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CO_2 effects on taxonomic composition and nutrient utilization in an Equatorial Pacific phytoplankton assemblage

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ABSTRACT: We report the results of a field incubation experiment demonstrating a substantial shift in the taxonomic composition of Equatorial Pacific phytoplankton assemblages exposed to CO_2 levels of 150 and 750 ppm (dissolved CO_2 ~3 to 25 µM). By the end of the experiment, the phytoplankton community in all samples was dominated by diatoms and *Phaeocystis* sp. However, the relative abundance of these phytoplankton taxa differed significantly between CO_2 treatments. Taxonomic pigment analysis and direct microscopic examination of samples revealed that the abundance of diatoms decreased by ~50% at low CO_2 relative to high CO_2, while the abundance of *Phaeocystis* increased by ~60% at low CO_2. This CO_2-dependent shift was associated with a significant change in nutrient utilization, with higher ratios of nitrate:silicate (N:Si) and nitrate:phosphate (N:P) consumption by phytoplankton in the low CO_2 treatment. Despite the significant changes in taxonomic composition and nutrient consumption ratios, total biomass and primary productivity did not differ significantly between the CO_2 treatments. Our results suggest that CO_2 concentrations could potentially influence competition among marine phytoplankton taxa and affect oceanic nutrient cycling.

KEY WORDS: Diatom · *Phaeocystis* · Carbon dioxide · Species composition · Nutrient utilization

INTRODUCTION

Over the past 2 decades, extensive laboratory and field research has been directed towards understanding the effects of atmospheric CO_2 variations on the productivity and species composition of terrestrial plant communities (Lemon 1983, Koch & Mooney 1996). By comparison, very few studies have examined the CO_2 responses of marine phytoplankton despite the established importance of these organisms in the global C cycle (Sarmiento & Siegenthaler 1992). Laboratory work suggests that CO_2 availability can potentially limit the growth of large marine diatoms (Riebesell et al. 1993), while recent field studies have provided preliminary information on the CO_2 sensitivity of oceanic primary production over various timescales (Chen & Durbin 1996, Hein & Sand-Jensen 1997, Tortell et al. 1997, 2000). Short-term CO_2 limitation of marine primary production has been observed (Chen & Durbin 1996, Hein & Sand-Jensen 1997), but the growth rates of phytoplankton assemblages in 3 to 6 d incubation experiments are generally unaffected by CO_2 manipulations (Tortell et al. 1997, 2000). At present, no information is available on the longer-term impacts of CO_2 on the ecology of marine phytoplankton communities.

Typical oceanographic incubation experiments usually last between 3 and 6 d before macro-nutrients are exhausted from bottles and cells enter stationary phase (e.g. Price et al. 1994). The timescale of such experiments appears to be shorter than that of *in situ* blooms

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(e.g. Coale et al. 1996)—due to the exclusion of metazoan grazers from bottles and the lack of advective nutrient supply—and may be insufficient to observe significant changes in community structure resulting from small differences in the competitive abilities of various phytoplankton groups. To examine the potential longer-term effects of CO_2 on phytoplankton communities, we employed a semi-continuous culture technique in which CO_2-manipulated seawater samples (150 and 750 ppm) were periodically diluted with high-nutrient, filtered seawater. Here, we report the results of these longer-term experiments demonstrating a CO_2 effect on the species composition of an Equatorial Pacific phytoplankton assemblage. We discuss the potential ecological, biogeochemical and paleoceanographic implications of our findings.

MATERIALS AND METHODS

We conducted a CO_2 manipulation experiment with a phytoplankton assemblage collected from high-nutrient upwelled seawater off the Peruvian coast (6° 36′ S, 81° 01′ W) in September 2000 (RV 'Melville', cruise COOK 001). Water samples were collected from ~15 m depth with an *in situ* pumping system, transferred into acid-cleaned 4 l polycarbonate bottles and incubated on deck in a flow-through seawater tank at ~30% surface irradiance (achieved with neutral density screening). In the seawater collected for incubations, concentrations of nitrate (N), silicate (Si) and phosphate (P) were 25, 26 and 2.3 µM respectively, total (>0.6 µm) chlorophyll *a* (chl *a*) was ~2 µg l^{-1} and dissolved Fe was present at non-limiting concentrations (i.e. >1 nM; E. Rue pers. comm.).

