Vol. 76: 149–157, 1991 | MARINE ECOLOGY PROGRESS SERIES
Mar. Ecol. Prog. Ser. | Published September 26

Diatom sources of ^{13}C-rich carbon in marine food webs

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ABSTRACT: We used stable isotope measurements to investigate the possible nutritional importance of diatoms for consumers in planktonic food webs. Several lines of evidence indicated that rapidly growing diatoms had ^{13}C-rich isotopic compositions in the Georges Bank (USA) ecosystem. Diatoms in spring blooms and in well-mixed summer waters were relatively rich in ^{13}C, with $\delta^{13}C$ values in the −15 to −19‰ range, while other phytoplankton and most particulate organic matter collected over a 13 mo period had ^{13}C-depleted values of −21 to −25‰. Culture experiments with nutrient-enriched seawater performed on Georges Bank and in Woods Hole Harbor (MA, USA) also showed a ^{13}C distinction between fast-growing diatoms with ^{13}C-rich contents and other algae that were depleted in ^{13}C. Zooplankton from central Georges Bank where diatoms are abundant had relatively high $\delta^{13}C$ values, consistent with an important nutritional role for ^{13}C-rich diatoms. We estimate that a minimum of 40% of the carbon present in zooplankton consumers of central Georges Bank is derived from diatoms. Bloom diatoms from the North Atlantic, northeastern Pacific, and the nearshore Gulf of Mexico also had ^{13}C-rich compositions, indicating that diatoms can be a source of ^{13}C-rich carbon in many marine food webs.

INTRODUCTION

Carbon isotopic measurements have been made in many marine food webs, with the consistent result that consumers are enriched in ^{13}C by 2 to 8‰ relative to particulate organic matter (POM) (Fry & Sherr 1984). Several reasons for this trophic ^{13}C increase have been advanced. The cycling of carbon in food webs may involve cumulative isotopic fractionation in loss of respiratory CO_2 (McConnaughey & McRoy 1979), or reflect reliance on carbohydrates and proteins that are relatively ^{13}C-rich (Fry et al. 1984, Stephenson et al. 1986). Another explanation is that among the phytoplankton, some groups or species are ^{13}C-rich, and these algae are heavily grazed and provide most of the carbon important in food webs. Algal groups that have been shown to be ^{13}C-rich in field collections include diatoms and large, filamentous cyanobacteria. These algae can be 3 to 7‰ enriched in ^{13}C relative to POC (particulate organic carbon) collected on filters, with $\delta^{13}C$ values of oceanic POC averaging near −23‰ and ^{13}C-rich diatoms and filamentous cyanobacteria averaging −15 to −20‰ (Craig 1953, Fry & Parker 1979, Gearing et al. 1984, Cifuentes et al. 1988). It is possible that the role of ^{13}C-rich diatoms had been underestimated in previous studies because these algae are heavily grazed, relatively rare, and therefore hard to sample.

Our investigations centered on the Georges Bank ecosystem (see Fig. 1) where diatoms are common in spring blooms, in tidally mixed waters of the central shoals region (< 60 m deep), and in surrounding frontal waters (O'Reilly & Evans-Zetlin 1982, Cura 1987, Horne et al. 1989). Dominance of large diatoms declines in deeper waters to the north and south of the central shoals, where resuspension of diatoms is less frequent (Cura 1987). Although diatoms are thus common and account for a substantial part of the high primary productivity of central Georges Bank (O'Reilly et al. 1987), we had no estimates of the overall food-web importance of diatoms for planktonic consumers on Georges Bank.

To document the occurrence and importance of ^{13}C-rich diatoms in the Georges Bank food web, we analyzed carbon isotopic compositions of POM, phytoplankton isolated from nets, phytoplankton grown in seawater enrichment cultures, and zooplankton consumers. We also measured zooplankton $\delta^{15}N$ to indicate zooplankton trophic level (Minagawa & Wada 1984, Fry 1988). The results indicate that diatoms from blooms and frontal areas have ^{13}C-rich compositions, and that these ^{13}C-rich labels can be traced into zoo-

0171-8630/91/0076/0149/$ 03.00

plankton grazers. Analyses of phytoplankton bloom samples from the Atlantic, Pacific and Gulf of Mexico confirmed that ^{13}C enrichment in diatoms is a common phenomenon in temperate and sub-tropical waters.

