

Phytoplankton carbon isotope fractionation during a diatom spring bloom in a Norwegian fjord

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ABSTRACT: The stable carbon isotope composition ($\delta^{13}\text{C}$) of particulate organic carbon (POC) was measured in 3 size fractions ($\text{POC}_{\text{total}}$, $\text{POC}_{>20\ \mu\text{m}}$, $\text{POC}_{<20\ \mu\text{m}}$) during a phytoplankton spring bloom dominated by the diatom *Skeletonema costatum* in Lindåspollene, a land-locked fjord in southern Norway. In addition to standard parameters for characterizing the phytoplankton bloom (chlorophyll, nutrient, and POC concentrations, and species composition), simultaneous measurements of $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC), total alkalinity and DIC concentration were obtained to determine temporal trends in dissolved carbon dioxide concentration and in carbon isotope fractionation (ϵ_p) of the POC size fractions. The carbon isotope composition of the $>20\ \mu\text{m}$ size fraction, which was dominated by diatoms, was ca 2‰ heavier than that of the $<20\ \mu\text{m}$ fraction, which was mainly composed of flagellates. $\delta^{13}\text{C}$ of both size fractions increased by about 3‰ over the course of the bloom. A 5‰ increase in $\delta^{13}\text{C}$ - $\text{POC}_{\text{total}}$ during the bloom resulted partly from a shift in the phytoplankton community from a flagellate- to a diatom-dominated one. Carbon isotope fractionation of all fractions decreased with declining $\text{CO}_2(\text{aq})$ concentration (14 to $>6\ \mu\text{mol l}^{-1}$). A positive correlation between ϵ_p and $[\text{CO}_2(\text{aq})]$ in the diatom size fraction was obtained for the period of exponential growth. Deviation from this correlation occurred after the peak in cell density and chlorophyll *a* (chl *a*) concentration, when POC still continued to increase, and may be related to changing phytoplankton growth rates or to possible effects of nutrient (nitrate) limitation on ϵ_p . Comparison of these results with those of previous field studies shows that, while an inverse relationship is consistently observed between ϵ_p and the ratio of instantaneous growth rate and CO_2 concentration $[\mu_r/[\text{CO}_2(\text{aq})]]$, considerable scatter exists in this relationship. While this scatter may have partly resulted from inconsistencies between the different studies in estimating phytoplankton growth rate, it could also reflect that factors other than growth rate and CO_2 concentration significantly contribute to determining isotope fractionation by marine phytoplankton in the natural environment.

KEY WORDS: $\delta^{13}\text{C}$ · Isotope fractionation · CO_2 · Phytoplankton · Diatom bloom

INTRODUCTION

The realization that the carbon isotope composition, $\delta^{13}\text{C}$, of terrestrial plants is largely determined by discrimination of the carbon-fixing enzyme Ribulose-1,5-bisphosphate-carboxylase-oxygenase against $^{13}\text{CO}_2$ (Park & Epstein 1960) was the crucial step that tied plant isotopic composition to properties of the environment, such as CO_2 concentration. Degens et al. (1968) were the first to experimentally demonstrate a positive relationship between photosynthetic discrimination

against $^{13}\text{CO}_2$ and the concentration of molecular dissolved carbon dioxide, $[\text{CO}_2(\text{aq})]$, in marine phytoplankton. This relationship was applied by Degens (1969) to interpret low $\delta^{13}\text{C}$ values of organic matter from ancient marine sediments as being the result of high $\text{CO}_2(\text{aq})$ concentrations at the time of formation. A close correlation between carbon isotope composition of particulate organic carbon and $\text{CO}_2(\text{aq})$ concentration was further substantiated for the contemporary ocean, and applied to hindcast the atmospheric partial pressure of CO_2 from plankton $\delta^{13}\text{C}$ of cretaceous sediments (Rau et al. 1989). Meanwhile, laboratory evidence has been accumulating to support a positive relationship between photosynthetic carbon isotope

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discrimination, ϵ_p , and $[\text{CO}_2(\text{aq})]$ of the medium (e.g. Pardue et al. 1976, Mizutani & Wada 1982, Hinga et al. 1994, Laws et al. 1995, 1997, Bidigare et al. 1997, Popp et al. 1998).

Aside from growing evidence that ϵ_p and $[\text{CO}_2(\text{aq})]$ may be positively related, other laboratory data suggest that physical factors such as temperature (e.g. Wong & Sackett 1978, Hinga et al. 1994, Johnston 1996), pH (Hinga et al. 1994), salinity (Leboulanger et al. 1995), light intensity (Korb et al. 1996) and daylength (Leboulanger et al. 1995) may also influence phytoplankton ϵ_p . In addition, carbon demand as represented by growth rate (e.g. Fry & Wainright 1991, Takahashi et al. 1991, Laws et al. 1995, 1997), variation in the inorganic carbon source, i.e. $\text{CO}_2(\text{aq})$ versus bicarbonate (Degens et al. 1968), passive diffusion versus active uptake of inorganic carbon (Sharkey & Berry 1985, Raven et al. 1993), differences in the carboxylating enzyme (Robinson & Cavanaugh 1995) and β -carboxylation reactions (Descolas-Gros & Fontugne 1990, Falkowski 1991) may cause significant variation in ϵ_p . To complete this list, phytoplankton species-specific differences (Wong & Sackett 1978, Falkowski 1991, Korb et al. 1996) and differences in nutrient utilization, i.e. NO_3^- versus NH_4^+ use (Guy et al. 1993), have been suggested to affect ϵ_p .

Among the numerous factors experimentally shown to influence phytoplankton isotope fractionation, not all are necessarily relevant under natural conditions in the field and only a few are likely to exert significant control at any given time and location. In order to iden-

tify the relevant parameters determining isotope fractionation in the field, it is therefore necessary to relate organic matter $\delta^{13}\text{C}$ to the environmental conditions under which it was produced. Vertical transport of particulate organic matter and its incorporation into sediments occurs to a large extent in episodic events often related to phytoplankton blooms (Berger & Wefer 1990). For the interpretation of sedimentary organic matter $\delta^{13}\text{C}$, it is of particular interest, therefore, to monitor organic matter isotope composition during bloom formation. Periods of bloom development, however, are generally characterized by systematic trends in environmental parameters which in themselves may affect the isotopic signal of the accumulating biomass. The intention of the present study, therefore, is to obtain synoptic information on the relationship between organic matter $\delta^{13}\text{C}$ and changing environmental conditions during the course of a phytoplankton bloom.

