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Effects of iron, silicate, and light on dimethylsulfoniopropionate production in the Australian Subantarctic Zone

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Abstract. Shipboard bottle incubation experiments were performed to investigate the effects of iron, light, and silicate on algal production of particulate dimethylsulfoniopropionate ($DMSP_p$) in the Subantarctic Zone (SAZ) south of Tasmania during March 1998. Iron enrichment resulted in threefold to ninefold increases in $DMSP_p$ concentrations relative to control treatments, following 7 and 8-day incubation experiments. Additions of Fe and Si preferentially stimulated the growth of lightly-silicified pennate diatoms and siliceous haptophytes, respectively, to which we attribute the increased $DMSP_p$ production in the incubation bottles. Both of these algal groups were previously believed to be low $DMSP_p$ producers; however, our experimental data suggest that addition of iron and silicate to the low-silicate low-iron waters of the SAZ will result in increased production of $DMSP_p$ by lightly silicified diatoms and siliceous haptophytes, respectively. Increased irradiance enhanced $DMSP_p$ production in iron-amended treatments with both low (0.5 nM) and high (5 nM) concentrations of added iron. However, the role of light in stimulating $DMSP_p$ production was apparently of secondary importance compared to the effects of iron addition. The combination of high irradiance and high iron enrichment produced the highest $DMSP_p$ production in the experiments, suggesting that iron and light may have a synergistic effect in limiting algal $DMSP_p$ production in subantarctic waters.

1. Introduction

Understanding the role of phytoplankton in biogeochemical cycling requires a synthesis of knowledge from many different scientific disciplines. It is now clear that phytoplankton interact intimately with the coupled ocean-atmosphere system [*DiTullio and Laws,* 1991; *Karl,* 1999] and hence may significantly influence global climate via the carbon cycle. Another important link between the atmosphere and marine biological production involves the sulfur cycle, via the biogenic gas dimethylsulfide (DMS) [*Charlson et al.*, 1987; *Andreae and Crutzen,* 1997; *Malin and Kirst,* 1999]. Certain species of marine phytoplankton are thought to impact significantly global sulfur emissions [*Andreae,* 1986] by producing very high cellular quantities of the DMS precursor dimethylsulfoniopropionate (DMSP) [*Challenger and Simpson,* 1948; *Keller et al.*, 1989]. DMS represents the major biogenic source of cloud condensation nuclei (CCN) in the marine atmosphere [*Ayers et al.*, 1997], and the production of CCN may be very important in affecting the overall radiation budget of the Earth because of associated effects on albedo [*Charlson et al.*, 1987; *Falkowski et al.*, 1992].

The global flux of biogenic DMS to the atmosphere is a function of both biological and physical processes and is estimated at 20-40 Tg S yr^{-1} [*Andreae and Crutzen,* 1997]. Although the oceanic DMS cycle is complex [*Malin et al.*, 1992], the oceanic flux of DMS to the atmosphere ultimately depends on the algal DMSP production rate, the DMS and DMSP consumption rate [*Kiene and Bates,* 1990; *Kiene,* 1996a], the DMSP degradation pathway [*Kiene,* 1996b; *Kiene et al.,* 1999], and various physicochemical factors such as diffusivity. Phytoplankton species composition and physiological state are two important factors that determine DMSP production rates [*Keller and Korjeff-Bellows,* 1996]. Conversion of $DMSP_p$ to DMS is primarily moderated by grazing processes [*Dacey and Wakeham,* 1986] and algal DMSP lyase activity [*Nishiguchi and Goff,* 1995; *Stefals et al.*, 1995]. Modeling global marine DMS production has proved rather difficult [*Kettle et al.*, 1999] because of the general lack of correlation between observed concentrations of chlorophyll (chl) and DMS in oceanic waters [*Andreae and Barnard,* 1984; *Andreae,* 1986; *Matrai et al.*, 1993], as well as the species variability in the cellular $DMSP_p$:chl *a* ratio [*Keller and Korjeff-Bellows.*, 1996]. In addition, experimental [*Kiene and Bates,* 1990; *Kiene et al.,* 1999] and modeling studies have implicated the importance of other trophic interactions such as bacterial metabolism on DMS concentrations [*Gabric et al.,* 1993].

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Polar and subpolar oceanic regions are especially important with respect to biological DMS fluxes to the atmosphere because of (1) the large areal extent of these regions, (2) the magnitude and duration of the phytoplankton spring blooms, (3) the prevalence of DMSP-producing prymnesiophytes, and (4) the relatively high wind speeds (facilitating sea-to-air DMS flux). In addition, recent modeling studies suggest that the Southern Ocean is likely to be impacted strongly by future climatic change [*Sarmiento et al.*, 1998]; thus it is particularly important that we understand the major controls on biogenic DMS production in this oceanic region in relation to environmental change. Measurements of methanesulfonic acid (MSA, the oxidation product of DMS) in Antarctic ice cores suggest a strong correlation between atmospheric DMS levels and glacial-interglacial climate variations, from which it has been inferred that biogenic DMS production was elevated during the during the Last Glacial Maximum (LGM) relative to interglacial levels [*LeGrand et al.*, 1991]. The glacial iron hypothesis postulates that lowered atmospheric pCO_2 during the LGM was primarily a result of increased primary and export production, fueled by elevated aeolian iron deposition over the Southern Ocean [*Martin*, 1990; *Watson et al.*, 2000]. This hypothesis also provides a plausible explanation for enhanced DMS production during the LGM in that increased primary production in the Southern Ocean would be expected to result in greater production of DMS by phytoplankton, especially if a shift in algal species composition occurred.

The results of in situ iron addition experiments provide clear support for this scenario. Iron addition was observed to stimulate increased algal $DMSP_p$ production and more than threefold increases in community DMS production during both the IronEx II experiment in the equatorial Pacific [*Turner et al.*, 1996] and the SOIREE (Southern Ocean Iron Release Experiment) experiment in the polar waters of the Southern Ocean [*Boyd et al.*, 2000]. Evidence from marine sediments implicates the present-day subantarctic region as the principal location of enhanced Southern Ocean export production during the LGM [*Kumar et al.*, 1995], moderated by increased dust deposition and a northward expansion of the seasonal ice zone at that time [*Moore et al.*, 2000]. However, it is difficult to extrapolate the results of iron fertilization studies in the equatorial Pacific and the polar Southern Ocean to the subantarctic waters, which are characterized by year-round low silicate concentrations (<5 μM), deep winter mixing, and a distinctly different phytoplankton community compared with the region south of the Polar Front [*Rintoul and Trull*, this issue; *Kopczynska et al.*, this issue]. *Curran et al.* [1998] have reported relatively high concentrations of $DMSP_p$ (>100 nM) and low concentrations of dissolved DMS (<10 nM) in waters of the Australian Subantarctic Zone (SAZ) during late spring and summer, although the factors that control biogenic production of $DMSP_p$ and DMS in this oceanic region are still poorly understood [*Jones et al.*, 1998].