METHODS

Sample collection. ***Georges Bank and Gulf of Maine:*** From 1988 to 1990, samples were collected from Georges Bank and the southern part of the Gulf of Maine (Fig. 1). POM samples were collected from surface water with a bucket, screened through a 100 µm

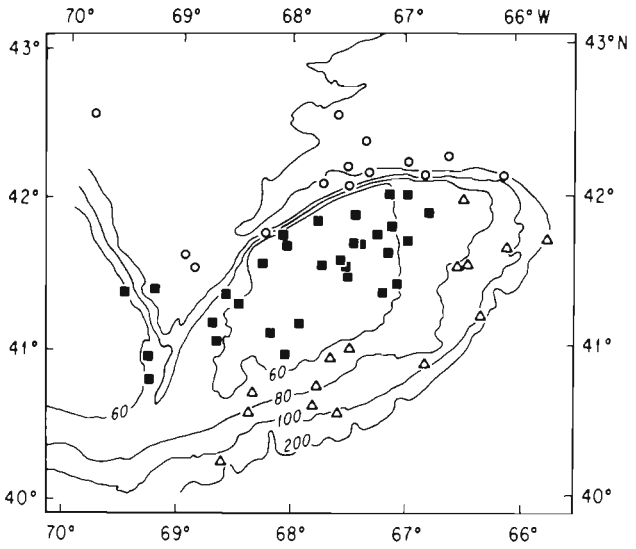

Fig. 1. Collection stations on Georges Bank and in the southern Gulf of Maine, USA. Stations were located in 3 areas: deep stratified waters of the southern Gulf of Maine (○), mixed shallow waters in central shoal areas (■), and deeper stratified waters along the southern and eastern flank of Georges Bank (△)

mesh net to remove large zooplankton, and either filtered onto precombusted (900 °C, 1 h) Whatman QM-A quartz fiber filters (effective pore size ca 1.2 µm) or, for net POM, filtered with a 20 µm mesh net, then washed onto a QM-A filter Large phytoplankton from spring blooms were obtained with 333 and 505 µm mesh nets. These net samples were visibly clogged with green phytoplankton, and were >95% purely algal when viewed under a dissecting microscope. In August 1988, net phytoplankton were obtained by pumping large volumes of seawater through a 20 µm mesh net. Retained material was then screened again to obtain algae between 40 and 110 µm and, when viewed under a Leitz compound microscope, judged to be >95% purely algal (mostly *Coscinodiscus* sp. centric diatoms).

Zooplankton samples were collected with bottom-to-surface or surface tows using 128 to 505 µm mesh nets. Individual animals >1 cm in length (larval fish, chaetognaths, amphipods, shrimp, euphausiids) were removed from zooplankton samples before analysis. One exception occurred in samples collected during August 1988, when zooplankton were wet-sieved into separate size categories spanning 64 to 8000 µm, and then analyzed.

Sediment trap materials collected between February and November 1982 from the southern margin of Georges Bank (Parmenter et al. 1983) were also analyzed for isotopic composition. These samples had been preserved with salt or sodium azide in moored traps, then stored frozen until analysis.

Other areas: For comparison with the Georges Bank results, POM and net phytoplankton were obtained from phytoplankton blooms in 3 other areas. POM and net phytoplankton from an offshore bloom of diatoms in the Mississippi River plume were collected 19 and 20 April 1988 in the area bounded by 27° 52′ N, 29° 07′ N, 89° 37′ W and 89° 45′ W. POM samples from the 1989 North Atlantic spring bloom were collected from 29 April to 3 May 1989 in the area bounded by 39° 57′ N, 40° 33′ N, 47° 02′ W and 47° 14′ W. POM was also collected during inshore upwelling conditions from 31 May to 10 June 1989 off the Washington coast at 48° 13′ N from 124° 57′ to 127° 14′ W.