MATERIALS AND METHODS

Location. Lindåspollene is a land-locked fjord ca 40 km north of Bergen, Norway (Fig. 1), known for an annual spring bloom that is generally dominated by the diatom *Skeletonema costatum* (e.g. Lännergren & Skjoldal 1976, see Aksnes & Lie 1990 for further references). Lindåspollene consists of 3 basins with a maximum depth of 90 m which are separated by shallow sills. The connection to the outer fjord, the Lurefjorden, is maintained by 3 shallow sills less than 3 m deep. The glacier-free watershed has an area of ca 35 km² and provides 70×10^6 m³ fresh-water annually to the fjord, which amounts to about half of its volume (Wassmann 1983). The tidal range is ca 50 cm and the concomitant water exchange during 1 tidal cycle is roughly 2% of the total volume (Wassmann 1983). The sampling station in the fjord was marked by a buoy.

Sampling. Sampling commenced in mid March of 1997, well before the onset of the diatom bloom. Data reported here cover the period from April 4 to 14, 1997, during which the development of a bloom of the diatom *Skeletonema costatum* was followed. During this period sampling was conducted between 13:00 and 15:00 h from a small rowboat with an outboard engine. At the beginning of the sampling program, maximum chlorophyll *a* (chl *a*) concentrations were at ca 2 m depth. All data presented here are from samples taken at this depth. Water samples were obtained with a hand-operated, 2 l Ruttner

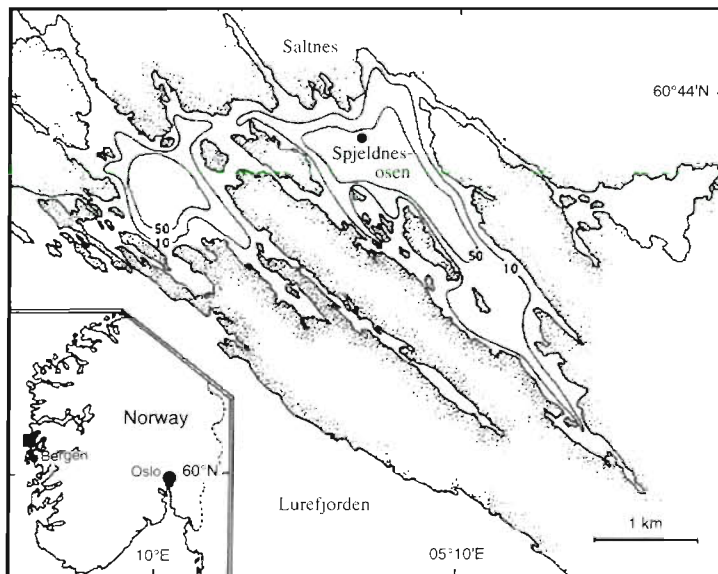


Fig. 1. Location of the sampling station in Lindåspollene. Inset map shows location of Lindåspollene (■) in southern Norway (modified after Aksnes & Lie 1990)

sampler in bottles thoroughly rinsed with water from the sampling depth. Samples for isotopic composition of particulate organic carbon ($\delta^{13}\text{C}$ -POC), isotopic composition of dissolved inorganic carbon ($\delta^{13}\text{C}$ -DIC), dissolved inorganic carbon concentration ([DIC]), alkalinity, nutrients, and phytoplankton community composition were taken from the same cast, and the water was stored in 1 l Schott flasks. Once ashore, samples for $\delta^{13}\text{C}$ -DIC, [DIC], alkalinity, and nutrients were fixed with mercury chloride (2%), and those for phytoplankton community composition with Lugol's iodine (Edler 1979). Every second day, additional phytoplankton community samples were fixed with 20% hexamine-buffered formalin solution (Edler, 1979). Samples for chl *a* and size-fractionated POC filtration were taken from repetitive casts to the same depth, stored in 1 l Schott flasks, and transported to the laboratory in a cooler for immediate filtration.

For temperature and conductivity (salinity) measurements (0 to 20 m), we used a hand operated probe (WTW LF 191) with a cable marked at 1 m intervals. Vertical chl *a* profiles (0 to 20 m) were obtained with an *in situ* fluorometer connected to a CTD (ADM) operating in storage mode.

Filtration. Samples for chl *a* determination were filtered onto glass-fiber filters (Whatman GF/C) and analyzed immediately. Samples for particulate organic matter (for later analysis of POC, PON [particulate organic nitrogen], and $\delta^{13}\text{C}$ -POC) were filtered onto glassfiber filters (Whatman GF/C) precombusted at 500°C for 12 h. Material for $\delta^{13}\text{C}$ -POC was filtered in duplicate (200 to 500 ml) from the same cast as the liquid samples (i.e. [DIC], $\delta^{13}\text{C}$ -DIC, etc.). For size fractionation of POC, 1 to 5 l of seawater from additional, repetitive casts was filtered through a 200 μm gauze (to remove zooplankton) and a 20 μm gauze, to obtain $\delta^{13}\text{C}$ -POC_{<20 μm} and $\delta^{13}\text{C}$ -POC_{>20 μm} samples. The POC on the 20 μm screen was washed off with GF/C-filtered seawater and filtered onto a glass-fiber filter. Except for the first 4 d, $\delta^{13}\text{C}$ -POC_{>20 μm} samples were taken in duplicate; $\delta^{13}\text{C}$ -POC_{<20 μm} was always sampled without replicates. All filters were stored in glass petri dishes and frozen at -20°C. The petri dishes were initially cleaned with a detergent free of organic substances.

Measurements. Chl *a* concentration was determined fluorometrically (Turner 10-AU-005) according to Edler (1979). POC, PON and the carbon isotopic composition of particulate organic matter were measured on the same filters with a continuous flow isotope ratio mass spectrometer (Europa Scientific, ANCA SL 20-20). Filters were thawed, acid fumed for 4 h, dried for 12 h at 60°C, and wrapped in Sn-vials prior to analysis. $\delta^{13}\text{C}$ -DIC was measured on a Finnegan MAT Delta-S isotope-ratio mass spectrometer after acidifying the

sample *in vacuo* with orthophosphoric acid and cryogenically trapping the released CO₂ (Mackensen et al. 1996). All values of carbon isotope composition are reported in δ -notation relative to VPDB (Vienna PeeDee Belemnite).