As part of the SAZ Project, shipboard bioassay experiments were conducted in the Australian subantarctic region during March 1998 to investigate the effects of iron, light, and silicate availability on phytoplankton production and associated biogeochemical processes [*Sedwick et al.*, 1999; *Boyd et al.*, this issue; *Hutchins et al.*, this issue]. These experiments afforded us an excellent opportunity to evaluate the effects of iron, light, and silicate on algal community composition and $DMSP_p$ production in subantarctic waters during the late summer and early fall. Our results suggest that each of these parameters, particularly iron availability, exert important controls on algal DMSP and DMS production in this region, and our observations are consistent with the idea that increased atmospheric iron inputs would have significantly stimulated DMS production in low-silicate subantarctic waters during the LGM.

2. Materials and Methods

Shipboard bottle incubation experiments were performed aboard RSV *Aurora Australis* on March 9-17, 1998, using seawater collected from the SAZ at 46°46'S, 142°E. These experiments included an iron and light interaction experiment (FePAR experiment) and an iron/silicate addition experiment (FeSi experiment). The site hydrography and general biological and chemical results from these experiments are described by *Sedwick et al.* [1999], *Boyd et al.* [this issue], and *Hutchins et al.* [this issue]. Trace metal clean seawater and resident plankton for the experiments were collected from the upper mixed layer at ~20 m depth using a dedicated clean pumping system [*Hutchins et al.*, 1998; *Sedwick et al.*, 1999]. Seawater was dispensed from the pump outlet into acid-cleaned 50 L polyethylene carboys then into 2.4 L polycarbonate bottles (for the FeSi experiment) and 24 L polycarbonate carboys (for the FePAR experiment) inside a container laboratory under Class-100 filtered air. Time zero measurements were taken for physical, chemical, and biological parameters in the starting seawater, then bottles and carboys were amended with iron and silicate (as described below) and set in deckboard incubators maintained at ambient sea surface temperature using flowing seawater.

The FePAR experiment aimed to investigate the relative importance of iron and light (but not silicate) in regulating phytoplankton processes. Because ambient Si levels (0.7 μM) were low and potentially limiting to diatom growth, purified (i.e., iron-free) sodium metasilicate solution was added to all FePAR experimental carboys to boost the Si concentration in the starting seawater to the estimated SAZ wintertime value of ~3.5 μM [*Boyd et al.*, 1999, this issue]. The FePAR experiment involved the following five treatments in the 24 L carboys: (1) control (no iron added, incubated at low light), (2) low-iron low-light (LILL) treatment, (3) high-iron low-light (HILL) treatment, (4) low-iron high-light (LIHL) treatment, and (5) high-iron high-light (HIHL) treatment. The low- and high-light treatments were incubated at 25% and 50% of daily incident surface irradiance, respectively. These irradiance levels were estimated using a vertical mixing model [*Boyd et al.*, this issue], with estimated mean in situ irradiance referred to as low light and a higher than mean irradiance referred to as high light. Light levels were simulated by covering the carboys with neutral density screening. Low- and high-iron enrichments (added as a solution of $FeCl_2$:EDTA (ethylenediaminetetraacetic acid) in a 1:1.5 ratio) corresponded to added Fe concentrations of 0.5 and 5 nM, respectively. During the course of the experiment the carboys were repeatedly subsampled (days 2, 4, and 7) under Class-100 conditions for biological and chemical analyses, including the $DMSP_p$, algal pigment, and cell count measurements presented here. No samples were taken for analysis of DMS from the carboys because of probable DMS losses during the subsampling procedure. The complete suite of other biologi-

cal and chemical measurements from the FePAR experiment is presented by *Boyd et al.* [this issue].

The FeSi experiment aimed to examine the role of iron and silicate in regulating algal production. In this experiment the 2.4 L incubation bottles were amended with Fe and/or Si (added as purified sodium metasilicate solution) as follows: (1) control (no additions), (2) +Fe (added concentration of 1.9 nM Fe), (3) +Si (added concentration of ~9 μM Si), and (4) +Fe+Si (added concentrations of 1.9 nM Fe and ~9 μM Si). For each treatment, duplicate 2.4 L bottles were sampled at each of three different time points during the experiment (days 2, 5, and 8). Destructive sampling was used so as to avoid spurious contamination of the samples. The FeSi experiment bottles were incubated at a mean irradiance of ~50% surface irradiance so as to approximate in situ irradiance. Concentrations of dissolved Fe in the starting seawater and in the water column were ~0.1 nM [*Sedwick et al.*, 1999]. The complete biogeochemical response of the algal community in this experiment is reported by *Sedwick et al.* [1999] and *Hutchins et al.* [this issue].

In both experiments, algal pigments in the incubation samples were analyzed using high-performance liquid chromatography (HPLC). Aliquots (0.5-2.0 L) from each incubation bottle were filtered through Whatman GF/F filters, which were frozen in liquid nitrogen for processing in our shore-based laboratory. Replicate subsampling for HPLC pigment measurements was not possible (except for initial concentrations) owing to sample volume limitations. Filters were homogenized with 1.5 mL 90% acetone and extracted for 4 hours at -20°C. The extracts were then centrifuged at -4°C, filtered, and then injected into an HP-1050 liquid chromatograph using an autosampler. The system was equipped with photodiode array and fluorescence detectors. The gradient elution program was a modification of the ammonium acetate method [*Wright et al.*, 1991] as described by *DiTullio et al.* [1993]. Phaeopigments were measured using HPLC pigment separations [*DiTullio and Smith*, 1996]. Phaeophorbides were quantified using both fluorescence detection and absorbance at 405 nm. The individual phaeophorbide peaks were summed and intepreted as an index of grazing activity in the incubation bottles. Pigment standards were prepared from unialgal cultures grown in our laboratory. The coefficient of variation from triplicate standard injections was typically <3%. Peak spectra from each eluted peak were compared to stored library spectra to confirm peak identity and determine relative peak purity. The algal pigment data were interpreted using the computer code CHEMTAX [*Mackey et al.*, 1996], which uses HPLC pigment concentrations to estimate the abundance of major algal classes relative to total chl *a* biomass. In the FeSi experiment an additional set of 2.4 L bottles was incubated for ^{14}C-chl *a* labeling to estimate absolute algal growth rates [*Redalje and Laws*, 1981; *Goericke and Welschmeyer*, 1993]. These bottles were incubated with ^{14}C for 24 hours, following a 5 day incubation without radioisotope to allow for pigment carbon pools to equilibrate, especially as a result of any cellular photoadaptive changes induced by ondeck incubation.