Cultures. To obtain mixed species cultures, we added nutrients (phosphate, nitrate, and in some cases silicate) to natural surface seawater from Georges Bank and Woods Hole Harbor. Final nutrient concentrations were ca 500 to 1000 µM N, 100 µM P, and, where added, 50 µM Si. Tris buffer was added to a final concentration of 2 mM in many experiments and the pH adjusted to 7.5–8.3 with HCl and NaOH to manipulate CO_2 [aqueous (aq)] concentrations in cultures. The resulting nutrient-enriched seawater medium was either filtered with a Whatman QM-A filter and inoculated with >20 µm POM, or left unfiltered with the natural phytoplankton assemblage as an inoculum. The enriched seawater was dispensed into 1 l clear polycarbonate bottles, and incubated in flowing seawater for up to 8 d on board ship or near a dock under natural day/night light cycles. A relatively small amount of algal growth occurred on walls, and algae were kept well suspended by natural rocking conditions of the outdoor incubations. Sealed bottles were sacrificed at 1 to 2 d intervals and subsamples taken for determination of pH, CO_2 (aq) calculated from acid titration (Parsons et al. 1984), chlorophyll *a* (Holm-Hansen et al. 1965), and $DI^{13}C$ (dissolved inorganic ^{13}C) and $\delta^{13}C$ of POM retained on QM-A filters. Subsamples of the seawater cultures were examined with 100 to 1000× magnification for identification of dominant phytoplankton species.

Isotopic discrimination factors or D factors (O'Leary

1981) for these closed-system experiments were calculated from the average differences between DIC and POM $\delta^{13}C$ values for the last 2 samples in each experiment. We used the last 2 samples because they best reflect new growth and were least affected by POM in inocula. Rearranging equations given in Mariotti et al. (1981),

$$D = (\delta^{13}C_{DIC} - \delta^{13}C_{cells})(f-1)/(\ln f)$$

where f is the fractional extent of reaction measured as loss of carbon from the DIC pool.

Analytical procedures. ***Filters:*** Filters were spotted with up to 20 drops of 1 N HCl containing 1 % chloroplatinic acid, dried without rinsing at 55 °C, and ground to a fine powder with 1 g CuO using a stainless steel mortar and pestle (Wig-L-Bug). Powdered filters were sealed in evacuated vycor tubes with 0.5 g copper metal, combusted at 750 °C for 3 h, then allowed to slowly cool to room temperature over 4 h. Combusted tubes were broken in an evacuated gas manifold, pure CO_2 isolated via cryogenic distillation and its mass estimated with a calibrated electronic manometer. Mass balance was used to correct filter results for blanks which averaged 12 µmol filter^{-1} and −24.4 ‰ $\delta^{13}C$. Corrections were typically < 0.5 ‰ $\delta^{13}C$ and always < 1‰.

Zooplankton, phytoplankton, and sediment trap material: Samples were dried in glass vials at 60 °C, acidified with 1 N HCl and redried. Lipids were extracted from some zooplankton samples with a 2:1 mixture of chloroform:methanol for 15 min at 60 °C (Folch et al. 1956). The extract containing lipids was discarded and the solid lipid-free residue redried for isotopic determination.

Dissolved inorganic carbon: DIC samples of 80 to 250 ml were collected in glass or polyethylene bottles, poisoned with 1 ml of saturated $HgCl_2$ solution, and stored tightly stoppered in the dark. Isolation of CO_2 from DIC samples for concentration and isotopic determinations followed procedures of Kroopnick (1974).

Isotopic determinations were made with Finnigan 251 or Delta S isotope ratio mass spectrometers. Measurements were made relative to commercial high-purity tank gases that had been calibrated against international standards. Results are reported relative to the isotopic compositions of nitrogen in air ($\delta^{15}N$) and carbon in PDB ($\delta^{13}C$), where

$$\delta^{13}C \text{ or } \delta^{15}N = ([R_{sample}/R_{standard}] - 1) \times 1000$$

and $R = {}^{13}C/{}^{12}C$ or ${}^{15}N/{}^{14}N$, respectively. Replicates carried through these procedures usually differed by less than 0.2 ‰ for POM, zooplankton or phytoplankton samples, and less than 0.1 ‰ for $DI^{13}C$. Samples that are ^{13}C-rich have less negative (higher) $\delta^{13}C$ values ralative to samples that are ^{13}C-depleted with more negative (lower) $\delta^{13}C$ values.

