

East–west gradients in the photosynthetic potential of phytoplankton and iron concentration in the subarctic Pacific Ocean during early summer

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Abstract

In the subarctic Pacific and its adjacent waters, the photochemical quantum yield (F_v/F_m) and the functional absorption cross section (σ_{PSII}) of photosystem II for surface phytoplankton were continuously measured during the early summer of 1999 using a fast repetition rate fluorometer. Concentrations of total dissolvable iron (TD-Fe) were also determined at each sampling station. The maximum value (0.61) of F_v/F_m was observed off the Aleutian Peninsula, where TD-Fe concentrations were relatively high. The Western Subarctic Gyre (WSG) and the Alaskan Gyre (AG), located in the northwest and northeast subarctic Pacific, respectively, were in high-nutrient, low-chlorophyll (HNLC) conditions. Surface TD-Fe generally remained in the WSG but was depleted (<0.01 nmol L⁻¹) in the AG. Nighttime F_v/F_m and σ_{PSII} in the WSG were significantly higher ($p < 0.01$) and lower ($p < 0.01$), respectively, than in the AG. Iron or nitrogen limitations generally lead to a decrease in F_v/F_m and an increase in σ_{PSII} . These results suggested that there was an east–west gradient (WSG $>$ AG) in the photosynthetic competence of phytoplankton in the subarctic Pacific and that the difference was probably caused by iron levels in seawater. Indeed, our iron enrichment experiment in the AG revealed that F_v/F_m increased from 0.27 to 0.49 and σ_{PSII} decreased from 496×10^{-20} to 365×10^{-20} m² photon⁻¹ after a 0.8 nmol L⁻¹ iron addition. At the same time, a dramatic floristic shift from phytoflagellates to diatoms was found by pigment signatures. Iron could principally control the photosynthetic physiology of phytoplankton in the whole subarctic Pacific.

The identification of factors controlling primary production is a key issue for a better understanding of the biogeochemical processes in high-nutrient, low-chlorophyll (HNLC) regions, where macronutrients (nitrate, phosphate, and silicate) are abundant and where phytoplankton stocks

in terms of chlorophyll *a* (Chl *a*) concentration are relatively low (<1 $\mu\text{g L}^{-1}$) throughout the year. It is now widely accepted that the northeast subarctic Pacific (i.e., Alaskan Gyre; AG) is one of the HNLC regions, together with the eastern equatorial Pacific and the Southern Ocean. HNLC conditions are mainly attributed to low Fe concentrations (Martin and Fitzwater 1988; Boyd et al. 1996; La Roche et al. 1996) and microzooplankton grazing (Frost 1991; Strom et al. 2000). Fe is required for the synthesis of chlorophyll and the reduction of nitrate and plays key roles in photosynthetic electron transport in the thylakoids of phytoplankton cells (Raven et al. 1999). Furthermore, it is known that the growth of large cells such as diatoms is more sensitive to Fe limitation than is the growth of small cells (Boyd et al. 1996). When the large-sized phytoplankton growth is restricted by Fe, the phytoplankton community becomes dominated by small algal cells that are accessible to grazing by microzooplankton. The high growth potential of these consumers ensures that they will always overtake and suppress increases in phytoplankton stocks (Strom et al. 2000). Maldonado et al. (1999) found that light could also be a co-

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limiting factor in phytoplankton growth in the AG during winter.

On the other hand, Fe limitation might be less severe in other regions of the subarctic Pacific. The northwest subarctic Pacific is often more productive in its lower trophic levels, especially during the bloom season from spring to early summer (e.g., Shiimoto et al. 1998; Obayashi et al. 2001). High Chl *a* concentrations of $>2 \mu\text{g L}^{-1}$ were observed, particularly in the western and southern edges of the Western Subarctic Gyre (WSG) and adjacent waters, where the Oyashio Current and East Kamchatka Current flowing near the Kamchatka Peninsula can intrude (e.g., Banse and English 1999; Obayashi et al. 2001). The Oyashio Current and East Kamchatka Current seem to contain relatively high concentrations of Fe. This speculation is consistent with the observation that there can be a 10- to 100-fold difference in the Fe concentration of coastal and oceanic surface waters (Sunda and Huntsman 1995). Moreover, most of the spring-time dust, which is a source of Fe, is generated in the arid regions of Asia, such as the Gobi Desert of China, and is transported eastward over the North Pacific by strong westerly winds (Duce and Tindale 1991). As a result, there is a strong gradient in the Fe flux between the western and eastern Pacific Ocean. Recently, Fujishima et al. (2001) showed that the dissolved Fe concentration in the deep water (>200 m) southwest of the WSG was $\sim 1 \text{ nmol L}^{-1}$, which was about twofold higher than that of the AG during the late summer of 1997.

Thus, Fe chemistry can be crucial in determining phytoplankton physiology and primary production in the whole subarctic Pacific Ocean. However, the difference in the physiological status of the phytoplankton assemblage between the northeast and northwest subarctic Pacific has never been reported. In addition, information on Fe concentrations in the subarctic Pacific is very limited. Here we report the photosynthetic potential of the surface phytoplankton community in the subarctic Pacific and its adjacent waters, such as the Bering Sea, during the early summer of 1999 as estimated by a fast repetition-rate (FRR) technique based on single-turnover flash saturation profiles of variable fluorescence (Kolber et al. 1998). The FRR technique has the advantage of being rapid, nondestructive, and able to measure the photochemical quantum efficiency (F_v/F_m) of photosystem II (PSII). The difference between the maximum (F_m) and minimum (F_0) chlorophyll fluorescence yields is called variable fluorescence, F_v . F_v/F_m is an index of the quantum yield for carbon fixation and oxygen evolution (Falkowski et al. 1994). Furthermore, the functional absorption cross-section (σ_{PSII}) of PSII can also be determined by this technique. This cross-section is a quantitative measure of the effective biophysical target size of the antenna pigments of PSII (Mauzerall and Greenbaum 1989). It is known that Fe or nitrogen limitations lead to a decrease in F_v/F_m and an increase in σ_{PSII} (e.g., Greene et al. 1992; Kolber et al. 1994). During the survey cruise, the concentrations of macronutrients and total dissolvable Fe (the sum of dissolved and labile particulate Fe at pH 3.2) were also determined at each sampling station. We also show the results of an Fe-enrichment bottle incubation experiment at the Canadian Ocean time series Station P (50°N, 145°W) in the AG. This experiment was

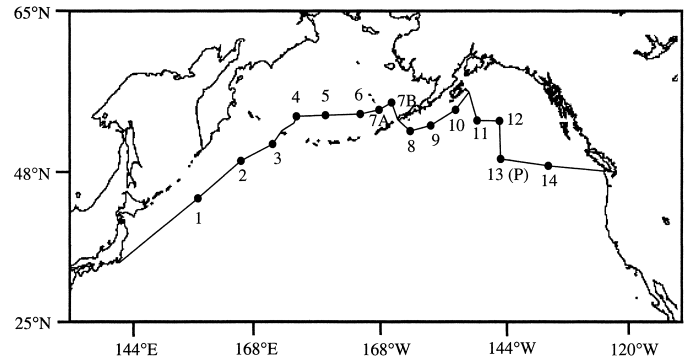


Fig. 1. Location of sampling stations and cruise track for the KH-99-3 cruise of R/V *Hakuho Maru*.

conducted to determine whether Fe affects photosynthetic physiology in terms of the PSII parameters and the abundance and composition of the phytoplankton assemblage. Changes over time in the concentrations of dissolved Fe and other trace metals (Mn, Ni, and Zn) stored in incubation carboys were also examined by inductively coupled plasma mass spectrometry (ICP-MS) or chemiluminescence for possible limitations of phytoplankton growth by these trace metals.

Materials and methods

This study was conducted during R/V *Hakuho Maru* cruise KH-99-3, which crossed the subarctic Pacific via the Bering Sea during the early summer (25 June–22 July) of 1999 (Fig. 1). This cruise had 15 observation stations, including the Japanese JGOFS time series Station KNOT (Sta. 1) and the Canadian Ocean time series Station P (Sta. 13). Following the hydrographic domains of Banse and English (1999), we have referred to 155–170°E as the Western Subarctic Gyre (WSG; Stas. 1–3), 175°E–170°W as the Bering Sea (Stas. 4–6), 150–170°W as a coastal domain off the Aleutian Peninsula (Stas. 7A–10), and 135–150°W as the Alaskan Gyre (AG; Stas. 11–14). The regions of $>155^\circ\text{E}$ and $<135^\circ\text{W}$, which were not mentioned by Banse and English (1999), have been defined as near Japan and near Canada, respectively. However, we will not discuss the latter two regions in this paper because macronutrients and Fe data were not available. Hydrographic data (seawater temperature, salinity, macronutrients, and Chl *a* determined by fluorometry) at each sampling station were obtained from the cruise report (Ocean Research Institute, The University of Tokyo 1999). Photosynthetically active radiation (PAR) was continuously measured on deck using a 2π Li-Cor quantum sensor, and the data were 10-min averaged.