DMS and DMSP measurements were performed using a liquid nitrogen cryogenic purge and trap apparatus as described by *Radford-Knoery and Cutter* [1993]. GF/F filtered seawater samples were sparged for 20 min with helium gas before injection onto a Chromosil 330 column (Supelco). The analysis was performed under isothermal conditions at 70°C with an HP 5890 Series II gas chromatograph equipped with a flame photometric detector using a DMS permeation device for calibration. Details of our method are described by *DiTullio and Smith* [1995]. $DMSP_p$ samples were filtered onto GF/F filters (50-300 mL) in triplicate, and the filters placed in 2 mL gas-tight Mini-nert reaction vials and capped with gas-tight sampling valves. The vials were filled with 5 N NaOH with no headspace and allowed to extract for 24 hours in the dark. Aliquots were then injected into helium-purged deep seawater to measure the DMS evolved from the base hydrolysis of $DMSP_p$.

3. Results

Sea surface temperature at 46°46'S, 142°E was 11.5°C with a mixed layer depth of ~80 m. Ambient concentrations of dissolved nitrate, silicate, phosphate, and iron in the upper mixed layer were >8 μM, 0.7 μM, 0.6 μM, and 0.05-0.11 nM, respectively, and the chl *a* level in the upper mixed layer was ~0.22 μg L^{-1}. CHEMTAX analysis indicated that chlorophytes (containing chl *b*) and haptophytes (containing 19'-hexanoyloxyfucoxanthin ; Hex) were the most abundant algal groups in the seawater collected at the start of the experiment [see *Hutchins et al.*, this issue], whereas flow cytometer measurements indicated that cyanobacteria accounted for ~85% of the initial total cell abundance of ~3 x 10^7 cells L^{-1} [*Boyd et al.*, this issue]. The apparent discrepancy between the algal abundances estimated by flow cytometry and HPLC pigment analyses is likely explained by the low biovolume of cyanobacterial cells relative to the eukaryotic algae.

3.1. Water Column DMS and DMSP

Surface water DMS concentrations were very low (<2 nM; Figure 1a) in our study area during March. In these subantarctic waters the $DMSP_p$ pool was typically greater than either the dissolved DMSP ($DMSP_d$) pool or the DMS pool in the upper mixed layer (Figure 1a), as has also been observed in this region during the early summer [*Curran et al.*, 1998]. Integrated DMS values (to 150 m) at 46°46'S, 142°E were 73 ± 22 μmol m^{-2}, as calculated from the average (± standard deviation) of four separate vertical profiles over the course of 4 days on station. In comparison, integrated DMS values in the Ross Sea during the spring *Phaeocystis antarctica* bloom were ~20,000-35,000 μmol m^{-2} [*DiTullio et al.*, 2000]. Integrated levels of DMS were consistently low in the SAZ waters throughout our study (Figure 1b) and were consistent with the generally low DMS levels previously reported for these waters during late spring to early summer [*Curran et al.*, 1998]. $DMSP_p$ concentrations were also very low and were considerably below values measured in this same region in late spring to early summer [*Curran et al.*, 1998], presumably because of the low algal biomass and the prevalence of algal species such as cyanobacteria and chlorophytes, which are not thought to be significant producers of DMSP [*Keller et al.*, 1989].

3.2. FePAR Experimental Results

The $DMSP_p$ concentrations in the FePAR experimental treatments increased up to 60-fold during the 7 day incubation period relative to initial concentrations, with the greatest response due to addition of both iron and light (Figure 2a).

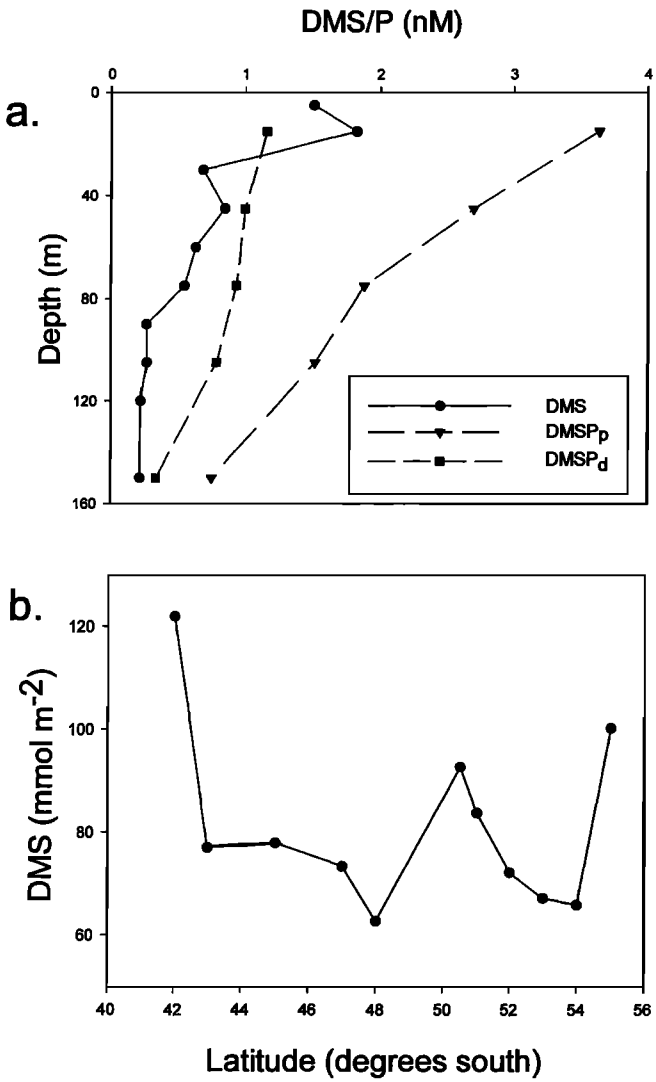

Figure 1. (a) Vertical profiles of dimethylsulfide (DMS) and particulate and dissolved dimethylsulfoniopropionate ($DMSP_p$ and $DMSP_d$, respectively) were collected at at 47°46'S and 142°E on March 9, 1998, prior to the start of our FePAR and FeSi experiments. Samples were collected using a conductivity-temperature-depth (CTD) profiler. (b) Integrated DMS (to 150m) during a transect of the SAZ in March 1998 along 142° E.