After approximately 3 and 8 d of incubation, ~90% of the contents of each bottle was removed (using a positive pressure sampling system) and replaced with 0.45 µm filtered seawater collected at the same time as the initial incubation water. Using this semi-continuous approach, we were able to observe the development of a phytoplankton assemblage over 3 successive transfers for a total of 11 d.

To control CO_2 concentrations in seawater samples, commercially prepared air mixtures containing 150 or 750 ppm CO_2 were bubbled into triplicate incubation bottles to obtain aqueous CO_2 concentrations of 5.7 and 28 µM (calculated using liquid–gas phase equilibria equations; Lewis & Wallace 1998). These CO_2 treatments were chosen to encompass a range from glacial atmospheric minima (~180 ppm; Petit et al. 1999) to values predicted to occur by the end of this century (IPCC 2001). As judged by periodic pH measurements, CO_2 concentrations in bottles equilibrated with the inflowing gas stream within ~8 h and remained nearly constant over the course of the incubations (±<10%). In the 150 and 750 ppm CO_2 treatments, seawater pH reached steady-state values of approximately 8.5 and 7.9 respectively, with corresponding CO_3^{2-} ion concentrations of 284 and 95 µM (calculated from the algorithm of Lewis & Wallace 1998). Total dissolved inorganic carbon (DIC) concentrations (i.e. $CO_2 + HCO_3^- + CO_3^{2-}$) were ~15% higher in the 750 ppm treatment (2188 vs 1888 µM), while seawater alkalinity was not altered by the CO_2 manipulations. Our experimental perturbations of the DIC chemistry in seawater samples (including pH changes) mimic those associated with photosynthetic CO_2 uptake as well anthropogenic CO_2 input to the oceans.

At various sampling points throughout the experiment, we measured total chl *a* (by fluorometric analysis), nutrient concentrations (with an autoanalyzer) and phytoplankton pigment concentrations by HPLC analysis as previously described (DiTullio & Smith 1996). The taxonomic composition of the phytoplankton assemblages was derived quantitatively from an analysis of pigment data using the CHEMTAX algorithm (Wright & van den Enden 2000) and qualitatively from microscopic examination of glutaraldehyde-preserved samples (1% final preservative concentration). Nutrient consumption was calculated as the difference between starting and final concentrations for each successive growth period. In each culture transfer, the incubation water was replenished before any of the macro-nutrients was completely consumed in the incubation bottles (<85% consumption).

Primary production was measured on Day 5 of the experiment. Subsamples (200 ml) were removed from grow-out bottles, incubated for 6 h with 20 µCi ^{14}C and harvested by gentle filtration onto GF/C filters. After overnight acidification with 1 ml of 1% H_3PO_4, radioactivity on filters was determined by liquid scintillation counting.

RESULTS AND DISCUSSION

The initial phytoplankton community (i.e. pre-incubation) was dominated by cryptophytes (~45% total chl *a*), but also contained significant biomass of prasinophytes, prymnesiophytes, chlorophytes and cyanobacteria (20, 13, 8 and 7% of total chl *a* respectively). Over the course of the experiment, diatoms and prymnesiophytes of the HAPTO4 pigment group—which includes *Phaeocystis*—became the dominant phytoplankton in all samples, accounting for ~90% of total community chl *a*. Total phytoplankton biomass did not differ significantly between the CO_2 treatments (Fig. 1a). However, the relative biomass of diatoms and prymnesiophytes was substantially different under low