DIC was determined coulometrically in duplicate with a system similar to that described by Johnson et al. (1987). In short, a defined volume of seawater is acidified with phosphoric acid, and the released carbon dioxide is bubbled into a titration cell and measured as electrons required to generate OH⁻ ions to titrate the acid formed in the reaction of CO₂ with ethanolamine. Alkalinities were titrated in duplicate with an automated, temperature-controlled system at 5°C, and total alkalinity determined using the Gran-plot approach (Almgren et al. 1988). Inorganic nutrients were measured with an auto-analyzer (Technicon AA II) using the methods of Armstrong et al. (1967) for NO₃⁻, Eberlein & Kattner (1987) for PO₄³⁻, and Grasshoff et al. (1983) for dissolved silica determination. Phytoplankton was identified, counted and measured ($n \geq 50$ for *Skeletonema costatum*) with an inverted microscope according to Utermöhl (1958).

Calculations. [CO₂(aq)] was calculated from total [DIC], alkalinity, salinity, temperature, and depth using dissociation constants of Goyet & Poisson (1989). $\delta^{13}\text{C}$ -CO₂(aq) was calculated from $\delta^{13}\text{C}$ -DIC measurements by combining the equations for ¹³C fractionation between DIC and CO₂(gas), and CO₂(aq) and CO₂(gas) of Zhang et al. (1995, their Eqs. 2 & 5 of Table 4). ϵ_p was estimated using

$$\epsilon_p = \frac{\delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{POC}}}{1 + \frac{\delta^{13}\text{C}_{\text{POC}}}{1000}} \quad (1)$$

Standard error estimates for ϵ_p were calculated from the standard deviation of ϵ_p obtained using Gauss' law of error propagation (Kreyszig 1982) divided by the number of replicates.

Since recovery of the material collected on the 20 μm screen was usually less than 100% (based on mass balance calculations), [POC]_{>20 μm} was calculated as the difference of [POC]_{total} - [POC]_{<20 μm} . Average growth rates (μ_{L+D} ; *L* and *D*: lengths of light and dark periods, respectively) were estimated independently from temporal changes in cell numbers of *Skeletonema costatum* and from changes in [POC]_{>20 μm} using least squares linear regression. Instantaneous growth rate (μ_i) was calculated according to

$$\mu_i = \frac{(L+D) \cdot \mu_{L+D}}{L - D \cdot r} \quad (2)$$

which corrects μ_{L+D} for *L* (cf. Laws et al. 1995, Rau et al. 1997). The average daylength during the study period was 13.7 h. We assumed the ratio of dark respiration

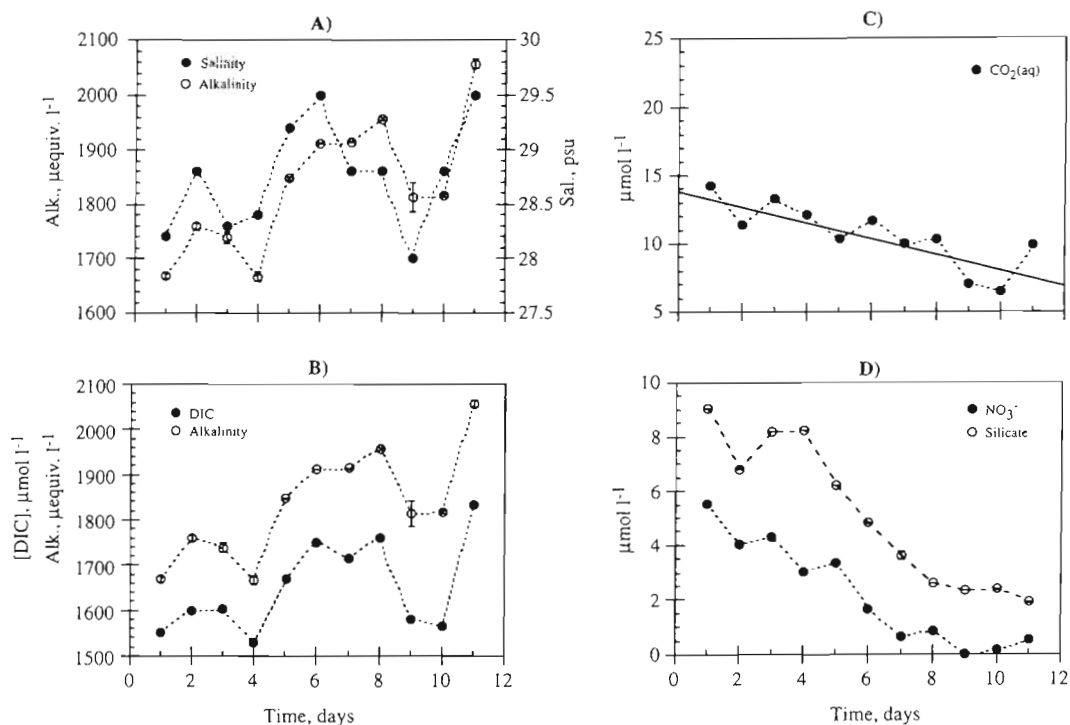


Fig. 2. (A) Salinity and alkalinity, (B) total dissolved inorganic carbon concentration, DIC, and alkalinity, (C) concentration of dissolved molecular carbon dioxide, CO₂(aq), and (D) concentrations of nitrate and silicate in Lindåspollene, Norway, during the sampling period. Error bars in alkalinity data represent ± 1 SD between replicate measurements

rate to light carbon assimilation rate, r , to equal 15% for D (Laws & Bannister 1980, Geider & Osborne 1989). The growth rate in the ratio $\mu_1/[\text{CO}_2(\text{aq})]$ was calculated with instantaneous growth rates obtained from temporal changes in *S. costatum* cell concentrations.

RESULTS

Sampling station

The sampling station was located roughly in the center of the inner basin (Spjeldnesosen) of Lindåspollene at a water depth of 65 m (Fig. 1). The upper 3 m were strongly stratified with temperature and salinity values ranging from 4.4 to 6°C and 21.6 to 29.2 practical salinity units (psu) at the surface; these values ranged from 5 to 5.2°C and 29.2 to 29.8 psu at 3 m depth. Between 3 and 10 m depth the temperature varied between 5 and 5.1°C, and the salinity increased steadily to approximately 31 psu.