Total dissolvable Fe analysis—For collecting seawater at each sampling station, two types of samplers were used: 12-liter lever-action Niskin samplers and 12-liter conventional Niskin samplers equipped with silicone tubing for closing the samplers. The inside walls of the sampling bottles were coated with Teflon. The cleaned samplers were loaded on a CTD-CMS (carousel multisampling system) connected to a titanium hydrowire. Water samples were usually collected

from 0, 10, 20, 30, 40, 50, 60, 80, 100, 125, 150, and 200 μM and then were adjusted to pH 3.2 by adding a formic acid–ammonium formate buffer solution without filtration. The Fe fraction in seawater was analyzed with an automatic analyzer described previously (Obata et al. 1997). The acidified seawater was pumped through a chelating resin column of 8-hydroxyquinoline (MAF-8HQ) immobilized on granular fluorinated metal alkoxide glass. Dissolved Fe concentrated onto the chelating resin column was eluted with 0.3 mol L⁻¹ hydrochloric acid and detected by a chemiluminescence method using the luminol hydrogen peroxide system in an aqueous ammonia medium. The detection limit (3SD) was 0.01 nmol L⁻¹. The Fe fraction determined in this study was defined as “total dissolvable Fe (TD-Fe).” The measurements were carried out on board ship.

Underway FRR fluorometer measurements—Water samples were continuously taken from the bottom of the research vessel at a depth of 5 m, using the ship’s underway pumping system, and then run through light-shaded rubber tubing and a light-shaded plastic debubbler (10 liters volume). The seawater then flowed through the dark sample chamber of a FRR fluorometer (FRRf, Chelsea Instruments) operated in a flow-through bench-top mode. The FRR technique is detailed in Kolber et al. (1998). The flow rate was adjusted to make a dark adaptation period of ~3 min (Behrenfeld and Kolber 1999) to open the reaction centers of PSII before FRRf measurements. The FRRf was set to deliver saturation flash sequences of 100 1- μs -duration flashes with 1- μs intervals between flashes. Acquisitions of a series of 16 flash sequences were internally averaged and were repeated five times with a 1-s interval between iterations. The FRRf usually operated at an interval of 15–30 min in the area from 35°16’N, 141°03’E (off Japan) to 57°42’N, 152°00’E (off Kodiak Island) during 25 June–11 July, and from 57°03’N, 151°31’E (off Kodiak Island) to 48°35’N, 127°08’W (off U.S.A.) during 15–22 July. The dark chamber of the FRRf was sometimes cleaned to avoid fouling during the cruise. The fluorescence data were processed with FRS software (Chelsea Instruments) to obtain F_v/F_m and σ_{PSII} . It is known that σ_{PSII} is wavelength dependent (Kolber et al. 1998). Because the peak excitation of the light-emitting photodiodes (LEDs) in our FRRf is 478 nm, with a 40-nm half-bandwidth, we limit our discussion to σ_{PSII} in those wavelengths. The PSII parameters obtained were compared to the specific growth rate of phytoplankton (Liu et al. 2002a) and photosynthesis–irradiance parameters (Yoshikawa 2002). It should be noted that their original data were reclassified into the hydrographic regime of this study for the comparison because Stas. 7A and 7B were set in Bering Sea stations both in Liu et al. (2002a) and Yoshikawa (2002), and Stas. 8 and 9 were in AG stations in Yoshikawa (2002).

In vitro Fe enrichment experiments—Seawater was collected from a depth of 5 m at Sta. 13 (Sta. P) using a non-toxic polypropylene bellows pump with silicon tubing. This seawater was immediately poured into 4-liter acid-washed polycarbonate carboys. Each carboy was either spiked with 0.8 nmol L⁻¹ (final concentration) FeCl₃ solution or left as a control (day 0) and was incubated on deck at surface water

temperature for 5 d. Duplicate carboys were prepared for each treatment. To minimize contamination during the incubation, carboys were placed in clean, heavy-duty polyethylene bags. Samples were collected around 1430 h on days 0, 2, 4, and 5. Sample treatments were carried out in a clean room under class 100 clean-air conditions on board ship.

Samples for dissolved trace metals were collected in low-density polyethylene Nalgene bottles. They were filtered through 0.2- μm Nuclepore filters, acidified to pH 2 with hydrochloric acid, and kept at room temperature for more than 1 yr. The aliquots were used for the determination of dissolved Fe (D-Fe), Ni (D-Ni), and Zn (D-Zn) with MAF-8HQ chelating column extraction followed by ICP-MS determination (Fujishima et al. 2001). Using the other aliquots of the samples, the concentration of dissolved Mn (D-Mn) was determined with an automatic analyzer based on chemiluminescence (Nakayama et al. 1989). A clean technique was used throughout the analysis.

Macronutrients (nitrate + nitrite, phosphate, and silicate) were measured by a BRAN + RUEBBE autoanalyzer on board ship. The difference in nutrient concentrations between days 0 and 5 of the experiment was used for calculations of the nutrient consumption ratio (Takeda 1988).

Nutrient consumption ratio

$$= ([M]_{\text{D5}} - [M]_{\text{D0}})/([N]_{\text{D5}} - [N]_{\text{D0}})$$

$[M]_{\text{D5}}$ and $[M]_{\text{D0}}$ are macronutrient or micronutrient concentrations ($\mu\text{mol L}^{-1}$) on days 5 and 0, respectively. $[N]_{\text{D5}}$ and $[N]_{\text{D0}}$ are concentrations ($\mu\text{mol L}^{-1}$) of nitrate + nitrite on days 5 and 0, respectively.

For FRRf measurements, water samples from the carboys were transferred in the clean room to 50-ml acid-cleaned polycarbonate bottles, which were covered with black plastic tape. For dark adaptation, samples were placed in a refrigerator adjusted to the surface water temperature for 30 min (Geider et al. 1993). Water samples were transferred to a 1-cm-pathlength quartz cuvette in an underlit condition and analyzed in the dark using the FRRf with a handmade cuvette folder following the same protocol used for the underway FRRf measurements. Triplicate samples were then analyzed, and five acquisitions were made per sample.

Water samples (200 ml) for Chl *a* were filtered onto 25-mm Whatman GF/F filters with a vacuum of <100 mm Hg. Chl *a* was extracted into *N,N*-dimethylformamide and measured by a Turner Designs fluorometer aboard ship (Suzuki and Ishimaru 1990). Furthermore, water samples (1 liter) for phytoplankton pigments were also filtered onto 25-mm GF/F filters on days 0 and 5, stored in a deep-freezer (–80°C) or liquid nitrogen, and analyzed by high-performance liquid chromatography (HPLC, Shimadzu) on land following the method of Suzuki et al. (in press). Increased ratios of pigment concentration were calculated as follows.

$$\text{Increased ratio} = [P]_{\text{D5}}/[P]_{\text{D0}}$$

$[P]_{\text{D5}}$ and $[P]_{\text{D0}}$ are pigment concentrations ($\mu\text{g L}^{-1}$) on days 5 and 0, respectively. Because of the limited water volume available, no replication was possible for the trace metals, macronutrients, Chl *a*, or HPLC pigment analyses. Duplicate water samples (1 ml) for ultraplankton (< ca. 5 μm in size),

including heterotrophic bacteria, were fixed with 0.2% (final concentration) paraformaldehyde and deep-frozen in a freezer (-80°C) or liquid nitrogen. Cell densities of ultraplankton were counted on land by a Becton Dickinson FACSCalibur flow cytometer following the protocol of Liu et al. (2002a,b).

Results

Hydrography—Surface water temperature gradually increased toward the east (6°C at Sta. 1 to 11°C at Sta. 14). Surface salinity ranged approximately between 32 and 33. The surface mixed layer, which was estimated from the maximum density gradient depth using discrete CTD data, was shallow throughout the survey area: the bottom depth of the surface mixed layer was 20–30 m in both the WSG and the coastal domain off the Aleutian Peninsula, 10–20 m in the Bering Sea, and 20–40 m in the AG; it was shallower than the euphotic layer throughout the cruise. Macronutrients were abundant along the cruise track, with only a few exceptions. Figure 2 shows the averaged macronutrient concentrations within the surface mixed layer at each sampling station. Nitrate + nitrite (Fig. 2A) was depleted at Sta. 7B in the coastal domain off the Aleutian Peninsula, which was the only shallow-water (<200 m depth) station during the cruise. In addition, surface silicate was almost depleted (0.02 – $0.71 \mu\text{mol L}^{-1}$) at Sta. 5, although surface nitrate remained at $>10 \mu\text{mol L}^{-1}$. Note that the standard deviations of macronutrient concentrations at Sta. 1, which is located on the edge of the WSG, were large. At this station, water samplings were conducted once a day for 2 d. The changes in macronutrient concentrations were probably due to the horizontal advection of the surface waters. Chl *a* concentrations were consistently low ($<1 \mu\text{g L}^{-1}$) within the surface mixed layer in both the WSG and AG, but relatively higher concentrations were sometimes observed in the Bering Sea and the coastal domain, especially at Sta. 10 (Fig. 2D). The Chl *a* and macronutrient data indicate that both the WSG and the AG were under HNLC conditions during the cruise.