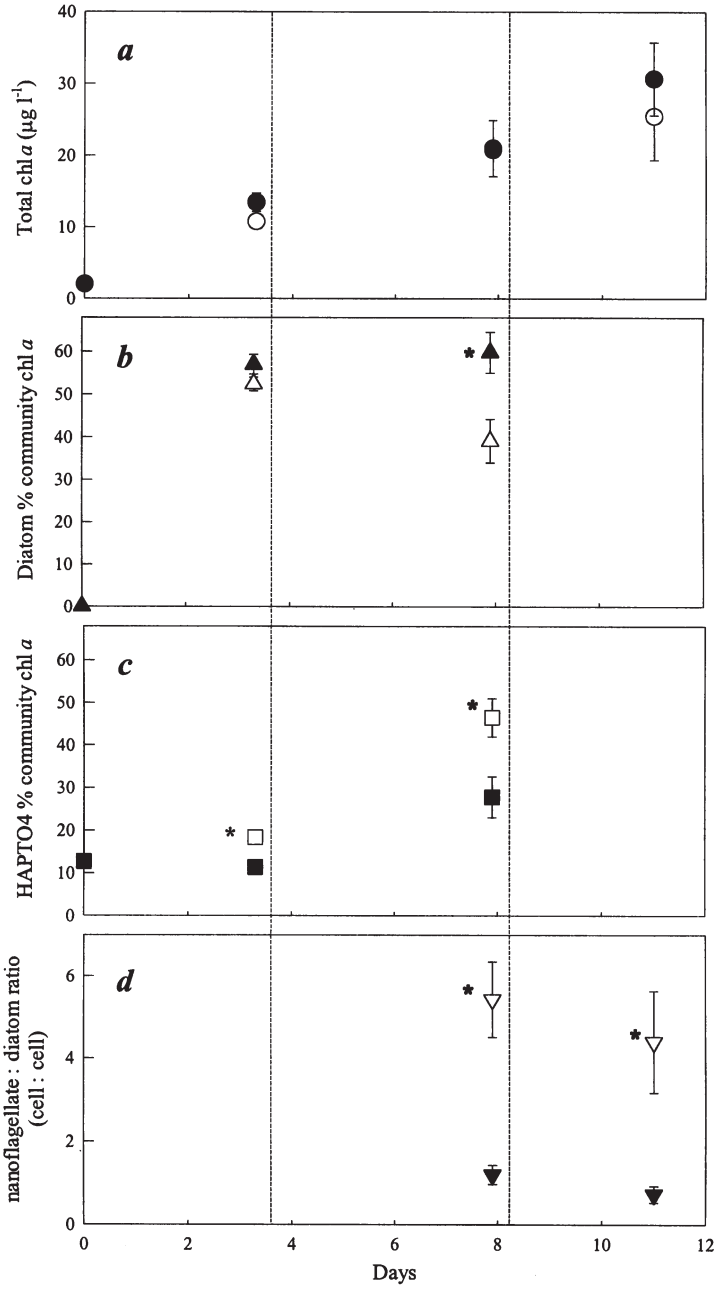

Fig. 1. Effects of CO_2 manipulations on the biomass and taxonomic composition of an Equatorial Pacific phytoplankton assemblage (triplicate treatments for each CO_2 level). (a) total chl *a* (> 0.6 µm); (b) abundance of diatoms (percent of total chl *a*) as determined by CHEMTAX analysis of phytoplankton pigment concentrations; (c) pigment-derived abundance of the HAPTO 4 prymnesiophytes which includes *Phaeocystis*; (d) ratio of nanoflagellate cells to diatom cells counted by microscopy in preserved samples from incubation bottles (see Fig. 2). Dashed lines on the figures indicate times when incubation samples were diluted (~10:1) with high-nutrient, filtered seawater. Asterisks next to symbols indicate a statistically significant difference between 150 (open symbols) and 750 ppm CO_2 (filled symbols) samples (n = 3, $p < 0.05$). Note that samples for total chl *a* and taxonomic pigment analysis were only collected on Days 0, 3.3 and 7.9, while preserved material for cell counts was only taken from the 7.9 and 11 d time points