Inorganic measurements

Over the sampling period, alkalinity showed a trend towards higher values, ranging from 1660 to

2060 $\mu\text{eq l}^{-1}$. Extreme values of alkalinity were correlated with extreme values of salinity (Fig. 2A), suggesting that the observed variability in alkalinity was driven by the mixing of different water masses.

Total [DIC] ranged from 1520 to 1820 $\mu\text{mol l}^{-1}$. Observed variability in [DIC] closely correlated with that in alkalinity (Fig. 2B). [CO₂(aq)], calculated from alkalinity and [DIC], decreased from 14 to ca 6 $\mu\text{mol l}^{-1}$ (Fig. 2C). Dissolved silicate concentrations decreased from 9 to 2 $\mu\text{mol l}^{-1}$, while nitrate concentrations diminished from 5.6 $\mu\text{mol l}^{-1}$ to exhaustion ($\leq 0.05 \mu\text{mol l}^{-1}$) on Day 9 (Fig. 2D). Phosphate concentrations, not presented here, decreased from initially 0.47 $\mu\text{mol l}^{-1}$ to a minimum value of 0.24 $\mu\text{mol l}^{-1}$ on Day 9. Although ammonium concentrations were not measured in this study, the observed drastic increase in the suspended organic matter C/N ratio at the time of nitrate exhaustion (Fig. 3C) suggests that either ammonium concentrations were too low to compensate for nitrate deficiency or that ammonium was not effectively used by the bloom-forming phytoplankton.

Plankton community

The plankton community was composed of cryptophytes, choanoflagellates, chrysophytes (e.g. *Apedi-*

nella spinifera), dinoflagellates (e.g. *Gyrodinium* sp. and *Gymnodinium* sp.), thecate and athecate smaller dinoflagellates, ciliates, and diatoms. Among the diatoms, *Skeletonema costatum* always dominated numerically, with 93 to 97 % of the diatom abundance. The remaining 3 to 8 % was comprised of *Thalassiosira nordenskjoeldii*, *Thalassionema nitzschioides*, *Pseudonitzschia cf. delicatissima* and *Chaetoceros* spp. Size-fractionated filtration separated the POC into diatom-dominated POC (>20 μm fraction) and flagellate-dominated POC (<20 μm fraction).

Biological/organic measurements

Chl *a* concentration and the abundance of *Skeletonema costatum* increased from 3 to 15 $\mu\text{g l}^{-1}$ and from ca 4×10^5 to 1.9×10^7 cells l^{-1} , respectively, during Days 1 through 7, and remained more or less constant thereafter (Fig. 3A). $[\text{POC}]_{<20 \mu\text{m}}$ varied between 200 and 500 $\mu\text{g C l}^{-1}$, with no consistent trend over the course of the bloom (Fig. 3B). In contrast, total [POC] and the calculated $[\text{POC}]_{>20 \mu\text{m}}$ increased drastically during bloom development from 301 to 1081 $\mu\text{g C l}^{-1}$ and from 54 to 759 $\mu\text{g C l}^{-1}$, respectively. POC build-up continued until Day 10, i.e. after chl *a* concentration and *S. costatum* cell numbers had reached their maximum (Fig. 3A, B). The carbon to nitrogen (molar) ratio of the suspended organic matter fractions ($\text{POC}_{\text{total}}$, $\text{POC}_{<20 \mu\text{m}}$, and $\text{POC}_{>20 \mu\text{m}}$) was minimal on Day 7 and increased to maximum values on Days 9 and 10 (Fig. 3C).

Average growth rate, μ_{L+D} , estimated from *Skeletonema costatum* cell numbers over the period of exponential cell division (Days 1 through 7) was 0.57 d^{-1} ($r^2 = 0.996$). Growth rate calculated from changes in $[\text{POC}]_{>20 \mu\text{m}}$ over the period of exponential increase in $[\text{POC}]_{>20 \mu\text{m}}$ (i.e. Days 4 to 9) yielded a value of 0.52 d^{-1} ($r^2 = 0.967$). Instantaneous growth rate, μ_i , was $1.97 \mu_{L+D}$.

Carbon isotopic composition

$\delta^{13}\text{C}$ -DIC ranged from 0.75 to ca 1.6‰, with highest values on Days 9 and 10 (Fig. 4A) coinciding with the peak in total [POC] (Fig. 4B). Carbon isotopic composition of the 3 POC fractions ($\text{POC}_{\text{total}}$, $\text{POC}_{>20 \mu\text{m}}$, $\text{POC}_{<20 \mu\text{m}}$) increased with time (Fig. 4C). The size fraction >20 μm (dominated by diatoms) was roughly 2‰ heavier than the <20 μm fraction (dominated by flagellates). The diatom isotopic composition increased from -23 to -20‰ and remained more or less constant after Day 7. The $\delta^{13}\text{C}$ of the flagellate-dominated fraction increased continuously from -24.6 to -21.2‰. The isotopic composition of total POC increased by roughly

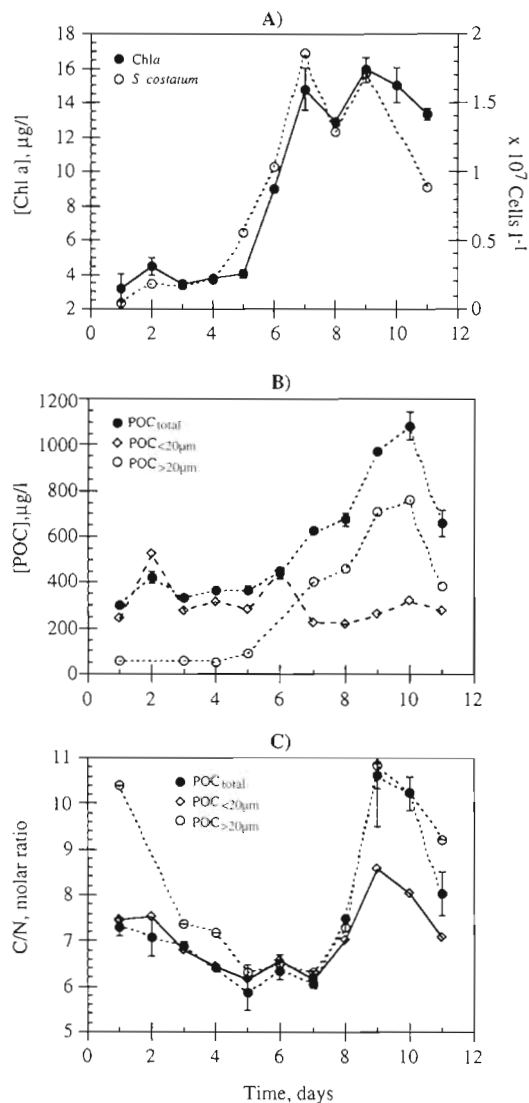


Fig. 3. (A) Concentration of chl *a* and abundance of *Skeletonema costatum*, (B) measured concentrations of $\text{POC}_{\text{total}}$ and $\text{POC}_{<20 \mu\text{m}}$, and calculated concentrations of $\text{POC}_{>20 \mu\text{m}}$, and (C) measured molar carbon to nitrogen ratios of POC size fractions in Lindåspollene during the sampling period. Error bars show ± 1 SD