Total dissolvable Fe concentration—Total dissolvable Fe (TD-Fe) concentrations within the surface mixed layer at each station were averaged and shown in Fig. 3A. It should be noted that the detection limit of the TD-Fe analysis was 0.01 nmol L^{-1} and that values below that limit were assumed to be zero. The TD-Fe within the surface mixed layer was often found at $<0.3 \text{ nmol L}^{-1}$ in the oceanic regions (i.e., the WSG, the Bering Sea, and the AG). Its concentrations at the AG stations (except Sta. 11) were below the detection limit. Concentrations were generally higher in the WSG, and the highest overall iron levels were found in the coastal domain off the Aleutian Peninsula (Stas. 7–10). Concentrations at Sta. 11 in the northern AG were as high as in the coastal domain, suggesting that Fe levels at this station were influenced by Fe inputs from coastal waters. Depth-integrated (0–200 m) TD-Fe concentrations (Fig. 3B) also showed that there was an east–west gradient to Fe distribution in the subarctic Pacific.

Underway FRRf measurements—The photochemical quantum efficiency (F_v/F_m) and the functional absorption

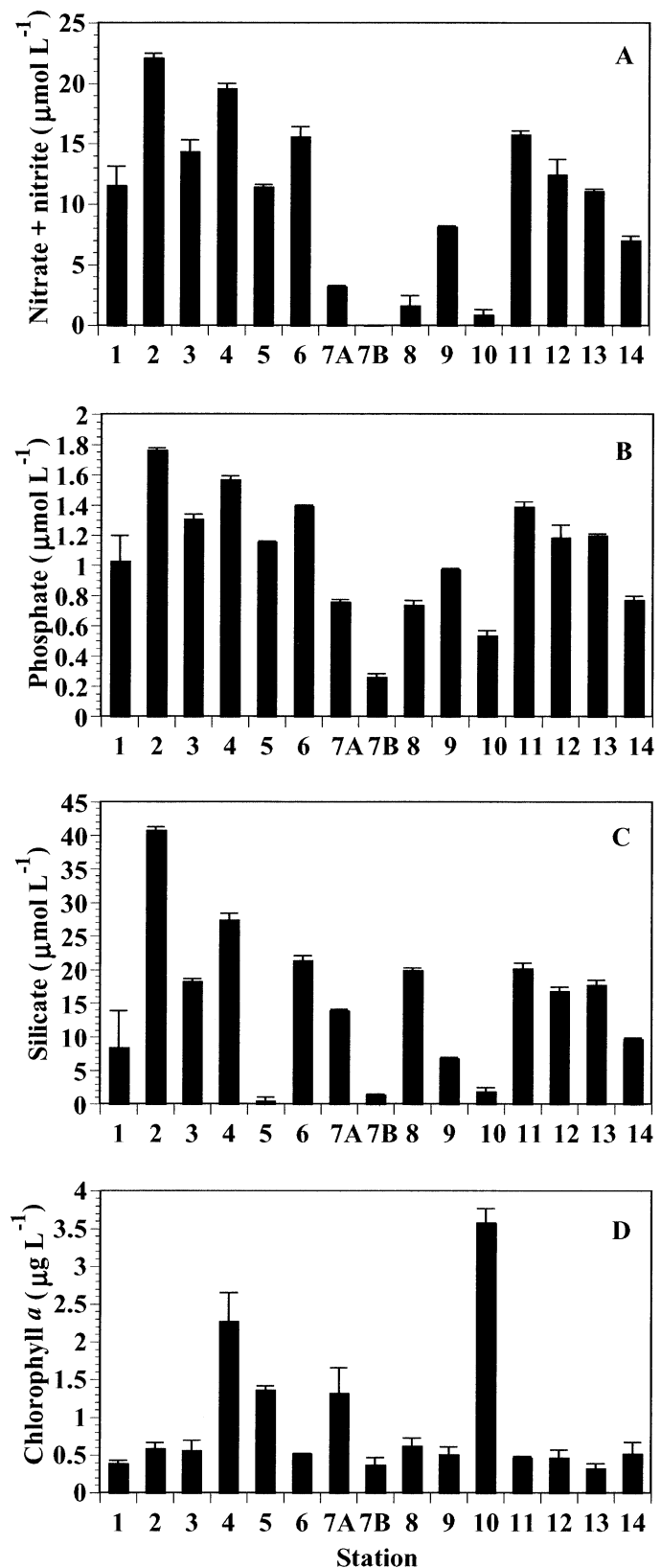


Fig. 2. Concentrations of (A) nitrate + nitrite ($\mu\text{mol L}^{-1}$), (B) phosphate ($\mu\text{mol L}^{-1}$), (C) silicate ($\mu\text{mol L}^{-1}$), and (D) Chl *a* ($\mu\text{g L}^{-1}$) in the surface mixed layer at each sampling station. Data presented are means \pm SD.

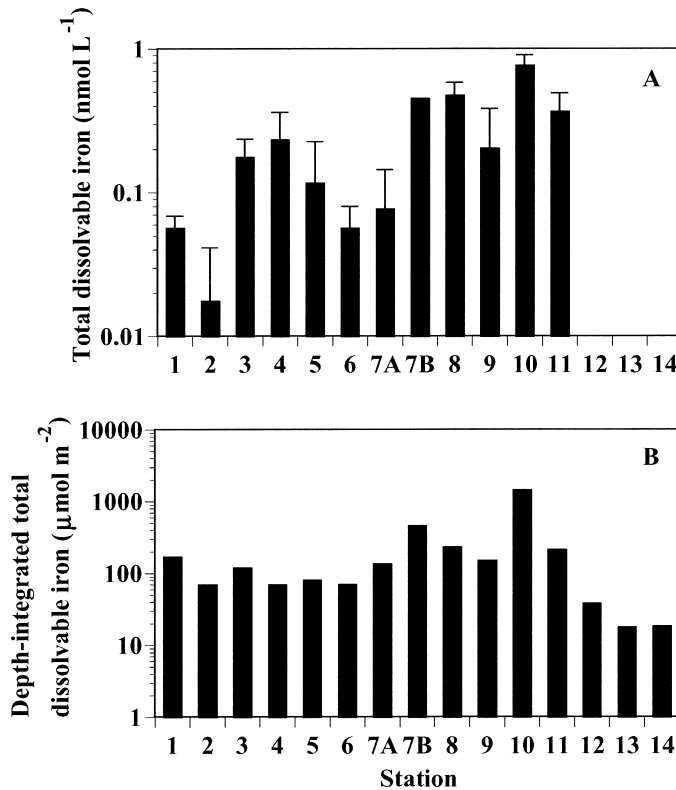


Fig. 3. Concentrations of (A) total dissolvable iron (nmol L^{-1}) and (B) depth-integrated (0–200 m) total dissolvable iron ($\mu\text{mol m}^{-2}$).

cross section (σ_{PSII}) of PSII changed between 0.12–0.61 and $180\text{--}750 \times 10^{-20} \text{ m}^2 \text{ photon}^{-1}$, respectively, throughout the cruise. Diurnal variations in F_v/F_m and σ_{PSII} often appeared (Fig. 4). Values of these parameters generally showed minima during the day and maxima at night in conjunction with the diel cycle in solar radiation (i.e., PAR). The amplitude of σ_{PSII} diurnal variation was particularly wide in the AG, where solar radiation was higher ($>1,500 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$). It is known that F_v/F_m and σ_{PSII} can be decreased by the photodamage of PSII units, the down-regulation of PSII reaction centers under excess solar radiation, or both (Vasiliev et al. 1994). To deduce the photosynthetic competence of phytoplankton, nighttime values of F_v/F_m and σ_{PSII} were used in this study because the irradiance effect could be neglected at night. In dark-adapted algae grown under nutrient-sufficient conditions, maximum values of F_v/F_m using the single-turnover flash technique are ~ 0.65 and independent of phytoplankton species (Falkowski et al. 1994). Table 1 shows that F_v/F_m in the AG was significantly lower than that in the WSG at night (Mann–Whitney U -test; $p < 0.01$). On the other hand, σ_{PSII} in the AG was ~ 1.2 times higher than that in the WSG at night (Mann–Whitney U -test; $p < 0.01$). A negative linear relationship between nighttime F_v/F_m and σ_{PSII} was observed (Fig. 5). Lower F_v/F_m and higher σ_{PSII} in the AG indicate that a nutrient (nitrate or iron) limitation of phytoplankton growth occurred. In fact, TD-Fe was generally depleted in the AG (Fig. 3B), although the macronutrients were abundant (Fig. 2). These results suggested

that an Fe limitation occurred in the AG. At Sta. 5, where silicate was almost depleted, the maximum value of F_v/F_m was ~ 0.4 , which was slightly lower than at the other stations in the Bering Sea. Although surface nitrate + nitrite was depleted at Sta. 7B (Fig. 2A), FRRf measurements unfortunately were not carried out at this station because of an intensive apparatus maintenance period. The maximum F_v/F_m value (0.61) was observed at $54^\circ 14' \text{N}$, $164^\circ 38' \text{W}$ (around Unimak Pass in the coastal domain off the Aleutian Peninsula) at dusk, at which time σ_{PSII} dropped to $287 \times 10^{-20} \text{ m}^2 \text{ photon}^{-1}$.