and high CO_2 conditions. After approximately 3 d of incubation, the biomass of HAPTO4 prymnesiophytes (hereafter referred to as prymnesiophytes) was significantly higher in the low CO_2 incubations relative to high CO_2 samples (*t*-test, $p < 0.05$), whereas diatom biomass was slightly (but not significantly) reduced at low CO_2 (Fig. 1b,c). By 7.9 d, prymnesiophyte biomass further increased at low CO_2 relative to high CO_2 and diatom biomass was significantly decreased in the low CO_2 samples (Fig. 1b,c; *t*-test, $p < 0.05$). At this time, the respective contributions of diatoms and prymnesiophytes to total community chl *a* were ~40 and 50% in the low CO_2 bottles, compared to 60 and 30% at high CO_2.

Using light microscopy, we identified dominant taxa in preserved samples from the algal assemblages collected on Days 8 and 11. The samples were composed mostly of diatoms (centric and pennate) and the nanoflagellate *Phaeocystis* sp. Without exception, the low CO_2 assemblages contained a significantly greater abundance of nanoflagellates (*Phaeocystis* sp.) relative to diatoms (Fig. 1d). In freshly collected samples from low CO_2 bottles, we observed a number of early-stage *Phaeocystis* colonies, mostly 4 cell clusters, but these were not well-preserved. Although the relative number of diatoms was reduced at low CO_2, we could not detect any qualitative differences in diatom species composition between the CO_2 treatments. We cannot, however, rule out such changes. From an ecological and biogeochemical perspective, changes in the relative abundance of various diatom species should be generally less important than shifts among major taxonomic classes.

The community shift from diatoms to *Phaeocystis* at low CO_2 was associated with a large change in nutrient consumption ratios. Phytoplankton assemblages in the high CO_2 bottles consumed NO_3^- and H_2SiO_3 in a ratio close to 1:1 (range 1.0 to 1.55), as is expected for a trace metal-replete diatom-dominated community (Brzezinski 1985). In contrast, N:Si consumption ratios in the low CO_2 assemblages ranged from 2.16 to 2.71 (Table 1). The CO_2-dependent difference in N:Si drawdown ratios was statistically significant at all sampling times (*t*-test, $p < 0.05$), but most pronounced after 7.9 and 11 d of incubation when the abundance of *Phaeocystis* relative to diatoms at low CO_2 was greatest. At the final sampling time point, we also observed a significant difference in N:P drawdown ratios between CO_2 treatments, with higher values in the 150 ppm assemblage (*t*-test, $p < 0.05$; Table 1). This result is consistent

Table 1. Nutrient consumption by Equatorial Pacific phytoplankton assemblages incubated with 150 and 750 ppm CO_2. *$p < 0.05$. Each row in the table gives total nutrient consumption calculated as the decrease in N, P, or Si concentration during the growth period indicated in the left-hand column

Time (d)	CO_2 (ppm)	N drawdown (mol l^{-1})	P drawdown (mol l^{-1})	Si drawdown (mol l^{-1})	N:P (mol:mol)	N:Si (mol:mol)
0 to 3.3	150	18.1 ± 0.3	1.08 ± 0.07	8.45 ± 0.6	16.9 ± 1.4	2.16 ± 0.2
	750	*15.3 ± 0.2	1.23 ± 0.03	9.93 ± 0.7	12.6 ± 1.0	*1.55 ± 0.1
3.3 to 7.9	150	21.7 ± 0.2	1.52 ± 0.02	8.0 ± 0.2	14.5 ± 0.4	2.71 ± 0.1
	750	21.1 ± 0.2	1.55 ± 0.10	*20.4 ± 0.51	13.9 ± 1.0	*1.08 ± 0.02
7.9 to 11.0	150	21.0 ± 0.2	1.40 ± 0.03	8.7 ± 1.2	14.6 ± 0.6	2.52 ± 0.3
	750	21.1 ± 0.3	*1.74 ± 0.02	*21.1 ± 0.7	*11.9 ± 0.4	*1.0 ± 0.04

with recent field data showing higher N:P consumption ratios in *Phaeocystis*-dominated assemblages relative to diatom-dominated populations (Arrigo et al. 1999).