There were no significant ($p > 0.05$; unpaired Student's T-test) differences in the $DMSP_p$ concentrations observed between the control and LILL treatments after 7 days (Figure 2a), although $DMSP_p$ in the LILL treatment was slightly higher than in the control treatment during the first 4 days of the experiment, suggesting transient stimulation in community $DMSP_p$ production (Figure 2a). The most significant ($p < 0.01$) increase in $DMSP_p$ concentration was observed in both high-Fe treatments (HILL and HIHL), with concentrations after 7 days elevated by approximately sevenfold and ninefold, respectively, compared to the control value (Figure 2a). The LIHL treatment displayed an intermediate response, with $DMSP_p$ values still significantly (threefold) higher ($p < 0.01$) than the control treatment and ~eighteenfold higher than the initial concentration after 7 days.

Over the course of the experiment, total cell abundances were relatively constant in the control and low-iron treatments, whereas total cell abundances in the HILL and HIHL treatments increased by 125 and 180%, respectively [*Boyd et al.*, this issue]. Similarly, the concentrations of chl *a* increased by ~85% in both high-iron treatments, with no significant increases observed in the other treatments, relative to the control. The relative increases in $DMSP_p$ concentrations in the high-iron treatments were significantly greater than corresponding increases in either cell abundances or chl *a* concentrations, which we attribute to a shift in the algal species composition in these treatments. Over the course of the experiment the $DMSP_p$:cell ratio for total autotrophic cells (cells counted by flow cytometry) increased by approximately twentyfold in the HIHL treatment (0.03-0.62 fmol $DMSP_p$:cell) (Table 1), whereas the $DMSP_p$:cell ratio for red fluorescent cells (cells counted by flow cytometry) increased by approximately tenfold (0.21-2.13 fmol $DMSP_p$:cell; Figure 2b). This difference may be explained by the fact that the total red fluorescent cells (predominantly diatoms and haptophytes) increased by approximately fivefold in the high-iron treatments, whereas total cells increased by only approximately twofold [*Boyd et al.*, this issue], and this latter group includes cyanobacteria, which typically have very low DMSP concentrations per unit biomass [*Keller et al.*, 1989]. Hence, the approximately sixtyfold increase in the $DMSP_p$ concentration observed in the HIHL treatment relative to the initial value (Figure 2) probably reflects a shift from cyanobacteria to DMSP-producing eukaryotic algae, as well as an increase in the $DMSP_p$ production by the red fluorescent eukaryotic cells (Figure 2).

The observed trend in $DMSP_p$:chl *a* ratios was similar to those for cellular $DMSP_p$ ratios in that HIHL treatment values (63.6 nmol $DMSP_p$ per μg chl) were approximately tenfold higher than the initial value (6.1 nmol $DMSP_p$ per μg chl) and approximately fourfold higher than in the control and LILL treatments (Table 1). In conjunction with the increases in the $DMSP_p$:chl *a* ratios in the high-iron treatments relative to the control the abundance of haptophytes increased, as estimated by increases in the Hex concentration (e.g., a 242% increase in the HIHL treatment, relative to the initial value; Figure 3a). However, the most significant change in algal species composition in the high-iron treatments was an increase in diatom population, as estimated by increases in fucoxanthin (Fuco) concentration and corroborated by microscopic observations [*Hutchins et al.*, this issue]. Concentrations of Fuco increased by more than 2000% in the HIHL treatment relative to the ini-

Table 1. Particulate DMSP Concentrations From FePAR I Experiment Normalized to Chl *a* Concentrations and Total Cell Number Estimated Using Flow Cytometric Analyses

	Treatment				
Time	Control	LILL	HILL	LIHL	HIHL
	$DMSP_p$:chl a (nmol μg^{-1})				
Day 0	6.1	6.1	6.1	6.1	6.1
Day 2	17.6	87.4	60.5	35.6	58.2
Day 4	18.9	18.1	17.8	16.0	31.3
Day 7	16.2	15.5	31.5	38.0	63.6
	$DMSP_p$:cell (fmol cell^{-1})				
Day 0	0.03	0.03	0.03	0.03	0.03
Day 2	0.01	0.24	0.20	0.20	0.47
Day 4	0.10	0.15	0.13	0.17	0.25
Day 7	0.17	0.16	0.57	0.39	0.62

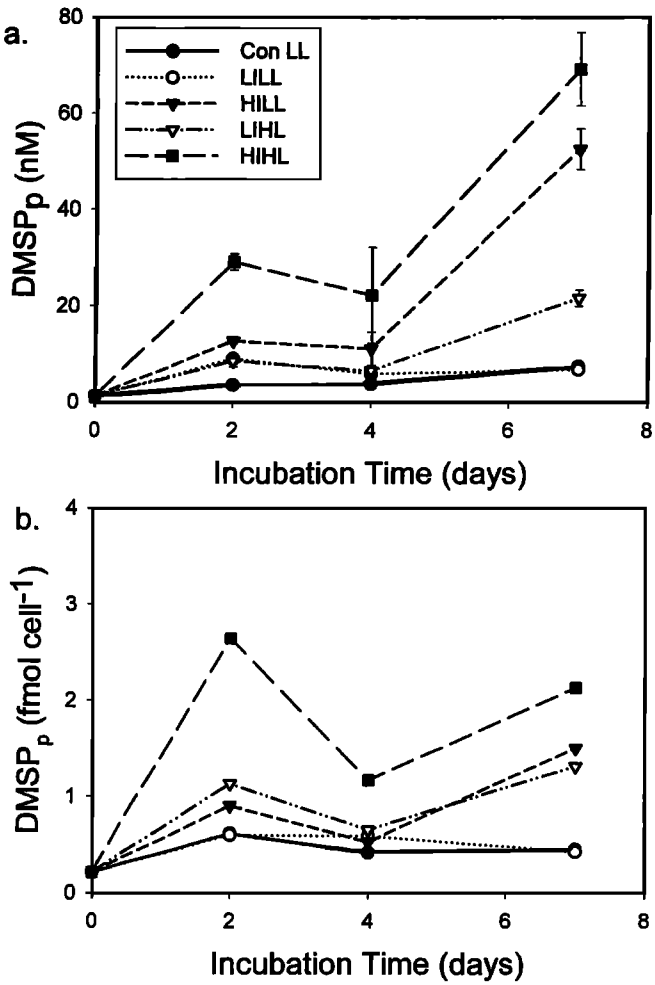

Figure 2. (a) Intracellular concentrations of particulate DMSP ($DMSP_p$) in the Fe and light interaction experiment (FePAR) performed on March 9-17, 1998. Experimental treatments include (a) control, LILL, HILL, LIHL, and HIHL. Mean irradiances and iron concentrations are described in section 2. Error bars represent the standard errors among triplicate samples. (b) $DMSP_p$:cell ratios in the FePAR experiment. Cell counts represent the number of red fluorescent cells measured by flow cytometry.