In vitro Fe enrichment experiment—Although duplicate incubation carboys were prepared for each treatment (Fe-supplemented or control), unfortunately, one carboy per treatment was clearly contaminated with $\sim 0.5 \text{ nmol L}^{-1}$ Fe during the experiment. Therefore, that series of the data will not be used hereafter. In the control carboy on day 0, macronutrients were abundant, and dissolved trace metals except Fe were detected (Table 1). Concentrations of macronutrients and dissolved trace metals except Fe in the Fe-supplemented carboy were almost the same as in the control carboy on day 0. Dissolved Fe (D-Fe) concentration in the Fe-supplemented bottle was 0.80 nmol L^{-1} on day 0 and decreased with time. Concentrations of macronutrients and dissolved zinc (D-Zn) and manganese (D-Mn) also decreased in both the control and Fe-supplemented carboys. In particular, D-Zn concentrations fell beneath the detection limit ($<0.41 \text{ nmol L}^{-1}$) in both carboys after day 4. On the other hand, dissolved nickel (D-Ni) concentrations were little changed in the carboys throughout the experiment. Table 2 shows that the silicate : nitrate + nitrite consumption ratio (1.4) in the control carboy was slightly higher than that (1.1) in the Fe-supplemented carboy. It is known that silicate : nitrate consumption ratios in Fe-limited conditions are higher than in Fe-abundant conditions (e.g., Takeda 1998). Although we could not separate nitrite from nitrite + nitrate in our experiment, the nitrite concentration can be ignored because nitrite was only $\sim 3\%$ of nitrate + nitrite concentrations in the surface water of the AG during the cruise (data not shown). The Mn : nitrate + nitrite consumption ratio in the control was markedly higher than in the Fe-supplemented carboy, in which the F_v/F_m ratio was low (0.27) on day 0 but increased to 0.49 on day 5 (Fig. 6). Furthermore, σ_{PSII} decreased from $496 \times 10^{-20} \text{ m}^2 \text{ photon}^{-1}$ on day 0 to $365 \times 10^{-20} \text{ m}^2 \text{ photon}^{-1}$ on day 5. These results suggest that the low F_v/F_m and high σ_{PSII} observed initially were constrained by the low concentration of Fe in the seawater and that the photosynthetic physiology of the phytoplankton assemblage was improved by Fe enrichment. F_v/F_m also increased to 0.39 in the control carboy on day 5, although σ_{PSII} stayed rather constant ($430\text{--}488 \times 10^{-20} \text{ m}^2 \text{ photon}^{-1}$ after day 2). These results suggest that the control carboy was inadvertently contaminated with a very small amount of Fe (up to 0.28 nmol L^{-1} , the analytical detection limit).

Chlorophyll *a* concentrations increased by 19 and 7 times, respectively, in the Fe-supplemented and control carboys during the 5-d incubation period (Fig. 7A). Furthermore, concentrations of major accessory pigments, which were analyzed by HPLC, also increased in the control and Fe-en-

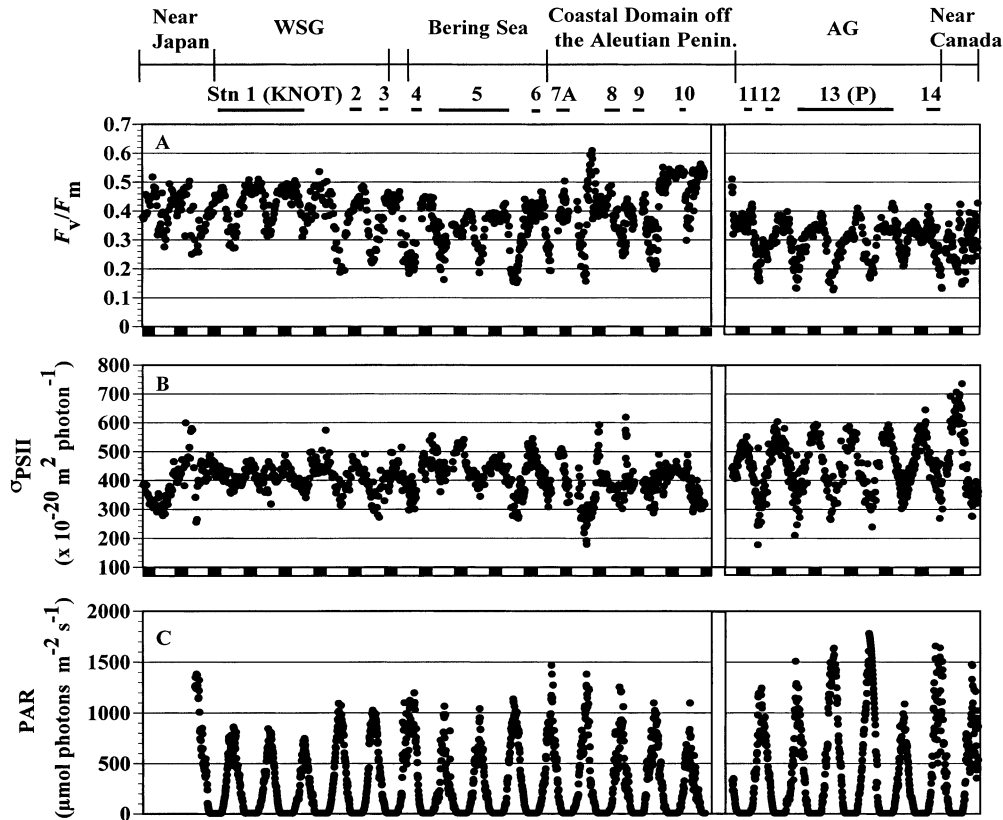


Fig. 4. Changes in (A) photochemical quantum efficiency (F_v/F_m), (B) the functional absorption cross section (σ_{PSII}) of photosystem II, and (C) photosynthetically active radiation (PAR) on deck during the underway monitoring.

riched carboys between days 0 and 5 (Fig. 8). In general, peridinin is a marker for dinoflagellates in the ocean, as is 19'-butanoyloxyfucoxanthin for pelagophytes; fucoxanthin for diatoms, pelagophytes, and prymnesiophytes; 19'-hexanoyloxyfucoxanthin for prymnesiophytes; and Chl *b* for green algae such as prasinophytes and chlorophytes (Jeffrey et al. 1997). However, the increased ratios of accessory pigments except fucoxanthin in the Fe-supplemented and control carboys were almost the same on day 5. Only the fucoxanthin concentration in the Fe-enriched carboy was three times higher than in the control on day 5. These data indicate that diatoms in particular suffered from Fe deficiency in the

phytoplankton assemblage and that this resulted in the differences in the values of the PSII parameters between the Fe-supplemented and control carboys. On day 0, the concentration of fucoxanthin ($0.049 \mu\text{g L}^{-1}$) was lower than 19'-hexanoyloxyfucoxanthin ($0.087 \mu\text{g L}^{-1}$) and rather close to 19'-butanoyloxyfucoxanthin ($0.028 \mu\text{g L}^{-1}$) and peridinin ($0.026 \mu\text{g L}^{-1}$), indicating that prymnesiophytes were initially predominant in the phytoplankton assemblage. Our flow cytometric (FCM) analysis revealed that cell densities of eukaryotic ultraplankton ($< \text{ca. } 5 \mu\text{m}$ in size) increased with time (Fig. 7B), but no difference was seen in cell densities in the Fe-supplemented and control carboys (Mann-

Table 1. Photosystem II and photosynthesis irradiance parameters and phytoplankton growth rate within the surface mixed layer during the cruise. Values indicate means \pm SD.

Parameter	WSG	Bering Sea	Coastal domain off the Aleutian Penins.	AG	Reference
F_v/F_m *	0.45 ± 0.03	0.38 ± 0.04	0.43 ± 0.05	0.33 ± 0.02	This study
σ_{PSII} * ($\times 10^{-20} \text{ m}^2 \text{ photon}^{-1}$)	445 ± 26	482 ± 30	430 ± 59	542 ± 34	This study
$P_{\text{max}}^{\text{B}}$ ($\text{mgC mg Chl } a^{-1} \text{ h}^{-1}$)	2.39 ± 0.72	$2.45 \pm 0.32 \dagger$	$2.95 \pm 0.42 \dagger$	$2.00 \pm 0.27 \dagger$	Yoshikawa (2002)
α^{B} ($\text{mg C } [\text{mg Chl } a]^{-1} \text{ h}^{-1}$)	0.0131 ± 0.0087	$0.0110 \pm 0.0026 \dagger$	$0.0125 \pm 0.0032 \dagger$	$0.0096 \pm 0.0033 \dagger$	Yoshikawa (2002)
Phytoplankton growth rate (d^{-1})	0.33 ± 0.12	$0.41 \pm 0.16 \dagger$	$0.45 \pm 0.10 \dagger$	0.20 ± 0.13	Liu et al. (2002a)

* Only nighttime data were used.