Statistical analyses were performed with procedures given in Sokal & Rolf (1981). Uncertainties given after mean values are 95 % confidence intervals.

RESULTS

Carbon isotopic compositions of phytoplankton, POM and zooplankton ranged from −15.5 to −26 ‰ on Georges Bank, a range of ca 10 ‰. Net and bulk POM collected together from the same stations did not differ significantly ($p > 0.05$, t-test) in carbon isotopic compositions (average $\delta^{13}C_{net} - \delta^{13}C_{bulk}$ difference = 0.6 ± 0.6 ‰, n = 21), and are therefore considered together as POM in further analyses.

There was limited evidence for ^{13}C-enriched POM and zooplankton $\delta^{13}C$ values where diatom production is most pronounced in the mixed central shoals and surrounding frontal areas (Fig. 2). In 2 of 7 POM collections (March and October 1988), and 2 of 6 zooplankton collections (March and August 1988), average values from the central shoals region showed significant ^{13}C enrichment relative to values from deeper stratified waters ($p < 0.05$, t-test). The strongest $\delta^{13}C$ differences between the 2 regions occurred during the 1988 spring bloom, and in late summer 1988. In the 1988 spring bloom, POM over the central shoals region was enriched in ^{13}C by 3.1 ‰ vs samples from deeper waters (−20.9 ± 0.5 vs −24.0 ± 0.7 ‰). DIC samples collected at the same time showed some evidence for ^{13}C-enrichment on Georges Bank. Six DIC samples collected on Georges Bank averaged 2.75 ± 0.2 ‰, and were 0.7 to 1.0 ‰ enriched in ^{13}C relative to the 1.7 and 2.1 ‰ values for 2 Gulf of Maine samples (Fig. 2).

No net phytoplankton were obtained in the spring 1989 sampling (no blooms of large phytoplankton were encountered), but bloom samples were again obtained in 1990. Combining the 1988 and 1990 data, samples collected towards the end of the spring bloom period in late March and early April were generally ^{13}C-rich, with $\delta^{13}C$ values of −20.6 to −18.4 ‰, averaging −19.4 ± 1.1 ‰ (Fig. 3). Only one April sample had a ^{13}C-depleted −21.7 ‰ value. This sample was collected in deep waters along the southern margin of Georges Bank while the other samples were collected in shallow shoals water.

Summer sampling showed that ^{13}C-rich values for net phytoplankton were not confined to bloom periods. In August 1988, large 40 to 60 µm diameter *Coscinodiscus* sp. had $\delta^{13}C$ values of −15.5 ‰ and were common in net samples from the central shoals region and the frontal areas to the northeast of the shoals. Chlorophyll and visual analyses showed that *Coscinodiscus* sp. did not dominate the bulk POM in these areas, which had fairly typical −21.2 to −21.9 ‰ values (Fig. 2). Other