tial concentration and by more than 370% relative to the control treatment concentration (Figure 3). Other large algal species also responded to the high-iron additions. For instance, autotrophic dinoflagellate abundance, as estimated from the concentration of peridinin, increased by ~900% in the high-iron treatments relative to the initial concentration; however, on the basis of CHEMTAX analysis these species still accounted for only a minor percentage (<1%) of the total chl *a* biomass [*Hutchins et al.*, this issue]. In addition, phaeopigment analyses provide evidence of significant grazing only in the high-iron treatments, in which the estimated concentrations of phaeophytin and total phaeophorbides increased by ~800 and 1200%, respectively, relative to the control treatment (Figure 4a).

3.3. FeSi Experimental Results

The FeSi experiment produced increases of 39, 61, and 159% in $DMSP_p$ concentrations in the +Si, +Fe, and +Fe+Si treatments, respectively, compared to concentrations in the control treatments. After 8 days incubation the $DMSP_p$ concentrations in all amended bottles were significantly higher than levels in the control treatments ($p < 0.01$; unpaired Student's T-test), with the highest $DMSP_p$ concentrations observed in the +Fe and +Fe+Si treatments (Figure 5a). As for the FePAR experiment, normalizing $DMSP_p$ concentrations to total cell numbers (Table 2) or to red fluorescent cell numbers (Figure 5b) yielded different results. Because cyanobacteria were initially numerically dominant at this station [*Hutchins et al.*, this issue], the observed decline in cyanobacterial abundance during the incubations, presumably due to grazing, explains the approximately twentyfold increase in the ratio of $DMSP_p$:total cells during the course of the experiment (Table 2). As already mentioned, cyanobacteria are expected to have low cellular $DMSP_p$ concentrations [*Keller et al.*, 1989]; thus the cellular $DMSP_p$ ratios based on total red fluorescent cells are more likely to portray accurately the actual changes in cellular $DMSP_p$ ratios during the course of the incubations. These data (Figure 5b) suggest that cellular $DMSP_p$ was significantly elevated in only the +Fe treatments, relative to the control ($p < 0.01$), whereas the +Si treatments had the lowest $DMSP_p$:cell ratios relative to the other treatments. However, the cellular $DMSP_p$ quotas in this study should be interpreted cautiously because of the importance of species differences in biovolume and $DMSP_p$ production. It is suggested that future studies perform $DMSP_p$ normalization using direct biovolume measurements.

Interestingly, $DMSP_p$:chl *a* ratios were lower in the +Fe and +Fe+Si treatments by 42% and 39%, respectively, relative to the controls after 8 days incubation (Table 2). Presumably, this observation reflects a significant increase in cellular chlorophyll content in response to iron addition [*Sunda and Huntsman*, 1997], as well as a shift in the algal assemblage from a haptophyte-dominated population (Hex) in the control treatment to a diatom-dominated population (Fuco) in the +Fe and +Fe+Si treatments, as indicated by pigment analyses (Figure 3b), CHEMTAX (Table 3), microscopy, and flow cytometry [*Hutchins et al.*, this issue]. Grazing processes stimulated the production of phaeophorbides in all the iron/silica amended treatments. For example, total phaeophorbide compounds as measured by HPLC [*DiTullio and Smith*, 1996] were 108%, 192%, and 575% higher in the +Si, +Fe, and +Fe+Si treatments, respectively, relative to the control samples (Figure 4). These increases in algal degradation products were positively correlated with absolute algal growth rates estimated from ^{14}C incorporation into chl *a* (Figure 4b). Whereas algal specific growth rates in the initial, control, and +Si treatments were ~0.3-0.4 d^{-1}, the +Fe and +Fe+Si treatments produced significantly higher algal growth rates of 0.9 and 1.4 d^{-1}, respectively (Figure 4b).

Measurements of DMS in the experimental treatments revealed a trend similar to the $DMSP_p$ data in that the largest increases in DMS levels were observed in the iron-amended treatments. After 8 days incubation the +Fe and +Fe+Si treatments contained 94% and 68% higher levels of DMS, respectively, relative to the control treatment, whereas DMS concentrations in the +Si treatment were similar to the control (Figure 6).

4. Discussion

In both of our experiments our results indicate that additions of iron and/or silicate to the subantarctic phytoplankton community resulted in significant increases in algal produc-