† The data were calculated after their original data had been reclassified into the hydrographic regime of this study (see text).

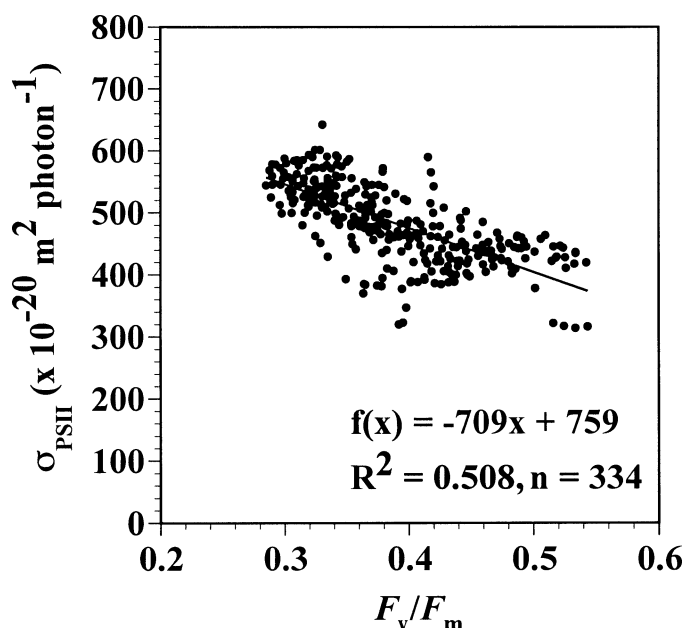


Fig. 5. (A) Relationship between nighttime F_v/F_m and σ_{PSII} ($\times 10^{-20} \text{ m}^2 \text{ photon}^{-1}$).

Whitney U -test; $p > 0.05$). The FCM and HPLC data suggest that the cell size of the fucoxanthin-containing diatoms were bigger than $\sim 5 \mu\text{m}$. Cell densities of the cyanobacterium *Synechococcus* and heterotrophic bacteria in the two carboys were also almost the same and decreased toward the end of the experiment (Fig. 7C,D).

Discussion

Comparison between the WSG and AG—During our cruise, macronutrients (nitrate, phosphate, and silicate) were abundant in the subarctic Pacific. These results are partly supported by satellite-derived surface nitrate at $>5 \mu\text{mol L}^{-1}$ in the oceanic regions of the subarctic Pacific during June

and July 1999 (J. I. Goes pers. comm.). Moreover, high levels of macronutrients in the study area in summer were also reported previously (e.g., Wong et al. 2002). On the other hand, D-Fe or TD-Fe data were limited in the study area. Surface D-Fe ($<0.45\text{-}\mu\text{m}$ fraction) and TD-Fe data in the subarctic Pacific and in the Bering Sea are compiled in Table 3. No comparable D-Fe or TD-Fe data are available in the coastal domain off the Aleutian Peninsula at the present time. In the northeast subarctic Pacific (i.e., AG), except for Sta. 11 ($55^{\circ}00'N$, $149^{\circ}59'W$), our TD-Fe data represented the lowest values in the previous TD-Fe values (Table 3). This suggests that the most serious Fe deficiency occurred in the AG during our observations. TD-Fe levels in the WSG stations were higher than those in the AG stations except Sta. 11 during our cruise (Fig. 3), indicating that there was an east–west gradient in surface Fe concentrations. The TD-Fe levels in the WSG (average 0.08 nmol L^{-1} , $n = 10$) roughly corresponded to the global mean (0.07 nmol L^{-1}) of dissolved Fe concentrations in surface oceanic waters (Johnson et al. 1997).

Although the sources of Fe in the subarctic Pacific have not been identified in detail (Harrison et al. 1999; Fujishima et al. 2001), the contribution of atmospheric Fe is considered to be crucial. The atmospheric Fe generated in the arid areas of East Asia is transported westward by strong westerly winds, especially in spring (Duce and Tindale 1991). According to Tegen and Fung (1994, 1995), annual atmospheric Fe fluxes to the WSG and AG were $0.75\text{--}1$ and $0.25\text{--}0.5 \text{ mmol m}^{-2} \text{ yr}^{-1}$, respectively. A higher D-Fe concentration ($>1 \text{ nmol L}^{-1}$) was also observed in the WSG in July (Kuma et al. 1998). A recent modeling study by Moore et al. (2002) reproduced the east–west gradient in D-Fe concentration in the surface mixed layer of the subarctic Pacific in January and June. Unfortunately, D-Fe or TD-Fe concentrations have not been measured concurrently (within a month) in the northeast and northwest subarctic Pacific except by Fujishima et al. (2001) and in our study. Furthermore, it should be pointed out that no clear seasonal changes in D-Fe or TD-Fe concentrations were observed at Sta. P (Table 3). Fur-

Table 2. Concentrations of macronutrients (nitrate, phosphate, silicate; $\mu\text{mol L}^{-1}$) and micronutrients (= trace metals nmol L^{-1}), and their consumption ratios (mol mol^{-1}) in the incubation carboys.

Treatment	Nutrient	Day 0	Day 2	Day 4	Day 5	Consumption ratio
Control	Nitrate + nitrite	11.2	12.0	10.7	9.79	1
	Phosphate	1.19	1.13	1.01	1.01	0.13
	Silicate	18.0	17.6	16.7	16.0	1.4
	Iron	N.D.	N.D.	N.D.	N.D.	—
	Zinc	0.73	0.69	N.D.	N.D.	—
	Manganese	1.0	1.1	0.91	0.74	0.18×10^{-3}
	Nickel	4.6	4.1	4.4	4.5	0.071×10^{-3}
Iron added	Nitrate + nitrite	11.2	12.1	10.1	7.52	1
	Phosphate	1.19	1.14	0.97	0.82	0.10
	Silicate	18.0	17.6	16.6	14.1	1.1
	Iron	0.80	0.57	0.38	0.30	0.14×10^{-3}
	Zinc	0.85	0.96	N.D.	N.D.	—
	Manganese	1.2	1.3	1.0	0.80	0.11×10^{-3}
	Nickel	4.8	4.9	4.6	4.5	0.082×10^{-3}

N.D., not detected ($<0.28 \text{ nmol L}^{-1}$ for iron and $<0.41 \text{ nmol L}^{-1}$ for zinc).

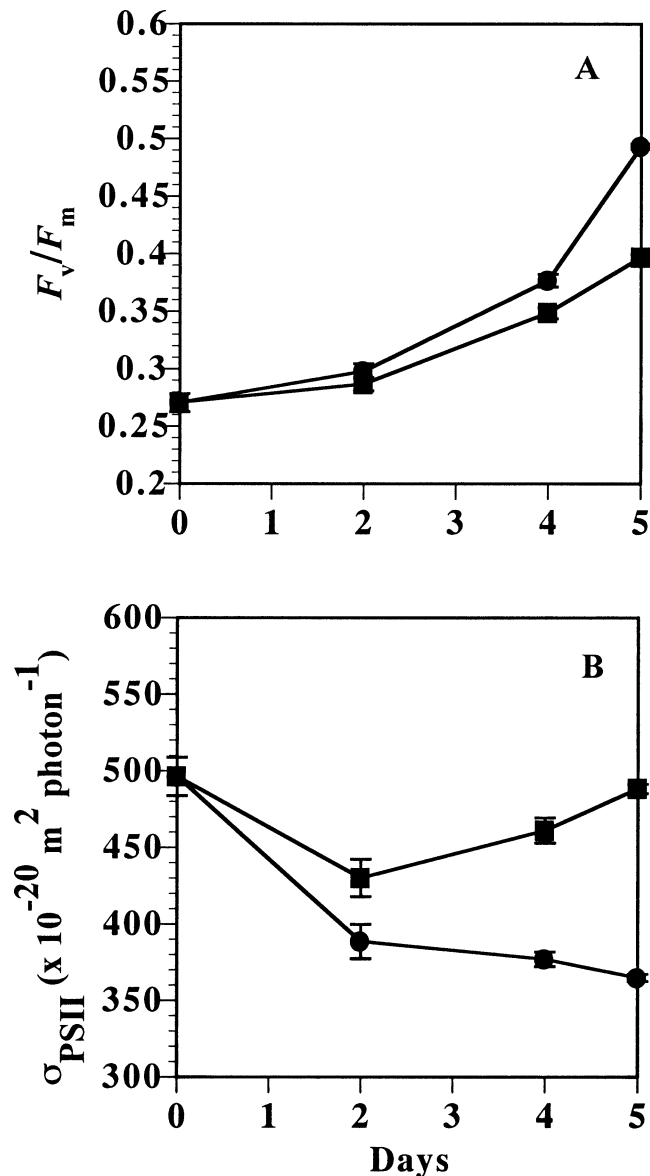


Fig. 6. Changes in (A) F_v/F_m and (B) $\sigma_{\text{PSII}} (\times 10^{-20} \text{ m}^2 \text{ photon}^{-1})$ over time during the iron enrichment experiment at Sta. P. Data presented are means \pm SE. Circles and squares indicate Fe added and controls, respectively.

ther studies are needed to confirm the east–west gradient in Fe concentration in the subarctic Pacific, especially in the WSG, where Fe data are more limited.