5‰ from -25 to -20‰. While initially $\delta^{13}\text{C}$ of total POC was close to that of the <20 μm size fraction, it gradually shifted over the course of the bloom towards the isotopic composition of the diatom-dominated size fraction (>20 μm , Fig. 4C).

Carbon isotopic fractionation

ϵ_p of the 3 size fractions ($\text{POC}_{\text{total}}$, $\text{POC}_{>20 \mu\text{m}}$, $\text{POC}_{<20 \mu\text{m}}$) was characterized by an overall decrease over the course of the bloom (Fig. 5A). A rapid decrease in ϵ_p of

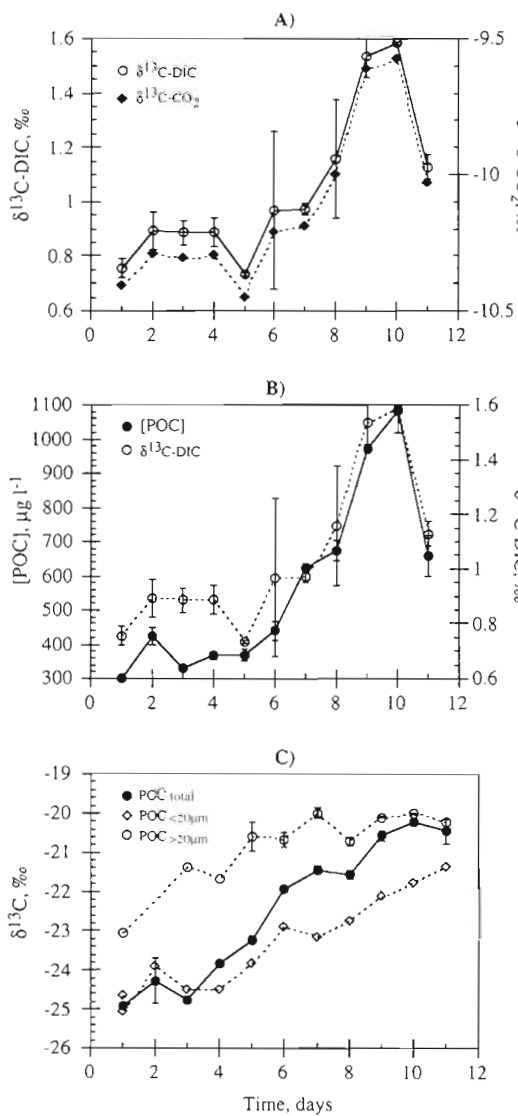


Fig. 4. (A) Carbon isotopic compositions of dissolved inorganic carbon, $\delta^{13}\text{C-DIC}$ (measured), and dissolved $\text{CO}_2(\text{aq})$, $\delta^{13}\text{C-CO}_2$ (calculated); (B) POC concentration in relation to $\delta^{13}\text{C-DIC}$; and (C) stable carbon isotopic composition of total POC, $\text{POC}_{<20 \mu\text{m}}$, and $\text{POC}_{>20 \mu\text{m}}$ at Lindåspollene during the sampling period. $\text{POC}_{>20 \mu\text{m}}$ sample of Day 2 was lost during analysis (see also Fig. 5A, B). Error bars show ± 1 SD

both total POC and the diatom size fraction ($\text{POC}_{>20 \mu\text{m}}$) occurred until Day 7, i.e. during the period of exponential increase in chl *a* and cell abundance of *Skeletonema costatum* (Fig. 3A). Whereas ϵ_p of total POC and of the $<20 \mu\text{m}$ size fraction continued to decrease until the end of the study, ϵ_p values of the $>20 \mu\text{m}$ fraction tended to level off after Day 7, when *S. costatum* cell numbers had reached their maximum. Similarly, when plotted against CO_2 concentration, ϵ_p of $\text{POC}_{>20 \mu\text{m}}$ decreased with $[\text{CO}_2(\text{aq})]$ during the development of the bloom and remained more or less con-

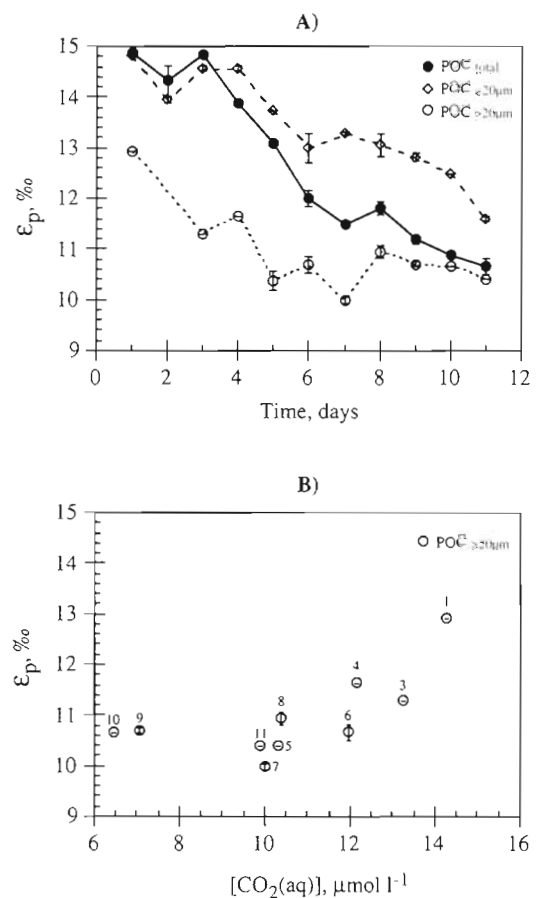


Fig. 5. (A) Carbon isotopic fractionation, ϵ_p , of total POC, $\text{POC}_{>20 \mu\text{m}}$, and $\text{POC}_{<20 \mu\text{m}}$ versus time and (B) ϵ_p of $\text{POC}_{>20 \mu\text{m}}$ as a function of $\text{CO}_2(\text{aq})$ concentration. In (B), numbers indicate sampling day. Error bars show ± 1 SE

stant with declining $[\text{CO}_2(\text{aq})]$ during the following days (Fig. 5B).