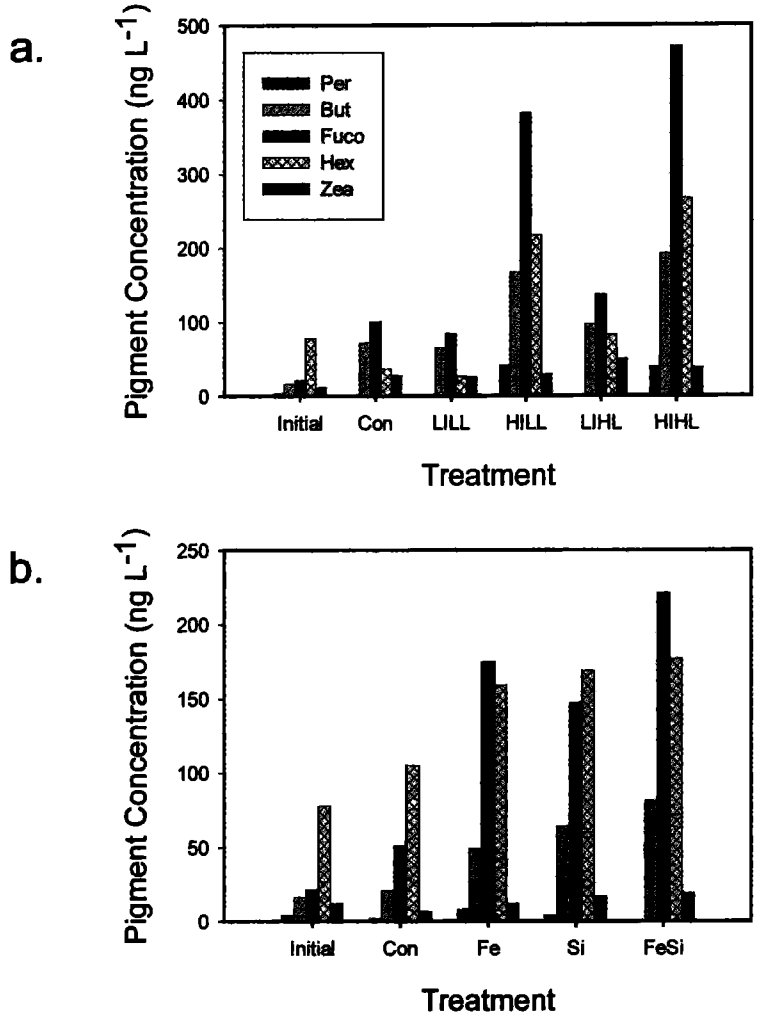

Figure 3. (a) Algal pigment concentrations in the FePAR experiment as measured by HPLC analyses at the end of the experiment. Concentrations of peridinin (Per), 19'-bututanoyloxyfucoxanthin (But), fucoxanthin (Fuco), 19'-hexanoyloxyfucoxanthin (Hex), and zeaxanthin (Zea) are pigment taxonomic indicators of dinoflagellates, pelagophytes, diatoms, prymnesiophytes, and cyanobacteria, respectively. Treatment designations are as described in Figure 2. (b) Pigment concentrations in the iron and silicate addition experiment (FeSi) at day 5 of the experiment. Experimental treatments include a control, an iron addition (+ 1.9 nM Fe), a silicate addition (+ 9 μM Si), and an iron and silicate addition (+FeSi). Because of the large sample volumes required for HPLC, dupolicate measurements were only possible for the initial sample.

tion of $DMSP_p$ (Figure 5) and DMS (Figure 6), as well as increases in community cellular $DMSP_p$ quotas (Tables 1 and 2). These increases were apparently mediated by shifts in community composition during the incubations, relative to the control treatments, to assemblages dominated by diatoms and/or type 4 haptophytes (Figure 3 and Table 3).

In both the FePAR and FeSi experiments, iron additions of ~2 nM or more were observed to promote the growth of diatoms relative to other algal species, as shown by increases in Fuco concentration, CHEMTAX analyses of pigment data (Table 3), and flow cytometry and microscopic cell counting [*Hutchins et al.*, this issue]. These diatoms were primarily small, lightly silicified pennate species, including *Nitzschia, Pseudo-nitzschia, Cylindrotheca,* and *Navicula*, which were apparently able to grow despite very low ambient silicate concentrations (<1 μM) in the starting seawater [*Hutchins et al.*, this issue]. The CHEMTAX analyses of the pigment data from the FeSi experiment suggest that diatoms accounted for 33% of total chl *a* in the +Fe treatments and 29% of total chl *a* in the +Fe+Si treatments, compared to 24% and 22% of total chl *a* in the +Si and control treatments (Table 3). Perhaps more significantly, diatom biomass accounted for a threefold increase in relative abundance in the iron-amended bottles, compared to the initial community composition in which diatoms accounted for 10% of total community chl *a* (Table 3).

The pigment data from the FeSi experiment show that addition of silicate, either with or without iron, stimulated the growth of haptophytes, as evidenced by increases in Hex concentrations. Shipboard flow cytometry measurements are consistent with this interpretation, indicating that the picoeukaryotic cells (0.2-2 μm) increased only in the +Si and +Fe+Si treatments [see *Hutchins et al.*, this issue]. The CHEMTAX pigment data analyses indicate that these algae were type 4 haptophytes, a group that includes *P. antarctica,*

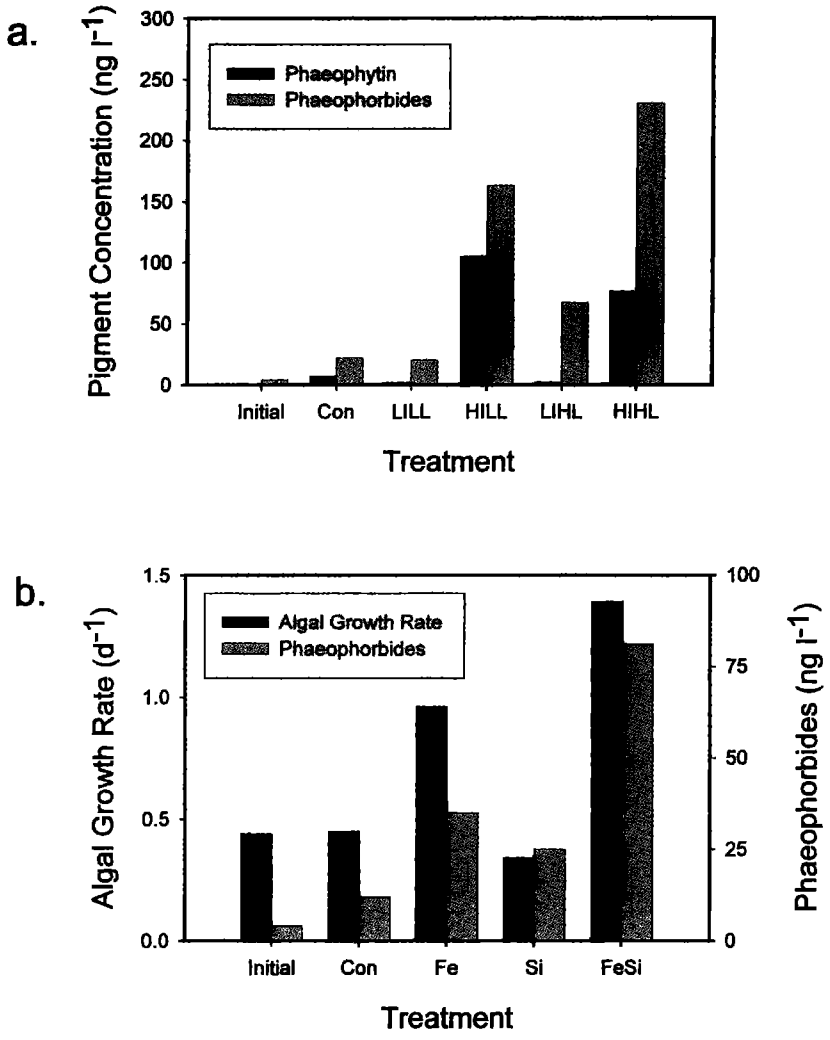

Figure 4. (a) Algal pigment degradation products in the FePAR experiment as measured by HPLC. The concentration of phaeophorbides was determined using the sum of of the concentrations from compounds with phaeophorbide-like spectra [*DiTullio and Smith*, 1996]. (b) Phaeophorbide concentrations in the FeSi experiment were calculated as described for the FePAR experiment. The absolute phytoplankton growth rate was estimated using ^{14}C incorporation into chl *a* [*Redalje and Laws*, 1981] following a 24 hour incubation started at day 5 of the FeSi experiment.