TD-Fe concentrations at Sta. 11 were higher (0.25–0.45 nmol L^{-1}) than at the other AG stations (Fig. 3), but the reasons for this are not clear. One possibility is the effect of the Alaska Stream Current, which flows near Sta. 11. This current could entrap iron-rich coastal water from off the Aleutian Peninsula and advect it seaward. However, the water temperature and salinity of Sta. 11 were almost the same as at the other AG stations (data not shown). Another possibility is that a sporadic atmospheric Fe input took place at Sta. 11. The F_v/F_m ratio (Fig. 4) and Chl *a* concentration (Fig. 2D) at this station were comparable to the other AG

stations, suggesting that the phytoplankton assemblage had not responded to Fe enhancement and that the Fe input occurred just before our observation.

Following the distribution of TD-Fe (except at Sta. 11), the photosynthetic potential of phytoplankton in the WSG was higher than in the AG as estimated by underway FRRf monitoring. Nighttime F_v/F_m values were 0.45 ± 0.03 and 0.33 ± 0.22 in the WSG and AG, respectively (Table 1). In nutrient-abundant and dark-adapted conditions, the maximum values of F_v/F_m using the single-turnover flash technique are approximately 0.65 and are independent of phytoplankton species (Falkowski et al. 1994). Therefore, 69 and 51% of PSII reaction centers were photochemically competent in the WSG and AG, respectively. The main reason for the reduction of F_v/F_m is probably the reductions of reaction centers and electron transfer proteins, which have been observed in Fe-starved prokaryotic (e.g., Sandmann and Malkin 1983) and eukaryotic algae (e.g., Greene et al. 1992). The level of σ_{PSII} in the AG was ~ 1.2 times higher than in the WSG at night (Table 1). According to algal culture (e.g., Greene et al. 1992; Davey and Geider 2001) and from in situ Fe fertilization experiments (Kolber et al. 1994; Boyd and Abraham 2001), Fe or nitrate limitations led to lower F_v/F_m and higher σ_{PSII} . In this sense, our underway FRRf and TD-Fe data clearly indicated that a serious Fe limitation occurred in the AG. Indeed, at Sta. P, F_v/F_m increased from 0.27 to 0.49 and σ_{PSII} decreased from 496×10^{-20} to $365 \times 10^{-20} \text{ m}^2 \text{ photon}^{-1}$ after an Fe addition of 0.8 nmol L^{-1} (Fig. 6). Although the level of σ_{PSII} can change with phytoplankton groups or species, a clear negative linear relationship between F_v/F_m and σ_{PSII} was observed in this study (Fig. 5). This suggests that a taxonomic effect on σ_{PSII} might only be a minor factor in the study area. The negative linear relationship between F_v/F_m and σ_{PSII} seems to be a paradox; that is, although lower σ_{PSII} can be expected in nutrient-limited cells, the opposite phenomenon appeared. The paradox could be related to the loss of functional PSII reaction centers (Falkowski et al. 1994). According to a traditional lake model for the transfer of excitation energy between PSII reaction centers (see Lavergne and Trissl 1995), when a reaction center cannot receive excitation energy from antenna pigments (i.e., it becomes nonfunctional) in a nutrient-limited condition, the energy can be transferred to other functional PSII reaction centers using the “extra” ensemble of antenna pigments. Therefore, σ_{PSII} might become higher under nutrient-depleted conditions. Although part of the excitation energy can dissipate thermally in the nonfunctional PSII reaction centers, σ_{PSII} would not be changed by the thermal dissipation of reaction centers (Falkowski et al. 1994).

The east–west gradient in the photosynthetic physiology of phytoplankton in the subarctic Pacific is supported by other parameters (see Table 1) measured in the same cruise: the specific growth rate of phytoplankton estimated by dilution technique (Liu et al. 2002a) and the photosynthesis–irradiance (PE) parameters for surface phytoplankton (Yoshikawa 2002). The specific growth rates of phytoplankton in the WSG were, on average, 1.7-fold higher than those in the AG (Liu et al. 2002a). This result probably arose from the difference in the photosynthetic competence of phyto-

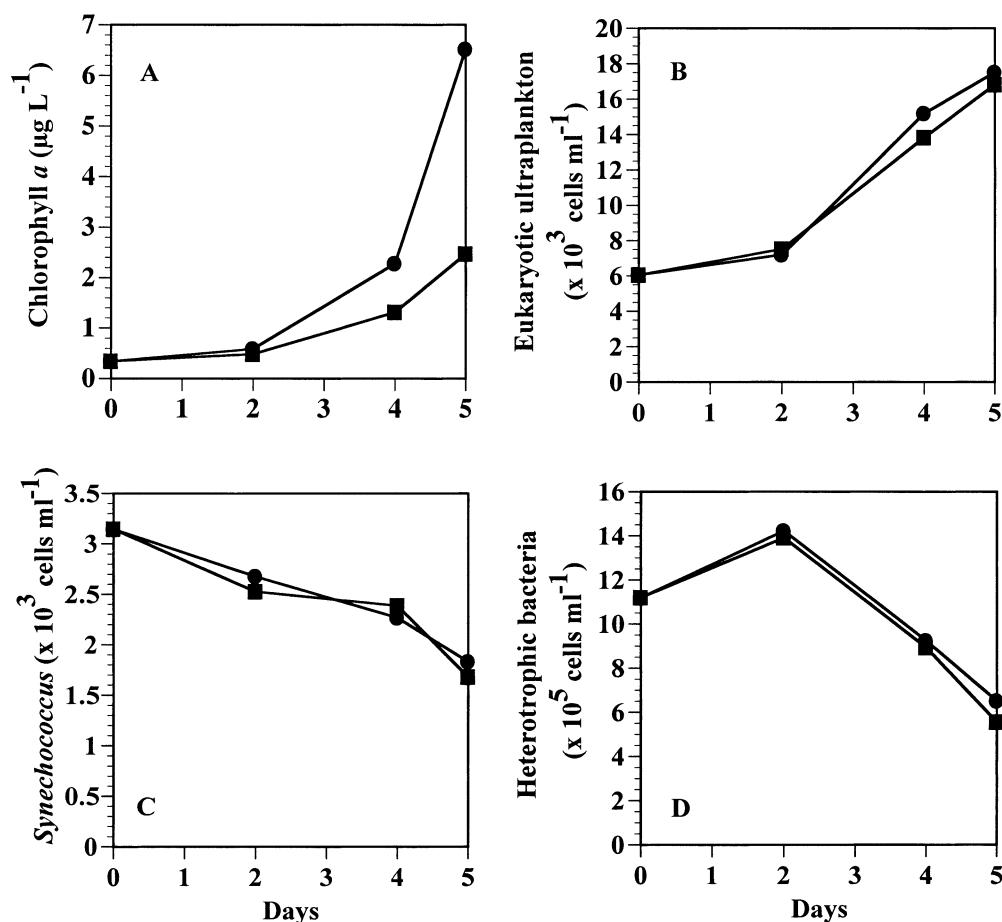


Fig. 7. Changes in (A) Chl *a* concentrations ($\mu\text{g L}^{-1}$), and cell densities of (B) eukaryotic ultraplankton ($\times 10^3 \text{ cells ml}^{-1}$), (C) cyanobacterium *Synechococcus* ($\times 10^3 \text{ cells ml}^{-1}$), and heterotrophic bacteria ($\times 10^5 \text{ cells ml}^{-1}$) with time during the iron enrichment experiment at Sta. P. Circles and squares indicate Fe added and controls, respectively.

plankton and a sufficient irradiance level during the cruise (Fig. 4C). According to T. Yoshikawa (pers. comm.), in the WSG and AG, photoinhibition for carbon fixation seldom occurred under light intensities of 0–2,500 $\mu\text{mol photons m}^{-2} \text{ s}^{-1}$. Both the maximum rate of photosynthesis normalized to Chl *a* concentration (P_B^{max}) and the initial slope of the PE curve (α^B) in the WSG were higher than those in the AG (Yoshikawa 2002). The decrease in both P_B^{max} and α^B has been observed in an Fe-starved diatom, *Chaetoceros muelleri* (Davey and Geider 2001). However, because diel variations of P_B^{max} and α^B with midday maxima and night minima have been noted in some observations (e.g., Prézelin et al. 1987), errors could be contained in the PE parameters of Yoshikawa (2002) when the data and nighttime PSII parameters were compared in Table 1.