An inverse linear relationship between ϵ_p and the ratio of cellular carbon demand to carbon supply (represented by $\mu_i/[\text{CO}_2(\text{aq})]$) is expected in cases of diffusive CO_2 uptake (Laws et al. 1995, Rau et al. 1996). Such a relationship has been shown under laboratory conditions for a marine diatom culture at $\mu_i/[\text{CO}_2(\text{aq})]$ values <0.3 (Laws et al. 1995) and has been found to deviate from linearity at values higher than 0.3 (Laws et al. 1997). Reliable estimates of the growth rate in the diatom ($\text{POC}_{>20 \mu\text{m}}$) size fraction in this study are limited to the period of exponential growth, lasting from Days 1 to 7. For this interval, the instantaneous growth rate calculated from cell concentrations was $\mu_i = 1.12 \text{ d}^{-1}$. Using this number in an ϵ_p versus $\mu_i/[\text{CO}_2(\text{aq})]$ plot also yields an inverse relationship for this data set (Fig. 6A), suggesting that the dependence of ϵ_p on the ratio of carbon demand to CO_2 supply may also hold true for natural phytoplankton populations during the development of diatom blooms.

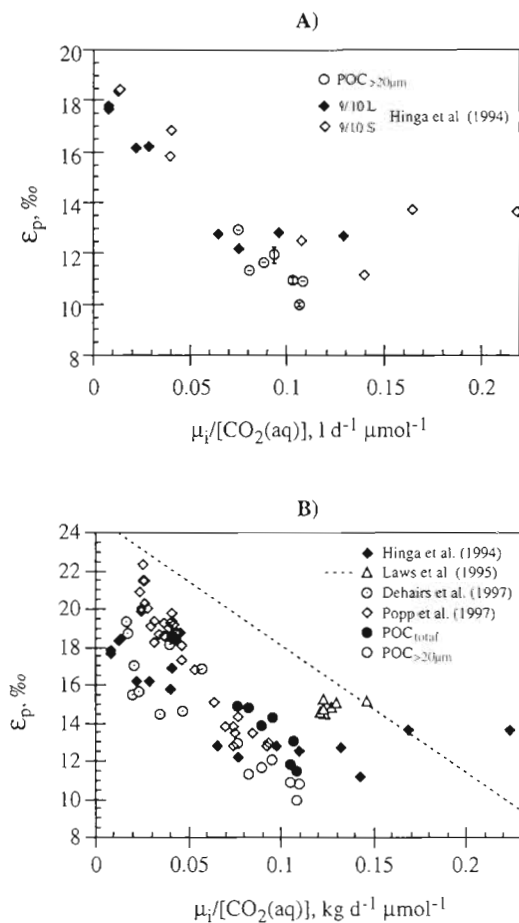


Fig. 6. (A) Carbon isotopic fractionation, ϵ_p , of $\text{POC}_{>20\mu\text{m}}$ (dominated by *Skeletonema costatum*) versus the ratio of instantaneous growth rate and CO_2 concentration, $\mu_i/[\text{CO}_2(\text{aq})]$. Error bars show \pm SE. (\blacklozenge, \circ) Data of Hinga et al. (1994) obtained in culture experiments with *Skeletonema costatum* (experimental runs 9 and 10 incubated under full light [L] and shaded light [S] conditions). (B) Comparison of data from this study with laboratory results obtained by Hinga et al. (1994) and Laws et al. (1995; dashed line), and field results obtained by Laws et al. (1995; triangles), Dehairs et al. (1997), and Popp et al. (1997). ϵ_p estimates from field measurements are for total suspended particulate organic matter. Note that $\text{CO}_2(\text{aq})$ concentrations in (B) are in $\mu\text{mol kg}^{-1}$.

DISCUSSION

Lateral advection and temporal variability

To investigate the temporal development of a phytoplankton bloom would ideally require repeated sampling within the same body of water. Due to lateral advection, this is rarely achieved in the natural environment if sampling is carried out at a fixed location. As indicated by significant changes in surface water salinity at the sampling site (Fig. 2A), lateral advection

also occurred during this study. Furthermore, total alkalinity and DIC both show considerable variability with time and correlate closely with salinity, indicating that the variability in these parameters may also be largely affected by lateral advection. This would imply that different water masses and hence different phytoplankton populations were sampled over the course of this study.

In contrast to salinity, alkalinity, and DIC, however, consistent temporal trends with little random variability were observed in biologically controlled parameters. Chl *a* concentration and the abundance of the dominant diatom species, *Skeletonema costatum*, for instance, both increased exponentially until the peak of the bloom, without any apparent variability corresponding to that observed in salinity (Fig. 3A). Similarly, a steady decline in inorganic nutrient concentrations, closely corresponding with the build-up of POC (Figs. 2D & 3B), gives little indication of random variability due to lateral advection in these parameters. A close correlation was further obtained between $\delta^{13}\text{C}$ -DIC and POC concentration (Fig. 4B), whereby the ^{13}C enrichment in DIC corresponds closely to that expected from the amount and isotopic composition of POC built up during bloom development (roughly 0.8‰ increase in $\delta^{13}\text{C}$ -DIC for $65 \mu\text{mol l}^{-1}$ POC formed). These findings suggest that in spite of lateral advection at the sampling site, the phytoplankton populations sampled during the course of this study had experienced a similar life history. Changes in nutrient concentrations, phytoplankton biomass, $\delta^{13}\text{C}$ of DIC and POC, ϵ_p , etc. are therefore considered to primarily reflect the development of a phytoplankton bloom, and not changes in water masses.

