudinal transects from oligotrophic waters at lower latitude to eutrophic waters at higher latitude in the northwestern and northern North Pacific Ocean (Kuma et al. 1996, 1998) and during a spring phytoplankton bloom in Funka Bay, Japan (Kuma et al. 2000a). If the organic ligand complexing with Fe(III) is produced by phytoplankton, it seems unlikely that all phytoplankton would produce similar amounts of the same ligand. The distribution of organic ligand probably reflects the distributions

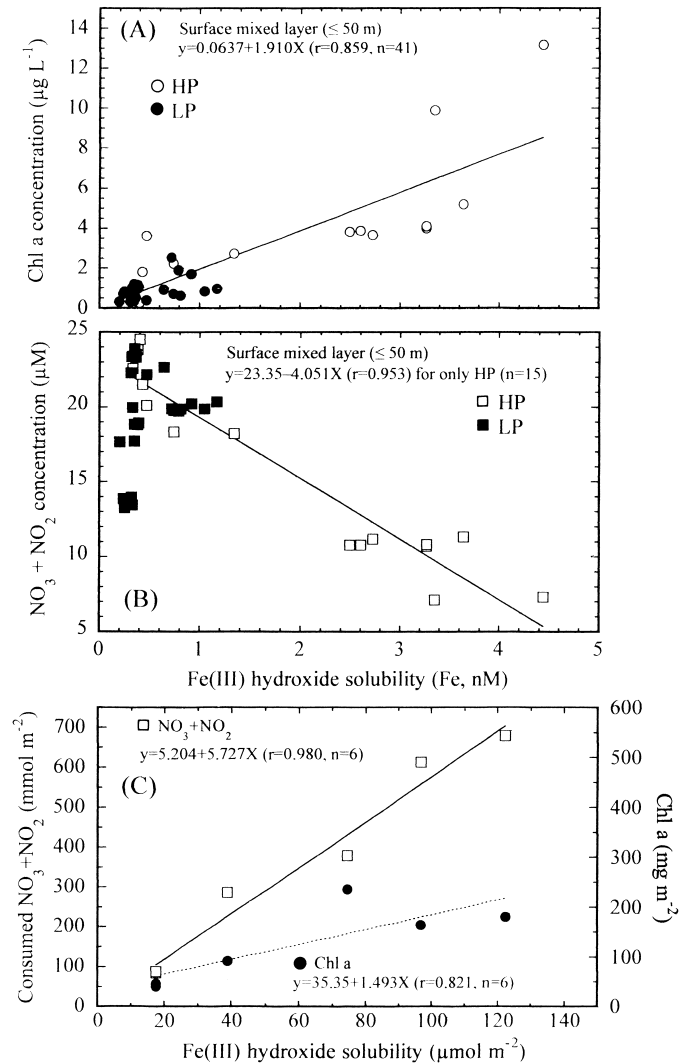


Fig. 6. (A) Chl *a* concentration and (B)  $\text{NO}_3 + \text{NO}_2$  concentration versus Fe(III) solubilities in the surface mixed layer ( $<50$  m depth) and standing stocks of consumed  $\text{NO}_3 + \text{NO}_2$  and (C) Chl *a* versus standing stock of Fe(III) solubility at the 0–50 m depth interval inside (HP) and outside (LP) the high-production patch area.

Table 1. Standing stocks of Fe(III) hydroxide solubility, Chl *a* and consumed  $\text{NO}_3 + \text{NO}_2$  at the 0–50 m depth interval in each station. The consumed  $\text{NO}_3 + \text{NO}_2$  at each depth was calculated by subtracting the  $\text{NO}_3 + \text{NO}_2$  concentration at each depth from that at 100 m depth.

Station	Fe(III) hydroxide solubility ( $\mu\text{mol m}^{-2}$ )	Chl <i>a</i> ( $\text{mg m}^{-2}$ )	$\text{NO}_3 + \text{NO}_2$ ( $\text{mmol m}^{-2}$ )
HP-1	74.5	235.9	379.3
HP-2	122.2	181.0	679.8
HP-3	96.8	164.5	613.7
knot (LP)	17.5	46.5	84.8
LP-1	17.5	40.2	88.2
LP-2	38.8	92.2	286.9

of particular source species, because many phytoplankton species occupy relatively distinct regional ranges in the surface water (Taylor and Waters 1982). Therefore, the distribution of Fe(III) solubility in surface waters within the restricted regional range in the present study would be expected to coincide with that of Chl *a* concentrations and to track trends in Chl *a*. The high Fe(III) solubility observed in the surface mixed layer at HP in this study may have been due to higher concentrations or stronger affinity of natural organic Fe(III) chelators released by dominant diatom species, such as *T. nordenskiöldii* and *F. oceanica*, smaller phytoplankton (<10- $\mu$ m cell size, no data) or bacteria during the spring bloom, although it is also possible that the higher Fe(III) solubility at the HP stations may have been due to coastal waters being advected offshore. The specific ligand or class of ligands and its source have to be identified in order to speculate as to the nature of organic Fe(III) chelators in the surface mixed layer.