Recently, Bowie et al. (2002) also showed a spatial association between TD-Fe concentrations and algal photosynthetic activity in the Atlantic. These data, as well as ours, indicate that most of the TD-Fe fraction (the sum of labile particulate and dissolved Fe) is biologically available, although it is thought that only dissolved ($<0.4\text{-}\mu\text{m}$ fraction) Fe species are taken up by phytoplankton (e.g., Morel et al. 1991). Bowie et al. (2002) proposed that labile particulate

Fe might be consumed by phytoplankton. It is surprising to note that the phytoplankton assemblage in the AG (except at Sta. 11) grew up even under very low TD-Fe concentrations ($<0.01 \text{ nmol L}^{-1}$). This is probably related to oceanic phytoplankton species having low Fe requirements or quotas (Sunda and Huntsman 1995). In addition, the phytoplankton assemblage could adapt to a low TD-Fe environment by reducing its dependence on Fe-requiring proteins in essential pathways, by efficient exchanges of Fe within intracellular pools, or both. A notable example is the replacement of the Fe-S protein ferredoxin by the non-Fe-containing protein flavodoxin within the photosynthetic electron transport chain, which has been detected in the AG (La Roche et al. 1996). Another possibility is that the phytoplankton assemblage might utilize Fe bound to siderophores, which could be produced by cyanobacteria, heterotrophic bacteria, zooplankton grazing, and cell lysis (Hutchins et al. 1999). Because some of the dissolved Fe bound to organic ligands cannot be detected by our method (Obata et al. 1997), the Fe bound to siderophores might be significant for the growth of the phytoplankton assemblage in the AG. In fact, high uptake rates of Fe bound to siderophores by bacteria and

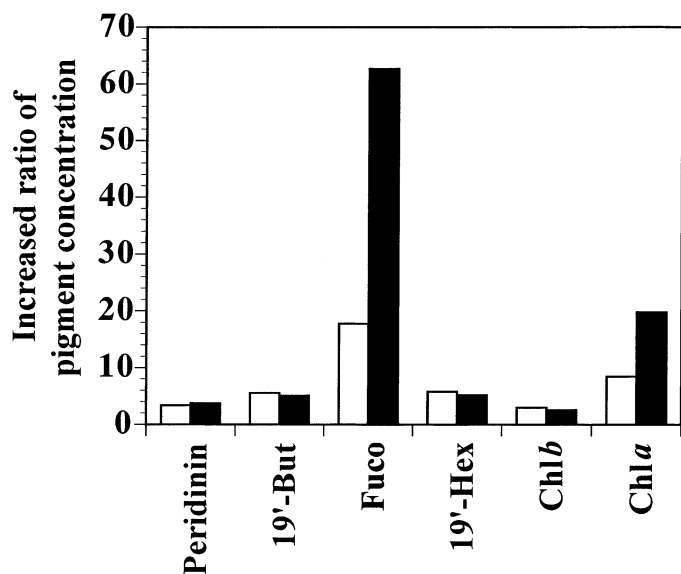


Fig. 8. Ratios of major accessory pigment concentrations increased between days 0 and 5 during the iron enrichment experiment at Sta. P. Open and hatched bars indicate the control and Fe-supplemented carboys, respectively. Abbreviations: 19'-But, 19'-butanoyloxyfucoxanthin; Fuco, Fucoxanthin; 19'-Hex, 19'-hexanoyloxyfucoxanthin; Chl *b*, chlorophyll *b*; Chl *a*, chlorophyll *a*.

phytoplankton have been observed in the AG (Maldonado and Price 1999).

Although the east–west gradients in the photosynthetic competence and specific growth rate (Liu et al. 2002a) of phytoplankton were observed together with TD-Fe concentrations, no difference in the Chl *a* concentration (Fig. 2D) was found between the WSG and AG (Mann–Whitney *U*-test; $p > 0.05$) during the cruise. The underway monitoring of nighttime *in vivo* chlorophyll fluorescence detected by a Turner Designs fluorometer also revealed that Chl *a* concentrations at a depth of 5 m in the WSG and AG were almost the same during the cruise ($0.36 \pm 0.16 \mu\text{g L}^{-1}$ in the WSG and $0.47 \pm 0.23 \mu\text{g L}^{-1}$ in the AG; mean \pm SD) (Suzuki et al. in press). Similar levels of phytoplankton stocks probably resulted from the top-down control by microzooplankton. According to Liu et al. (2002a), specific microzooplankton grazing rates in the WSG and AG were 0.34 ± 0.19 and $0.20 \pm 0.10 \text{ d}^{-1}$ during the cruise, respectively, indicating that microzooplankton grazing activity in the WSG was higher than in the AG. Furthermore, the microzooplankton grazing rates were approximately balanced with the phytoplankton growth rates (Table 1) in the two gyres (Liu et al. 2002a). Therefore, it is considered that both Fe concentration and microzooplankton grazing played a crucial role in controlling the phytoplankton stocks in the subarctic Pacific Ocean under HNLC conditions during the early summer of 1999.

In vitro Fe enrichment experiment at Sta. P.—The fluctuation patterns in F_v/F_m over time were different from a previous *in vitro* Fe enrichment experiment by Boyd et al. (1998), who measured F_v/F_m using 3-(3,4-dichlorophenyl)-1,1-dimethylurea (DCMU) at the same site in May 1995.

They showed that transient increases in F_v/F_m between days 1 and 2 were observed only in carboys supplemented with 3.5 nmol L^{-1} chelated Fe and not in contaminated controls with 1.8 nmol L^{-1} Fe, although the Chl *a* concentrations increased ~ 20 -fold in both carboys during the 6-d experiment. The reason for the difference in F_v/F_m trends between the present study and that of Boyd et al. (1998) is unknown. In both investigations, diatoms (fucoxanthin) became predominant at the end of the experiment. Boyd et al. (1998) speculated that the difference in F_v/F_m in the treatment and control carboys might be due to the form in which the Fe was added (chelated Fe in treatments vs. probably nonchelated Fe in controls). In this study, FeCl_3 was added to the carboy, and F_v/F_m increased exponentially with time in the Fe-supplemented and control carboys. According to Geider et al. (1993), trends in F_v/F_m , determined by using the DCMU and the pump and probe technique, which has single-turnover excitation flashes like the FRR technique, were similar to each other, although their absolute values were generally different. These results indicate that the methodological difference between DCMU and FRR techniques cannot account for the different trends in F_v/F_m . Further studies are needed to examine the response of F_v/F_m to Fe additions with a different Fe form at Sta. P.

The biological response in our experiment was generally similar to those reported by other researchers (e.g., Coale 1991; Boyd et al. 1996, 1998); that is, Fe enrichment led to an increase in Chl *a* concentration largely because of increased net growth of diatoms and a concomitant decrease in macronutrient concentrations. Although we did not quantify the algal cells in the carboys microscopically because the samples were not in good preservation, a 60-fold increase in the concentration of fucoxanthin, which is a diatom marker (Jeffrey et al. 1997), was found in the Fe-supplemented carboy (Fig. 8), indicating that diatoms became predominant in the phytoplankton community. The silicate : nitrate + nitrite consumption ratio in the control was slightly higher than in the Fe-supplemented carboy (Table 2). Our results were consistent with observations that silicate : nitrate consumption ratios increase under Fe limitation (e.g., Takeda 1998), but the difference in our consumption ratios between the control and Fe-supplemented carboys were smaller than those reported previously. This was most likely because of the contamination of Fe in the control carboy as described above. As for dissimilarities with previous studies, the cell densities of the cyanobacterium *Synechococcus* and heterotrophic bacteria decreased with time in the two carboys (Figs. 8C,D). However, Coale (1991) reported that the cell densities of cyanobacteria as observed by epifluorescent microscopy increased about two- and fourfold in control and Fe-supplemented carboys, respectively, at Sta. P in August 1987. Changes in the cell density of heterotrophic bacteria in Fe enrichment experiments at Sta. P have not been reported except in our study. Unfortunately, the causes for the decrease we observed in *Synechococcus* and heterotrophic bacteria are unclear. The decrease in heterotrophic bacteria might be related to a low dissolved organic carbon concentration (Kirchman et al. 1990), high microzooplankton feeding (Rivkin et al. 1999), or both, which were previously observed at Sta. P. Although heterotrophic bacteria contain

Table 3. Concentrations (nmol L⁻¹) of dissolved iron (D-Fe) and total dissolvable iron (TD-Fe) in surface mixed layer or <40 m depth in the subarctic Pacific and the Bering Sea.