The observed variability in CO_2 concentration, on the other hand, may reflect at least partly the changes in DIC and alkalinity caused by lateral advection. Whereas both DIC and alkalinity varied by less than 20% over the study period with no consistent trend, $[\text{CO}_2(\text{aq})]$ decreased to about half of its pre-bloom concentration. This steady decline in surface water $[\text{CO}_2(\text{aq})]$ can be largely attributed to photosynthetic carbon fixation with its corresponding increase in seawater pH.

On the last day of sampling the consistent trends between nutrient decline and $[\text{POC}]$ build-up vanished. POC concentration and $\delta^{13}\text{C}$ -DIC dropped steeply and nitrate concentration increased (Figs. 2D & 4B), suggesting that on this day a fundamentally different water mass entered the fjord. In fact, the strong northerly winds with velocities close to 30 knots that swept in on Day 11, are known to cause sudden changes in coastal water masses along the Norwegian coast (Sætre et al. 1988).

Temporal trends

The temporal trends in nutrient concentrations and biological parameters suggest that we were indeed following the development of a phytoplankton bloom from the beginning until the end of the growth period. *Skeletonema costatum* abundance and chl *a* concentration increased exponentially until nitrate became the limiting nutrient, with concentrations dropping to $\leq 0.6 \mu\text{mol l}^{-1}$ (Eppley et al. 1969; Figs. 2D & 3A). At this stage, on Day 7, build-up in diatom cell density and chl *a* concentration ended, while the POC concentration continued to increase until nitrate exhaustion (Day 9, Fig. 3A, B). This rise in [POC] was paralleled by a near doubling in the C/N ratio of phytoplankton organic matter (Fig. 3C). Such an increase in the phytoplankton C/N ratio is typical for nitrogen-limited phytoplankton (Banse 1974, 1994, Sakshaug & Holm-Hansen 1977), and indicates phytoplankton bloom termination due to nitrate depletion (see Sakshaug et al. 1983, Sakshaug & Olsen 1986 for a comprehensive treatment of nutrients limiting phytoplankton blooms in Norwegian fjords).

Carbon isotope composition

$\delta^{13}\text{C}$ of the $<20 \mu\text{m}$ size fraction was consistently lighter by ca 2‰ than that of the $>20 \mu\text{m}$ fraction. This offset may be due to the different phytoplankton taxonomic groups in each size class. Whereas the smaller fraction mostly contained naked flagellates, the larger one was completely dominated by the diatom *Skeletonema costatum*. Previous observations have shown planktonic diatoms to be isotopically heavier than flagellates under identical environmental conditions (Wong & Sackett 1978, Gearing et al. 1984, Goering et al. 1990, Fry & Wainright 1991). Possible reasons for heavy diatom $\delta^{13}\text{C}$ could be higher growth rates (Banse 1982, Fry & Wainright 1991), as well as a generally larger cell size and carbon content per cell, leading to higher carbon demand of diatoms compared to other taxonomic groups (e.g. Laws et al. 1995, Rau et al. 1996).

The difference in $\delta^{13}\text{C}$ between the 2 size fractions also explains part of the ca 5‰ rise in $\delta^{13}\text{C}$ -POC_{total} observed over the course of the bloom. At the onset of the bloom the isotopically lighter $<20 \mu\text{m}$ fraction contributed $>80\%$ to the POC. This fraction decreased to $<30\%$ of POC towards the peak of the bloom (Fig. 3B). A 3 to 5‰ shift in $\delta^{13}\text{C}$ -POC during spring bloom conditions was also found by Cifuentes et al. (1988) in the Delaware estuary, USA, by Nakatsuka et al. (1992) in a mesocosm experiment, and by Rau et al. (1992) during the JGOFS North Atlantic Bloom Experiment. Over the

first half of the study of Rau et al. (1992) $\delta^{13}\text{C}$ -POC decreased from -22.9 to -19.9% . At the same time the diatom to prymnesiophyte pigment ratio shifted from 0.7 to 2. A similar change in the relative ratio of diatom to flagellate POC occurred during Days 4 to 7 in this study, with a corresponding 2.4‰ change in $\delta^{13}\text{C}$ of total POC. The $\delta^{13}\text{C}$ of the diatom size fraction increased by only 1.6‰ over this period (Fig. 4C), suggesting that the potential effect of changing environmental conditions (e.g. CO_2 concentration) on phytoplankton isotopic composition would have been significantly overestimated if based on changes in $\delta^{13}\text{C}$ of total POC.

Carbon isotope fractionation

ϵ_p of the diatom size class (POC _{$>20 \mu\text{m}$}) steadily decreased during the period of exponential growth (Fig. 5A, Days 1 to 7) and leveled off after the peak in cell density and chl *a* concentration. Decreasing ϵ_p closely corresponds to a concomitant decline in surface water $\text{CO}_2(\text{aq})$ concentration (Fig. 5B), suggesting that molecular CO_2 , at least in part, served as the source of inorganic carbon utilized by the phytoplankton.

Deviation of the isotopic signal from the correlation of ϵ_p with $[\text{CO}_2(\text{aq})]$ obtained during bloom development occurred after Day 8. Since chl *a* concentrations and *Skeletonema costatum* cell numbers started to level off at this point, this deviation may reflect a drop in phytoplankton growth rates. However, POC _{$>20 \mu\text{m}$} further increased until Day 10 (Fig. 3B), indicating that photosynthetic carbon fixation continued at about the same rate for another 2 d. During Days 9 and 10, ϵ_p should, therefore, be expected to roughly follow the trend of the previous days. On the other hand, on these days phytoplankton growth was evidently nitrate-limited (Fig. 2D). In a comparison of ϵ_p responses of a marine diatom obtained in nitrate-replete batch cultures and nitrate-limited chemostat cultures we have observed a large offset in isotope fractionation between the 2 approaches, with higher ϵ_p values for N-limited cells (Riebesell et al. unpubl.). Based on this finding, the observed deviation from the ϵ_p versus $[\text{CO}_2(\text{aq})]$ correlation, which yielded higher ϵ_p values under nitrate-limiting conditions than expected for the corresponding $\text{CO}_2(\text{aq})$ concentrations, may also be interpreted as the result of a shift from nitrate-replete to nitrate-limited growth.