Taken together, our nutrient data, biomass estimates and microscope observations demonstrate that diatom abundance was decreased in low CO_2 incubation bottles in favor of non-siliceous phytoplankton taxa—*Phaeocystis* in particular. Despite the large community shift we observed in response to our CO_2 manipulation, primary productivity (6.4 ± 0.5 g C l^{-1} d^{-1}) and total biomass (~20 ± 3 µg chl *a* l^{-1}; Fig. 1a) did not differ significantly between the CO_2 treatments at any sampling point during the incubation. This suggests that oceanographic techniques that measure characteristics of entire phytoplankton communities rather than individual taxa may be inadequate to detect potential ecological responses to CO_2 variations.

Thus far, the role of inorganic C in the ecology of marine phytoplankton has received little attention owing to its abundance in seawater relative to other potentially limiting nutrients. However, free CO_2 constitutes less than 1% of the total inorganic C pool in the oceans (Morel & Hering 1993) and its concentration is at or below that required for half saturation of RubisCO, the central C fixing enzyme in photosynthesis (see Badger et al. 1998). It has been suggested that CO_2 could limit C fixation by marine phytoplankton—large diatoms in particular—and some experimental support for this exists (Riebesell et al. 1993). However, most phytoplankton compensate for the low CO_2 affinity of RubisCO by utilizing cellular C-concentrating mechanisms based on the active uptake of CO_2 and/or HCO_3^- from the environment (see Raven 1997). Cells that possess such active C uptake mechanisms generally show a high affinity for CO_2 (Raven & Johnson 1991) and little evidence of growth-rate limitation over a typical range (~5 to 30 µM) of oceanic CO_2 concentrations (Raven 1997, Tortell et al. 2000).

The apparent lack of CO_2 effects on the steady-state growth rates and bulk productivity of phytoplankton assemblages does not preclude long-term changes in species composition resulting from species-specific CO_2 responses. Indeed, the results of our study indicate that such CO_2-dependent taxonomic shifts can occur in the absence of a detectable difference in total primary productivity or biomass (Fig. 1). Species-specific CO_2 responses could result from taxonomic differences among phytoplankton in the physiological mechanisms of inorganic C acquisition (Raven 1991, Tortell 2000). For example, laboratory studies with freshwater phytoplankton have demonstrated that differential C uptake kinetics between green algae and cyanobacteria determine the outcome of competition between these phytoplankton in C-limited chemostats (Williams & Turpin 1987). Furthermore, direct manipulation experiments in lakes have shown that low CO_2 concentrations favor the growth of cyanobacteria over other phytoplankton species (Shapiro 1973). More generally, the well-documented association between pH and phytoplankton species composition in lakes has been attributed by a number of authors to the differential CO_2 affinity of various phytoplankton species (Moss 1973, Talling 1976).

Phytoplankton species-pH associations have also been observed in coastal marine environments where CO_2 concentrations can fall to values as low as 100 ppm (~3 µM; Codispoti et al. 1982, Bates et al. 1998). Such low CO_2 environments are often dominated by nanoflagellates including *Phaeocystis* even when Si is present in non-limiting concentrations (Hinga 1992, Brussard et al. 1996). Though causality cannot be inferred from this qualitative observation—owing to the covariance between CO_2 concentrations and a number of physical and chemical variables—the apparent dominance of nanoflagellates over diatoms in many low CO_2 environments is consistent with our incubation results. If indeed *Phaeocystis* has a competitive advantage over diatoms at low CO_2, we should expect to find characteristic differences in the C uptake systems of these phytoplankton groups. At present, such physiological differences cannot be discerned owing to a lack