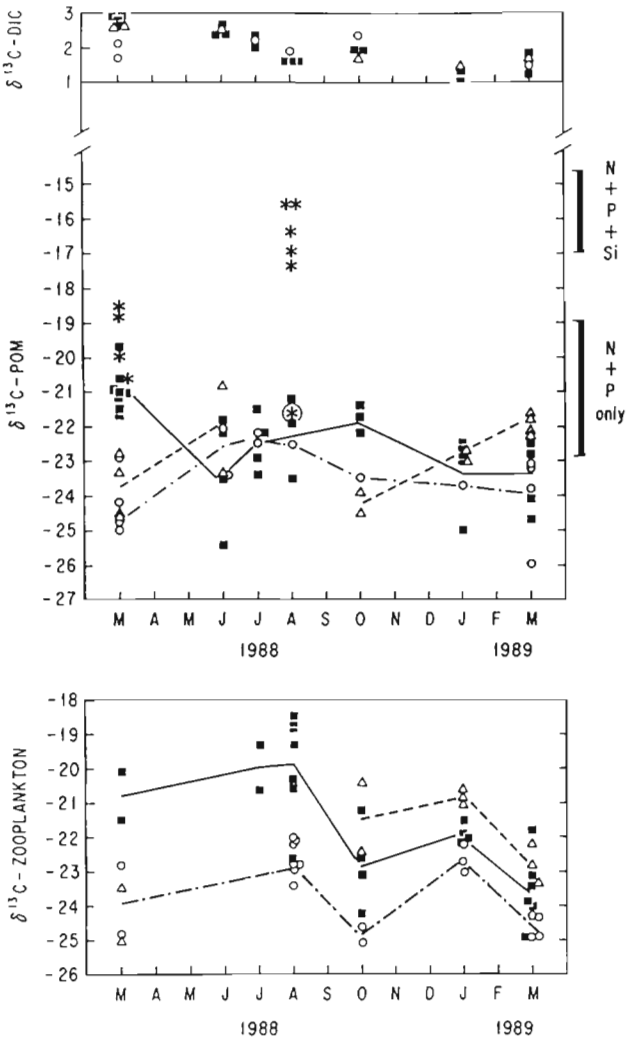

Fig. 2. Seasonal variations in $\delta^{13}C$ values of dissolved inorganic carbon (top), net phytoplankton and particulate organic material (middle), and zooplankton (bottom) in the Georges Bank region. Symbols as in Fig. 1, with net phytoplankton indicated by ✻ and (✻) for central Georges and the Gulf of Maine, respectively. Lines connect average values in each subarea: mixed waters on Georges Bank (——), stratified waters on Georges Bank (– – –) and stratified waters in the Gulf of Maine (· – –). Bars at right of center panel show algal culture results extrapolated to field POM values (extrapolated values were calculated using fractionation factors listed in Table 1 and assuming an average value of 2‰ for $DI^{13}C$)

phytoplankton collected on this August cruise also lacked a ^{13}C-rich composition, e.g. large >100 µm long *Orthoceratium longipes* dinoflagellates from the Gulf of Maine had a −21.6‰ value.

We also studied algal $\delta^{13}C$ in semi-natural seawater enrichment cultures. As in natural samples, $\delta^{13}C$ values of phytoplankton were 15 to 25‰ depleted in ^{13}C relative to DIC, reflecting isotopic fractionation in photosynthetic uptake of carbon (Fig. 4). Cultures with added N + P + Si had significantly smaller average discrimination factors than cultures with added N + P only (17.9 ± 0.4 vs 22.5 ± 0.6‰; Table 1). Phytoplankton in cultures with added Si had faster growth rates (Table 1) and were dominated by pennate and centric diatoms of the genera *Skeletonema, Leptocylindricus, Asterionella, Ditylum,* and *Coscinodiscus.* Phytoplankton in cultures without added silica had slower growth rates and were dominated by cryptomonads, dinoflagellates and chrysophytes, with few diatoms. Culture experiments showed that isotopic fractionation declined with increasing growth rates (Fig. 5) and was not strongly correlated with other factors that included incubation

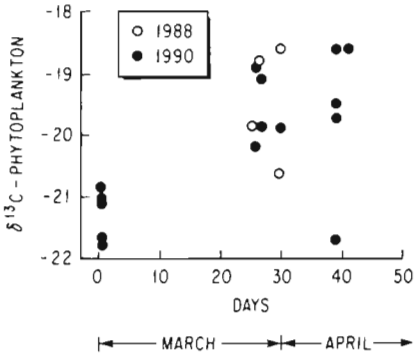

Fig. 3. $\delta^{13}C$ values of net phytoplankton collected during spring bloom periods on Georges Bank, 1988 and 1990