In previous studies (Kuma et al. 1996, 1998), we estimated how strong ligands must be to be measured by the Fe(III) hydroxide solubility experiments. More than 85% of the organic ligands complexing with Fe will be detected at a conditional stability constant with respect to  $\text{Fe}^{3+}$  of  $K'_{\text{FeL}_1, \text{Fe}^{3+}} = 10^{21} \text{ M}^{-1}$ . In the equatorial Pacific Iron-Ex II study (Coale et al. 1996), Rue and Bruland (1997) found two classes of Fe(III)-binding organic ligands in surface waters by use of a highly sensitive competitive ligand equilibration/cathodic stripping voltammetry method: a strong ligand class ( $L_1$ ) with a conditional stability constant  $K'_{\text{FeL}_1, \text{Fe}^{3+}} = 5 \times 10^{23} \text{ M}^{-1}$  and a mean concentration of  $0.31 \pm 0.08 \text{ nM}$  and a weaker class ( $L_2$ ) with a conditional stability constant  $K'_{\text{FeL}_2, \text{Fe}^{3+}} = 6 \times 10^{22} \text{ M}^{-1}$  and a mean concentration of  $0.19 \pm 0.09 \text{ nM}$ . The total Fe(III)-binding ligand concentrations seen in Iron Ex II ( $\sim 0.5 \text{ nM}$ ) agree well with the Fe(III) solubility values ( $0.3\text{--}0.9 \text{ nM}$ ) in the surface mixed layer at the LP in the present study. In addition, the initial 2 nM mesoscale iron injection in the primary Iron-Ex II study resulted in a fourfold increase ( $\sim 2 \text{ nM}$ ) in the total Fe(III)-binding ligand concentrations. In particular, the stronger ligand class ( $L_1$ ) increased from 0.3 to 1.3 nM. Fe-binding ligand measurements in the iron fertilization experiment in the polar Southern Ocean also revealed that the Fe(III)-binding ligand concentrations increased from 3.5 to 8.5 nM inside the phytoplankton bloom patch (Boyd et al. 2000). In laboratory culture experiments, there is evidence for extracellular siderophores, specific Fe(III)-uptake chelators, production by marine phytoplankton, and bacteria under iron-deficient conditions (Trick et al. 1983*a,b*; Reid et al. 1993; Wilhelm and Trick 1994; others). Contrary to the concept of a siderophore, which is supposed to be released under iron-deficient conditions, the ubiquitous coccolithophore *Emiliania huxleyi* was found to release iron-complexing ligands in response to the iron addition (Boye and van den Berg 2000). Therefore, it is very difficult to determine whether the observed high Fe(III) solubility in the surface mixed layer at HP in the present study was due to the biological production of Fe(III)-binding ligands under Fe supply by atmospheric input or iron-deficient conditions. The Fe(III) solubility minima observed in the subsurface (40–125 m) was probably due to the consumption or degradation of both the surface-

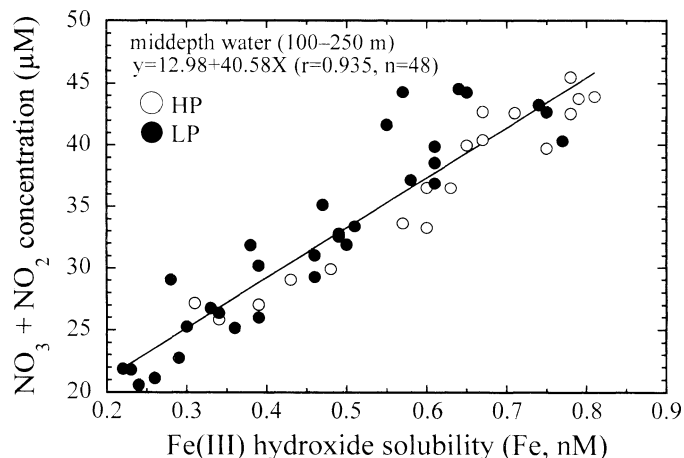


Fig. 7.  $\text{NO}_3 + \text{NO}_2$  concentration versus Fe(III) solubility in the middepth waters (100–250 m depth) inside (HP) and outside (LP) the high-production patch area.