of data on C acquisition in *Phaeocystis*. Preliminary studies indicate that *P. globosa* is capable of utilizing HCO_3^- as a source of inorganic C for photosynthesis (Elzenga et al. 2000) as has been observed in a number of diatom species (Korb et al. 1997). However, the affinity of the C transport system in *Phaeocystis* (and in many diatoms) remains to be determined. Comparative studies of C uptake in marine phytoplankton, as well as direct laboratory competition experiments, will be necessary to understand how CO_2 concentrations could influence phytoplankton species succession in productive marine waters.

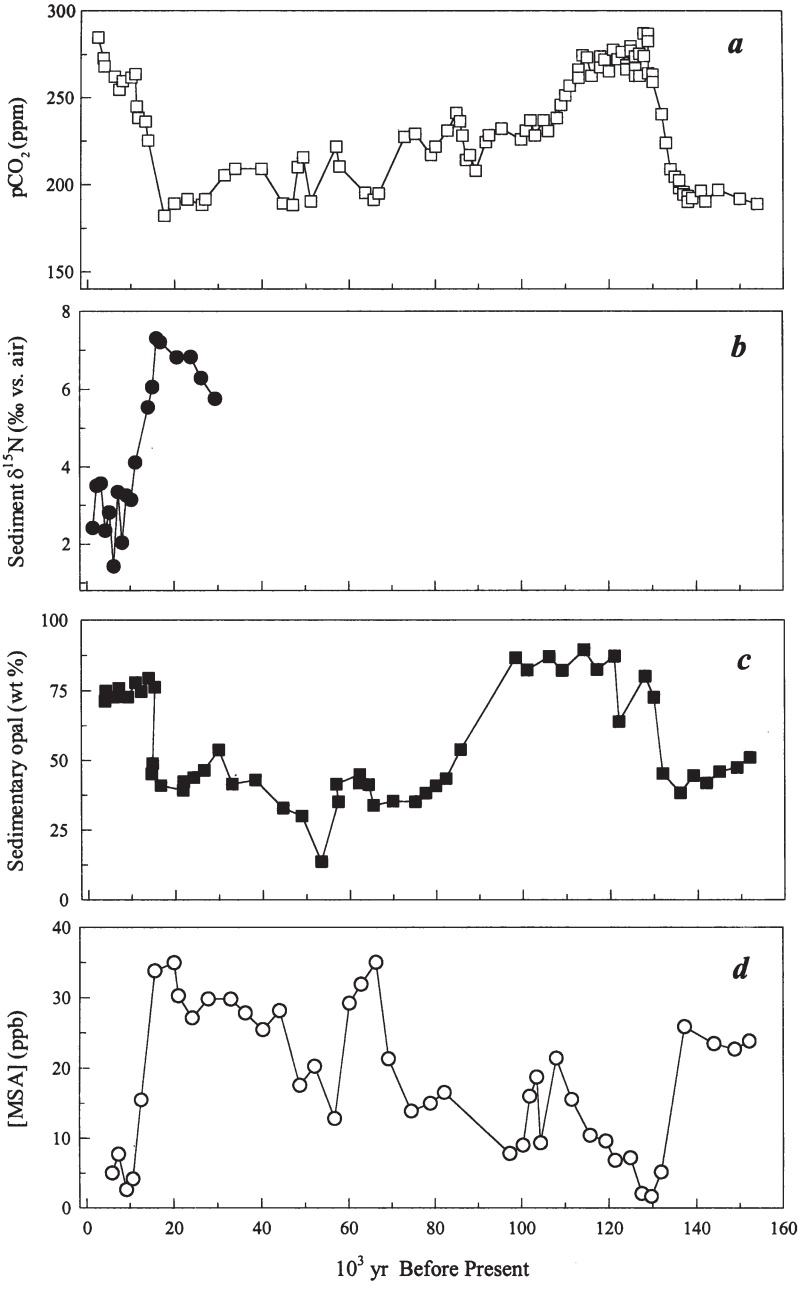

Fig. 2. Compilation of Vostok ice core records and Southern Ocean sedimentary data showing: (a) changes in atmospheric CO_2 concentrations; (b) relative N consumption based on bulk sediment $\delta^{15}N$ values; (c) biogenic Si export to the sediments; and (d) atmospheric concentrations of methylsulfonic acid (MSA)—an oxidation product of dimethylsulfide. Data are replotted from Petit et al. (1999) (CO_2), François et al. (1997) ($\delta^{15}N$), Mortlock et al. (1991) (opal fluxes) and Legrand et al. (1991) (MSA). These manuscripts should be consulted for a detailed explanation of measurement protocols, age models and data interpretation

Potential CO_2 effects on phytoplankton community structure may have important implications for ocean biogeochemistry. Paleooceanographic data suggest that decreased CO_2 in the glacial atmosphere (180 ppm; Petit et al. 1999) was accompanied by a lowering of Si:N utilization ratios by phytoplankton in the Antarctic zone of the Southern Ocean (Fig. 2). During low CO_2 periods, the fractional consumption of N in the Antarctic ($\delta^{15}N$ of sediment) appears to have increased (François et al. 1997), whereas both the relative utilization of Si in surface waters and the export of biogenic Si to the sediments are believed to have decreased (Mortlock et al. 1991, De La Rocha et al. 1998). It has been suggested that oceanic Fe fertilization may have caused this change in nutrient cycling by lowering Si:N consumption ratios in diatoms (Hutchins & Bruland 1998, Takeda 1998). However, several authors have also argued that shifts in phytoplankton community composition towards non-siliceous species such as *Phaeocystis* may have occurred during glacial times (Martin 1992, Moore et al. 2000). Such a species shift is consistent with ice core records suggesting a glacial increase in southern hemispheric concentrations of dimethylsulfide (Legrand et al. 1991; Fig. 2d). This compound is produced in particularly high quantities by *Phaeocystis* and other prymnesiophytes (Keller et al. 1989).