Location	Latitude	Longitude	Month	Year	D-Fe	TD-Fe	Reference
NE subarctic Pacific							
	55°50'N	147°50'W	Aug	1987	0.07–0.10	—	Martin et al. 1989
	45°00'N	142°87'W	Aug	1987	0.08	—	Martin et al. 1989
	49°17'N	138°40'W	May, Sep	1995	0.1–0.4	—	La Roche et al. 1996
	55°00'N	149°59'W	Jul	1999	—	0.28–0.45	This study
	55°01'N	144°59'W	Jul	1999	—	<0.01–0.01	This study
	49°00'N	135°00'W	Jul	1999	—	<0.01	This study
Sta. P in the NE subarctic Pacific							
	50°00'N	145°00'W	Aug	1987	0.05	—	Martin et al. 1989
	50°00'N	145°00'W	May, Sep	1995	0.1–0.6	—	La Roche et al. 1996
	49°53'N	144°54'W	Sep	1997	<0.28	—	Fujishima et al. 2001
	50°00'N	145°00'W	Sep	1997	0.07–0.21	0.15–0.25	Nishioka et al. 2001
	50°00'N	145°00'W	Feb	1998	0.06–0.12	0.01–0.12	Nishioka et al. 2001
	50°00'N	145°00'W	Jun	1998	0.07–0.08	0.1–0.12	Nishioka et al. 2001
	50°00'N	145°00'W	Sep	1998	0.09	0.09	Nishioka et al. 2001
	50°00'N	145°00'W	Feb	1999	0.21–0.23	0.29–0.31	Nishioka et al. 2001
	49°59'N	145°08'W	Jul	1999	<0.28	<0.01	This study
NW subarctic Pacific							
	45°00'N	165°00'E	Oct	1993	—	0.22	Takeda 1998
	47°30'N	175°30'E	Jul	1994	0.28–1.04	—	Kuma et al. 1998
	43°00'N	175°30'E	Jul	1994	0.34–0.4	—	Kuma et al. 1998
	44°05'N	161°44'E	Sep	1997	<0.28	—	Fujishima et al. 2001
	44°08'N	155°12'E	Jun	1999	—	0.05–0.22	This study
	50°00'N	165°18'E	Jul	1999	—	<0.01–0.05	This study
	52°07'N	170°41'E	Jul	1999	—	0.11–0.21	This study
Bering Sea							
	53°30'N	175°59'E	Jul	1997	<0.28–0.48	—	Fujishima et al. 2001
	57°24'N	179°54'E	Jul	1997	0.3–0.78	—	Fujishima et al. 2001
	55°07'N	175°00'E	Jul	1999	—	0.14–0.38	This study
	55°03'N	180°	Jul	1999	—	0.07–0.24	This study
	55°01'N	172°00'W	Jul	1999	—	0.03–0.07	This study

higher Fe:C ratios (1.5–2 times) than phytoplankton and might compete with phytoplankton for the limited Fe resources (Maldonado and Price 1999), there was no difference in the cell densities of heterotrophic bacteria between the Fe-supplemented and control carboys in this study.

Concerning the possible limitations of phytoplankton growth by the other trace metals, initial concentrations of D-Zn and D-Mn were <1.5 nmol L⁻¹ and decreased with time in the carboys (Table 2). The latter result suggests that D-Zn and D-Mn were also bioavailable, although some portions of these elements might be adsorbed on the walls of the carboys during incubation (Coale 1991). Zn occurs in carbonic-anhydrase and can limit the growth of phytoplankton that require the enzyme for acquisition of inorganic carbon (Morel et al. 1994). Mn is an essential component of the water oxidation complex in PSII; four Mn per PSII are involved in O₂ evolution (Raven et al. 1999). It should be noted that the initial D-Zn and D-Mn concentrations were clearly higher than the TD-Fe (Fig. 3A), suggesting that Zn

and Mn were not the primary limiting micronutrients. This speculation was supported by the trace metal (Fe, Mn, Cu, and Zn)-enrichment experiments of Coale (1991), who clearly showed that Fe was the most influential micronutrient for phytoplankton growth among the trace metals at Sta. P during summer. However, he also noted that the addition of small amounts of Mn or Zn had a positive effect on the phytoplankton growth at Sta. P. The Mn:nitrate + nitrite consumption ratio in the control was remarkably higher than in the Fe-supplemented carboy, but the reasons remain unclear. D-Ni concentrations changed little in either the control or Fe-supplemented carboys (Table 2), although Ni is known to be involved in urease and is used for the hydrolysis of urea (Peers et al. 2000). Urea might be a minor nitrogen source in our experiment.

Bering Sea and coastal domain off the Aleutian Peninsula—In the Bering Sea, nitrate + nitrite, phosphate, and TD-Fe levels were similar to those in the WSG (Fig. 3), but

surface silicate was almost depleted at Sta. 5 where the Chl *a* concentration was elevated (Fig. 2). According to Suzuki et al. (in press), diatoms were predominant in the phytoplankton assemblage at Sta. 5, as estimated by HPLC pigment analysis. These results suggest that diatom blooms occurred at Sta. 5. Liu et al. (2002a) showed that the specific growth rates of total phytoplankton at Sta. 5 were higher ($>0.5 \text{ d}^{-1}$) than at the other stations in the Bering Sea, as estimated by the dilution technique, but the nighttime F_v/F_m values (~ 0.4) at this station were slightly lower (Fig. 4). The causes of the different trends between the growth rates and F_v/F_m are unclear. Levels of irradiance, TD-Fe, and macronutrients except silicate were almost the same throughout the Bering Sea stations. Although F_v/F_m is sensitive to nitrogen or Fe starvation (Falkowski et al. 1994), the effect of silicate concentration on F_v/F_m for diatoms has not yet been evaluated. According to Ragueneau et al. (2000), silicon metabolism and photosynthesis are not directly coupled in diatoms. In this sense, F_v/F_m might not be changed by silicate concentration.

The recent modeling study of Moore et al. (2002) suggested that Fe limitation occurred in the surface mixed layer of the oceanic Bering Sea during summer. In fact, the TD-Fe concentrations in the Bering Sea were low ($<0.38 \text{ nmol L}^{-1}$), and 42% of PSII reaction centers were nonfunctional, as estimated by the averaged nighttime F_v/F_m values (Table 2) in the Bering Sea, although nitrate + nitrite was abundant. These data seemed to support the results of Moore et al. (2002). However, silicate limitation also could have taken place in the oceanic Bering Sea during summer, since silicate was almost depleted at Sta. 5.

In the coastal domain off the Aleutian Peninsula, F_v/F_m sometimes increased to >0.5 , suggesting that the photosynthetic potential of the phytoplankton assemblage was higher in this region. The maximum F_v/F_m value (0.61) was observed at the edge of the continental shelf (around Unimak Pass), the site of the so-called "green belt," which is a highly productive habitat. According to Springer et al. (1996), annual primary production in the vicinity of the green belt can be as high as $175\text{--}275 \text{ g C m}^{-2} \text{ yr}^{-1}$ and 270% greater than in the region of the Bering Sea examined in this study. Relatively higher phytoplankton growth rates (Liu et al. 2002a) and PE parameters (Yoshikawa 2002) were also observed in the coastal domain (see Table 1). These higher rates were probably caused by sufficient amounts of macronutrients and Fe. A typical example was Sta. 10, where both the F_v/F_m and TD-Fe concentration were relatively high, and measurable macronutrients remained in the water.

Recently, Behrenfeld and Kolber (1999) showed a nocturnal decrease in F_v/F_m caused by Fe-limited cyanobacteria in the South Pacific Ocean. During our cruise, no nocturnal decrease in F_v/F_m was found. According to Liu et al. (2002b), *Prochlorococcus* were not detected, but *Synechococcus* abundances were relatively high ($\sim 5 \times 10^4 \text{ cells ml}^{-1}$) in the surface mixed layer of Stas. 9 and 11. In addition, Suzuki et al. (in press) showed that the range of contributions of cyanobacteria to chlorophyll biomass was 10–45% in the surface mixed layer of Stas. 9 and 11. However, TD-Fe remained at relatively high concentrations at those stations (Fig. 3). Therefore, the effect of iron-limited cyano-

nobacteria on the diel change in F_v/F_m was probably minor in our study area.

Conclusion—It is widely accepted that the northeast subarctic Pacific is one of the HNLC regions, whereas the northwest subarctic Pacific is sometimes more productive in its lower trophic levels, especially in the bloom season from late spring to early summer. Here, we showed that Fe could play a role in the difference. Although the east–west gradient in atmospheric Fe flux into the subarctic Pacific was introduced by Duce and Tindale (1991), our study reported for the first time that there were east–west gradients in the photosynthetic potential of phytoplankton and TD-Fe concentration in the macronutrient-rich subarctic Pacific. We conclude that it is Fe that may well control the photosynthetic physiology of phytoplankton, and Fe supply has a crucial effect on biota and carbon cycling in the whole subarctic Pacific. Indeed, in our subnanomolar Fe-enrichment experiment at Sta. P, the photosynthetic competence of phytoplankton was much improved, and a dramatic floristic shift from phytoflagellates such as prymnesiophytes to diatoms was observed using pigment signatures. Such a floristic shift to diatoms probably leads directly to an increase in the flux of sinking particulate organic carbon and, thus, carbon export to the deep ocean.

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