silicoflagellates, and *Parmales* species [*Mackey et al.*, 1996]. CHEMTAX analyses suggest that these type 4 haptophytes accounted for 34% of total chl *a* in the +Si and +Fe+Si treatments compared with 23% and 24% of total chl *a* in the control and +Fe treatments, respectively (Table 3). These observations suggest that the growth of type 4 haptophytes was promoted by silicate addition, implying that these were siliceous type 4 haptophytes, such as silicoflagellates or the little studied group of chrysophytes described as *Parmales* [*Marchant and McEldowney*, 1986; *Booth and Marchant*, 1987], rather than nonsiliceous species such as pelagophytes and *P. antarctica*, which have no known silicate requirements [*Hutchins et al.*, this issue]. It is possible, however, that different haptophyte species responded to additions of silicate alone compared to the treatment when silicate and iron were added together.

The pigment data from both experiments indicate that type 3 haptophytes and dinoflagellates did not significantly contribute to the community biomass in the bottles amended with iron and/or silicate. The CHEMTAX analyses of our pigment data from the FeSi experiment suggest that type 3 haptophytes, which include coccolithophorids such as *Emiliania huxleyi*, accounted for <7% of the total chl *a* biomass in the iron and/or silicate treatments, relative to ~16% of chl *a* in the control treatments.

Concentrations of peridinin, indicative of dinoflagellates, were also typically low in iron and/or silicate amended bottles in both experiments (Figure 3), and CHEMTAX analyses suggest that dinoflagellate biomass represented only ~1% of the total chl *a* biomass in all iron/silicate treatments. Thus our data are not consistent with the idea that type 3 haptophytes or dinoflagellates were responsible for the increase in $DMSP_p$ production observed in our iron and silicate addition experiments.

These results clearly implicate diatoms and/or siliceous type 4 haptophytes as the organisms responsible for the increased $DMSP_p$ and DMS concentrations measured in samples incubated with iron and/or silicate in that both groups were significant contributors to the total algal biomass in these

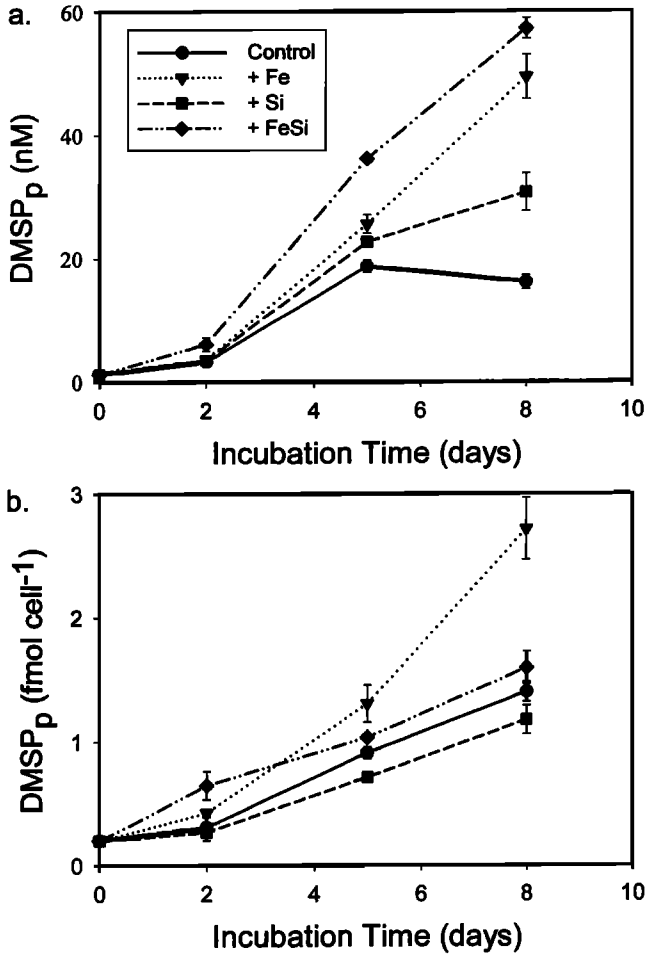

Figure 5. (a) $DMSP_p$ concentrations in the FeSi experiment. Treatment designations are described in Figure 3. Error bars represent the standard error from triplicate measurements on duplicate bottles. Error bars on some samples were smaller than the symbols. (b) $DMSP_p$:cell ratios from the FeSi experiment. Cell counts represent the red fluorescent cells measured by flow cytometry (mostly diatoms and haptophytes).

treatments. We recognize that it is not possible to identify unequivocally either of these groups as the major $DMSP_p$ producers in these experiments, particularly if changes in community $DMSP_p$ production reflect species-specific physiological changes mediated by iron and/or silicate, rather than changes in algal species composition. With this caveat in mind we interpret our experimental results on the basis of the significant changes in algal species composition that resulted from iron and silicate addition, as inferred from our pigment data. In the FeSi experiment the observed increases in $DMSP_p$ concentrations in the +Si and +Fe+Si treatments (Figure 5), in association with the significant increases in type 4 haptophyte abundance and little or no increase in diatom abundance (Table 3), relative to controls, suggest that siliceous type 4 haptophytes were responsible for most of the $DMSP_p$ production in these treatments. This interpretation is consistent with the idea that type 4 haptophytes are significant producers of DMSP in the marine environment [*Keller et al.*, 1989].

However, this same interpretation does not readily explain our observations for the iron-amended samples in the FeSi experiments. In these treatments, increased $DMSP_p$ concentrations, and elevated cellular $DMSP_p$ quotas based on total eukaryotic cells (Figure 5), are associated with a significant increase in the relative abundance of diatoms but not type 4 haptophytes, relative to the control treatments (Table 3). These observations provide strong circumstantial evidence that the lightly silicified pennate diatoms that proliferated in the +Fe treatments were major producers of the $DMSP_p$ and DMS measured in these samples. This conclusion is further supported by a comparison of the experimental results from the FePAR and FeSi experiments, which reveals that the additional Fe added in the FePAR experiment (5 nM in FePAR versus 1.9 nM in FeSi) resulted in proportionally higher $DMSP_p$ (compare Figures 2 and 5) and Fuco concentrations but not Hex (Figure 3), thus clearly implicating diatoms as responsible for the increased DMSP production in iron-amended samples. Following this line of reasoning, we suggest that both diatoms and type 4 haptophytes contributed to the production of $DMSP_p$ in the +Fe+Si treatments of the FeSi experiment.