The relationship between ϵ_p and $\mu_i/[\text{CO}_2(\text{aq})]$ obtained for the $>20 \mu\text{m}$ size fraction dominated by *Skeletonema costatum* largely agrees with experimental results of Hinga et al. (1994) for the same species (Fig. 6A). These authors grew *S. costatum* in dilute batch cultures at different $\text{CO}_2(\text{aq})$ concentrations and

growth rates. The 2 data sets differ from each other at low $[\text{CO}_2(\text{aq})]$ [i.e. high values of $\mu_i/[\text{CO}_2(\text{aq})]$], where isotope fractionation reported by Hinga et al. (1994) also clearly deviated from a linear ϵ_p versus $\mu_i/[\text{CO}_2(\text{aq})]$ correlation. This difference could be related to the fact that calculations from the data set of Hinga et al. (1994) were based on a single growth rate for the entire range of CO_2 concentrations in each of the experimental runs (see Table 1 in Hinga et al. 1994). Lower growth rates under low $[\text{CO}_2(\text{aq})]$, for example, could reconcile the observed differences. It should be noted here that ϵ_p estimates from field measurements are for total suspended particulate organic matter (i.e. with contributions from heterotrophic organisms and detrital organic material), whereas experimental data correspond to pure algal biomass. An offset of 1.4‰ between phytoplankton and bulk particulate organic matter has been estimated by Laws et al. (1995). Applying this offset to the experimental data of Hinga et al. (1994) would lower ϵ_p values in their data set by this amount.

Comparison of data obtained in this and in the study of Hinga et al. (1994) with previous field investigations (Laws et al. 1995, Dehairs et al. 1997, Popp et al. 1997) in an ϵ_p versus $\mu_i/[\text{CO}_2(\text{aq})]$ plot shows reasonable agreement between these data sets (Fig. 6B). Still, for any given value of $\mu_i/[\text{CO}_2(\text{aq})]$, ϵ_p spans a range of several per mille. Part of this range may be due to different approaches in determining phytoplankton growth rate. Dehairs et al. (1997) measured $\delta^{13}\text{C}$ -POC in the Southern Ocean between 47° and 55°S and estimated instantaneous growth rates from carbon-specific production rates (24 h ^{14}C incubations) corrected for the phytoplankton proportion of total [POC]; ϵ_p was calculated assuming a constant $\delta^{13}\text{C}$ - $\text{CO}_2(\text{aq})$ of -10‰ (Dehairs et al. 1997). The growth rate in the study of Laws et al. (1995) in the Equatorial Pacific was estimated from $[\text{CO}_2(\text{aq})]$ data using a linear regression between $\mu_i/[\text{CO}_2(\text{aq})]$ and ϵ_p obtained from N-limited *Phaeodactylum tricornutum* chemostats, corrected for photoperiodic length and respiration. As discussed below, application of this relationship to carbon isotope data obtained from N-replete natural populations may be problematic. To estimate photoperiodic growth rate, Popp et al. (1997) used Eppley's (1972) growth rate versus temperature relationship and assumed temperature-limited growth for their WOCE SR-3 data (obtained between 45° and 65°S for suspended particulate organic matter). Since this relationship predicts maximum potential growth rates for any given temperature, it is likely to overestimate phytoplankton growth rates in the field. Actual values of $\mu_i/[\text{CO}_2(\text{aq})]$ for the data of Popp et al. (1997) are therefore likely to be lower than those plotted in Fig. 6B, which would result in closer agreement with the other results.

As discussed earlier, considerable variability in phytoplankton isotope fractionation may also result from differences in species composition. The fact that this may also have contributed to the large scatter of ϵ_p in the comparison of field data presented in Fig. 6B is indicated by the data set of Dehairs et al. (1997). For $\mu_i/[\text{CO}_2(\text{aq})]$ values of 0.035 to 0.04, for example, these authors obtained ϵ_p values of 14.5 and 18.5‰. Whereas the lower value corresponded to a phytoplankton community dominated by diatoms, the high ϵ_p value was obtained for phytoplankton composed of equal proportions of diatoms, green algae, and prymnesiophytes (Fig. 4 in Peeken 1997). Lower isotope fractionation for diatoms and diatom-dominated phytoplankton is, in fact, consistent with differences in $\delta^{13}\text{C}$ observed between the 2 size fractions in this study, as well as with earlier reports on diatoms being isotopically heavier than other phytoplankton species (e.g. Fry & Wainright 1991, Pancost et al. 1997).

As previously noted (Pancost et al. 1997, Popp et al. 1997), a considerable offset exists between the bulk of the field estimates and results obtained in culture experiments with the marine diatom *Phaeodactylum tricornutum* by Laws et al. (1995, dashed line in Fig. 6B). While this offset may be due to species-specific differences in ϵ_p responses related to, among other factors, cell size (Rau et al. 1996), cell geometry (Rau et al. 1997, Popp et al. 1998) or carbon acquisition mechanisms (Raven et al. 1993), it may also reflect differences in the nutritional status of the phytoplankton. Whereas experiments by Laws et al. (1995) were conducted in N-limited chemostats, Hinga et al. (1994) used N-replete batch culture incubations. In accordance with the latter study, all field estimates presented in Fig. 6B were determined on particulate organic matter produced under N-replete conditions.

Conclusions

A steady increase in the carbon isotope composition of total organic matter over the course of the diatom bloom was partly caused by a shift in species composition from a flagellate- to a diatom-dominated community. Isotope fractionation of the >20 μm size fraction, dominated by the diatom *Skeletonema costatum*, correlated with surface water CO_2 concentration over the period of bloom development. Deviation from this correlation occurred after cell density and chl *a* concentration had peaked and may be related to changes in phytoplankton growth rate and/or possible effects of nitrogen-limited growth on isotope fractionation. Comparison with field data from previous investigations shows general agreement in the presence of an inverse relationship between ϵ_p and $\mu_i/[\text{CO}_2(\text{aq})]$, with rela-

tively good correspondence in the slope of this relationship. However, there is considerable scatter in ϵ_p for any given ratio of growth rate and CO_2 concentration.

The results of this study show that changes in environmental conditions, for example as encountered during the course of a phytoplankton bloom, are imprinted in the carbon isotope composition of the particulate organic matter produced. In addition to CO_2 concentration and growth rate, isotope fractionation of marine phytoplankton may also be influenced by taxon-specific differences and the nutritional status of the cells. While taxon-specific biomarkers can help to resolve species-related variability in the isotopic signal, the utility of sedimentary organic matter $\delta^{13}\text{C}$ as a proxy for growth rate or $[\text{CO}_2(\text{aq})]$ may be further complicated by the potential influence of other environmental factors on phytoplankton isotope fractionation.

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