produced and the upwelled organic ligands. However, the solubility minima might be related to the change in ligand size fraction rather than consumption or degradation of the ligands themselves if the ligands binding Fe associate with large organic colloids of which the size normally increased sharply to much  $>25 \text{ nm}$  in this depth range in oceanic waters (Wells and Goldberg 1991). In middepth waters (100–250 m depth), the Fe(III) solubility levels appeared to increase with increasing  $\text{NO}_3 + \text{NO}_2$  concentration (Fig. 4). When the nutrient data at 100–250 m depth from all stations are used, the correlation coefficient ( $r$ ) between the solubility and  $\text{NO}_3 + \text{NO}_2$  is 0.935 ( $n = 48$ ) (Fig. 7). The increase in Fe(III) solubility with nutrient concentrations is likely related to the decomposition and transformation of sinking organic matter and is due to the formation of organic Fe(III) chelators through the decomposition of biogenic organic matter. The organic Fe(III) chelators in middepth waters are regulated by biological uptake and regeneration processes that occur for major nutrients and dissolved Fe (Martin et al. 1989). This interpretation is remarkably consistent with that for a humic-type fluorescence of dissolved organic matter that correlated well with nutrients and apparent oxygen utilization (AOU) in middepth waters in the open ocean (Hayase et al. 1988; Hayase and Shinozuka 1995). It has been suggested that fluorescent humic substances are regenerated in the water column by the oxidation and remineralization of settling organic particles (Hayase et al. 1988; Hayase and Shinozuka 1995) and that the complexation of iron with natural organic ligands, such as humic acid, increase the iron solubility at pH levels near 8 (Liu and Millero 1999). The chemical composition of organic Fe(III) chelators in middepth waters may differ from those that were released by particular phytoplankton or bacteria species through their metabolism in the surface waters. As another possible interpretation for the increase in Fe(III) solubility with depth in middepth waters, heterotrophic bacteria in middepth waters may release ligands (siderophores) that could be different from those released by phytoplankton.

Bruland et al. (1991) suggested that eolian input caused the surface-enriched dissolved Fe profile observed in the ol-

igotrophic North Pacific central gyre. In addition, Kuma et al. (2000a) reported surface-enriched dissolved Fe profiles during the beginning of the spring phytoplankton bloom, and surface-depleted dissolved Fe profiles were observed at the bloom peak in Funka Bay (Japan). The changes in patterns of dissolved Fe profiles in the bay may reflect temporal variations in the atmospheric input from land close to this bay and biological processes. Therefore, the near-surface (0-m depth) enriched dissolved Fe profiles in our study (Fig. 5) could be due to eolian Fe input. The depletion of dissolved Fe in the surface waters at 10–75 m depth probably resulted from active removal of dissolved Fe by phytoplankton, and the increase in dissolved Fe with depth in middepth waters (100–250 m depth) was probably due to the remineralization of sinking particulate organic matter (Kuma et al. 1996, 1998; Johnson et al. 1997a,b).

Another feature associated with the iron profiles was the difference in iron concentration between the Fe(III) solubility ( $<0.025 \mu\text{m}$ ) and dissolved Fe ( $<0.2 \mu\text{m}$ ) concentration at HP and LP (Fig. 5). The higher Fe(III) solubility than the dissolved Fe concentration in the surface waters probably resulted from active removal of dissolved Fe and release of natural organic Fe(III) chelators by phytoplankton or bacteria. However, in middepth waters, the Fe(III) solubility was generally lower than the dissolved Fe(III) concentration. The colloidal iron phases in middepth waters may have been present in the  $0.2\text{-}\mu\text{m}$  fraction. These phenomena were also observed in the water column of the eastern Indian Ocean and the northwestern North Pacific Ocean (Kuma et al. 1996). Wu and Luther (1994) reported that the colloidal Fe concentration in the  $0.2\text{-}0.4 \mu\text{m}$  size fraction in the water column of the western North Atlantic Ocean was relatively high ( $0.2\text{-}0.3 \text{ nM}$ ) at  $50\text{-}750 \text{ m}$  depth. Recently, Nishioka et al. (2001) have reported vertical distributions of soluble Fe ( $<200 \text{ kDa}$  or  $<0.03 \mu\text{m}$ ) and dissolved Fe ( $<0.1$  or  $<0.2 \mu\text{m}$ ) at  $0\text{-}1000 \text{ m}$  depth in the northeastern North Pacific Ocean. Soluble Fe concentrations exhibited a nutrient-like profile and increased with depth up to  $0.34\text{-}0.57 \text{ nM}$  at  $600\text{-}1000 \text{ m}$  depth. Small colloidal Fe below  $100 \text{ m}$  depth represented  $13\%\text{-}50\%$  of dissolved Fe ( $<0.2 \mu\text{m}$ ). The small colloidal Fe concentrations were generally low in the surface mixed layer and suddenly increased with depth at  $100\text{-}200 \text{ m}$  depth. The sudden increase in the small colloidal Fe concentrations in middepth waters reported by Nishioka et al. (2001) is remarkably consistent with the increase in the difference between the dissolved Fe concentration and the Fe(III) solubility at  $100\text{-}200 \text{ m}$  depth in the present study (Fig. 5). These increases at  $100\text{-}200 \text{ m}$  depth were probably due to the formation of colloidal Fe ( $<0.2\text{-}\mu\text{m}$  size) and organic Fe(III) chelators through the oxidative decomposition of sinking biogenic organic matter. Wells and Goldberg (1991, 1992, 1993) have reported that marine small colloids ( $<0.12\text{-}\mu\text{m}$  size) are at least three orders of magnitude more abundant than larger submicrometer particles and that small colloids commonly aggregate in ocean waters.

These results suggest that the Fe(III) solubility in the surface waters is strongly related to the formation of organic Fe(III) chelators and the biological activity. However, the

chemical composition and the vertical distribution of organic Fe(III) chelators in the surface waters are still unknown.

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