In general, the production of $DMSP_p$ by marine diatoms has not been considered as a major source of DMS in oceanic regions, on the basis of laboratory studies of cultured diatoms [*Keller and Korjeff-Bellows*, 1996]. However, there are exceptions to this rule, such as some species of Arctic diatoms [*Matrai and Vernet*, 1997] and sea ice diatoms, which are thought to be significant $DMSP_p$ producers in both Arctic and

Table 2. Particulate DMSP Concentrations From the FeSi Experiment Normalized to Chl *a* Concentrations and Total Cell Number Estimated Using Flow Cytometric Analyses

	Treatmant			
Time	Control	Fe	Si	FeSi
	$DMSP_p$:chl a (nmol μg^{-1})			
Day 0	5.7	5.7	5.7	5.7
Day 2	15.9	11.9	11.5	20.3
Day 5	62.3	34.0	56.6	36.1
Day 8	53.8	30.9	68.3	32.8
	$DMSP_p$:cell (fmol $cell^{-1}$)			
Day 0	0.03	0.03	0.03	0.03
Day 2	0.05	0.06	0.05	0.10
Day 5	0.31	0.45	0.27	0.39
Day 8	0.52	0.57	0.78	0.71

Table 3. CHEMTAX Analysis of Algal Pigment Data From the FeSi Experiment

Treatment	% Diatoms	% Type 3 Haptophytes	% Type 4 Haptophytes
Initial	10.2	16.4	20.8
Control	22.1	18.2	23.1
+ Si	23.7	2.3	33.6
+ Fe	32.8	6.6	24.5
+ FeSi	29.2	0.0	34.4

Values represent the percentages of total algal community chl *a*. Type 3 haptophyes include the coccolithophorids, whereas the type 4 haptophytes include *Phaeocystis antarctica* and siliceous haptophytes such as silicoflagellates and *Parmales*. The entire CHEMTAX output from the experiment displaying all taxonomic results is presented elsewhere [*Hutchins et al.*, this issue].

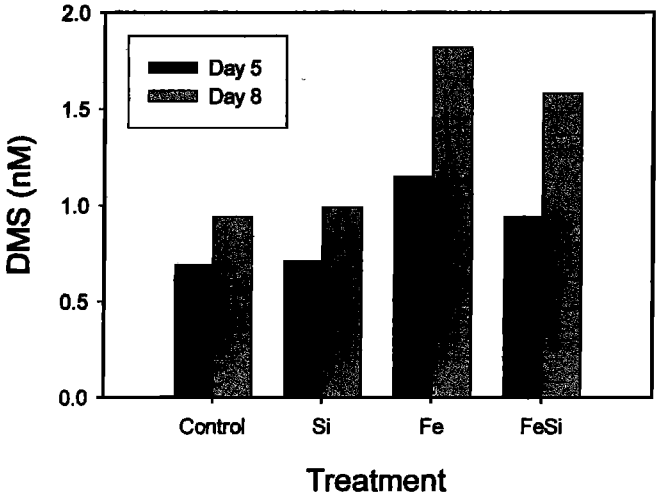

Figure 6. DMS concentrations in the FeSi experiment. Abbreviations and nutrient concentrations added to each treatment are described in Figure 3. DMS concentrations represent the average of duplicate measurements.

Antarctic waters [*Levasseur et al.*, 1994; *DiTullio et al.*, 1998]. Our results suggest that the small, lightly silicified diatom species that bloomed in our iron addition experiments are potentially very important with respect to marine $DMSP_p$ production in the subantarctic region, as are the siliceous type 4 haptophytes that apparently responded to additions of silicate. On the basis of these results we suggest that transient inputs of iron and/or silicate into subantarctic surface waters, as afforded by dust deposition, advective inputs from shelf sediments, or vertical mixing might be expected to produce blooms of these algal species and thus significant local production of DMSP and DMS.

Our results from the FePAR experiment also suggest that increased light intensity stimulated community $DMSP_p$ production. These data corroborate the results of previous laboratory studies, which revealed that enhanced light intensities stimulate $DMSP_p$ and DMS production in some polar algal species [*Baumann et al.*, 1994; *Matrai et al.*, 1995]. Over the range of iron and light levels examined in the FePAR experiment our results suggest that irradiance is of secondary importance to iron availability in stimulating $DMSP_p$ production by the subantarctic algal community (Figure 2). However, in the absence of a high-light control treatment in this experiment (i.e., high-light, no added iron) the apparent enhancement of community $DMSP_p$ production under high-light conditions could be interpreted as a result of decreased algal iron requirements under increased irradiance [*Raven*, 1990; *Sunda and Huntsman*, 1997], rather than a direct result of increased irradiance on algal $DMSP_p$ production. Nevertheless, on the basis of our experimental results the effect of variations in irradiance on algal iron requirements would be expected to moderate algal $DMSP_p$ production in subantarctic waters, such that increased irradiance would be expected to increase community DMSP production.

The glacial iron hypothesis [*Martin*, 1990] contends that enhanced deposition of iron-bearing mineral aerosol during the LGM stimulated the biological pump, primarily in the Southern Ocean, thus causing a large drawdown in atmospheric CO_2 concentration. An enhanced flux of aeolian iron into the ocean at the LGM might have also enhanced algal production of DMSP and DMS, relative to interglacial conditions, which offers an explanation for the high concentrations of both MSA and iron-bearing dust in glacial age ice core samples from Vostok, Antarctica [*LeGrand et al.*, 1991; *Martin*, 1992]. Studies of the marine sediment record lend support to the glacial iron hypothesis and suggest that enhanced aeolian iron deposition during the LGM allowed high export production north of the present-day Antarctic Polar Front (i.e., in the present-day subantarctic region) [*Kumar et al.*, 1995], which presumably also altered the algal community structure in this region [*Moore et al.*, 2000]. The results from our shipboard experiments lend support to the idea that increased aeolian iron deposition over this area of the Southern Ocean could have moderated a dramatic increase in algal DMSP and DMS production during the LGM. On the basis of our experimental data we suggest that enhanced deposition of aerosol iron in the low-silicate, low-iron subantarctic waters during the last glacial period may have resulted in the proliferation of small, lightly silicified pennate diatoms, which produced significant quantities of $DMSP_p$ and DMS. Light silicification could result in enhanced Si dissolution rates in sinking diatoms leading to a reduction in the Si flux to subantarctic sediments. We believe that these results demonstrate a potentially important linkage between the biogeochemical cycles of iron, carbon, and sulfur in the subantarctic Southern Ocean, which clearly warrants further field studies in this region.

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