The factors that might have triggered a shift from diatom-dominated to *Phaeocystis*-dominated phytoplankton communities in the glacial Antarctic have not been identified. Our observations provide a speculative CO_2-dependent mechanism for this shift, with lower glacial atmospheric P_{CO_2} potentially encouraging the relative success of *Phaeocystis*. If low surface water P_{CO_2} does indeed favor the success of *Phaeocystis*, evidence for abundant *Phaeocystis* in glacial Antarctic waters would imply lower surface water P_{CO_2}, suggesting that this region played an important role in reducing atmospheric CO_2 to glacial values. Reduced glacial surface water P_{CO_2} in the Antarctic is

consistent with greater biological production (Sarmiento & Togweiller 1984, Martin 1992) and/or intensified water column stratification in this region (François et al. 1997), but inconsistent with a reduction in gas exchange between the Antarctic surface ocean and atmosphere (Stephens & Keeling 2000). The enhancement of *Phaeocystis* abundance during glacial times may have acted as a positive feedback on climate change through a stimulation of DMS production, enhanced cloud formation and increased albedo (Legrand et al. 1991).

To our knowledge, the data presented in this article provide the first direct evidence that CO_2 concentrations can influence the species composition of a marine phytoplankton assemblage. The extent to which our preliminary results may be generalized to other oceanic ecosystems remains to be determined. Future studies will need to examine the effects of finer-scale CO_2 variations (e.g. 180 to 280 ppm) on the species composition of marine phytoplankton communities. In addition, more information is needed on the physiological mechanisms of inorganic C acquisition in a variety of marine phytoplankton taxa. Such information will inform our understanding of how phytoplankton species may respond differentially to natural and anthropogenic CO_2 variations in the oceans.

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