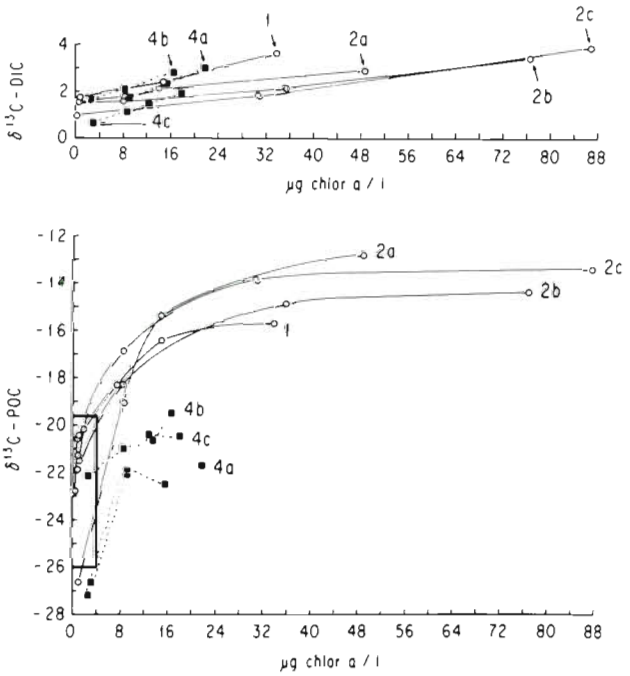

Fig. 4. Carbon isotopic changes during phytoplankton growth in culture experiments performed on Georges Bank (see Table 1). Diatoms growing in cultures with added silica (▫) had higher $\delta^{13}C$ values than did algae growing in cultures that lacked silica amendment (▪). For reference, framed area shows normal range of POM $\delta^{13}C$ values from Georges Bank

Table 1 Carbon isotopic discrimination factors (D) for phytoplankton grown in seawater enrichment cultures

Expt[a]	Temp. (°C)	pH[b]	CO_2 (aq)[c] (μM)	Growth rate[d] (doublings d^{-1})	POC (μg l^{-1}) Initial	Final	D[e] (‰)
Si+N+P added							
(1) Georges Bank	20–23	8.62	2	1.16	140	820	19.0
(2a) Georges Bank	20–23	7.58[f]	35	1.79	250	1600	16.6
(2b) Georges Bank	20–23	8.42	4	1.11	380	2240	17.4
(2c) Georges Bank	20–23	8.46[f]	4	1.50	180	2040	17.5
(3a) Woods Hole	14–20	8.58[f]	3	–	300	5990	18.4
(3b) Woods Hole	14–20	8.49[f]	3	–	1090	6850	18.5
						$\bar{x}$ ± 95 % CL:	17.9 ± 1.0
N + P added							
(4a) Georges Bank	20–23	7.63[f]	30	0.54	260	920	24.7
(4b) Georges Bank	20–23	8.15	8	0.34	420	790	22.7
(4c) Georges Bank	20–23	8.36[f]	4	0.59	260	780	22.1
(5a) Woods Hole	14–20	8.37[f]	5	–	300	2160	20.9
(5b) Woods Hole	14–20	8.51[f]	3	–	1090	5450	22.3
						$\bar{x}$ ± 95 % CL:	22.5 ± 1.7

[a] Expts 1, 2 and 4 were conducted in August 1988 shipboard over central Georges Bank for 4 to 6 d, and Expts 3 and 5 were conducted in October 1989 in Woods Hole Harbor for 6 to 8 d. Inocula included < 20 μm POM (Expts 3a, 4a to c and 5a) or POM > 20 μm and < 110 μm (other experiments)
[b] Average of pH measurements for the final 2 samples of each experiment
[c] Calculated from total CO_2 (DIC) and pH according to Butler (1982)
[d] Estimated from chlorophyll increase between last 2 bottles harvested
[e] D determined from average values of final 2 bottles in each experiment (see 'Methods')
[f] Buffered with Tris

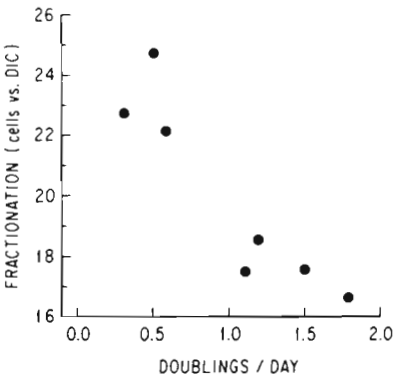

Fig. 5. Carbon isotopic fractionation in seawater enrichment cultures as a function of phytoplankton growth rate (from Table 1)

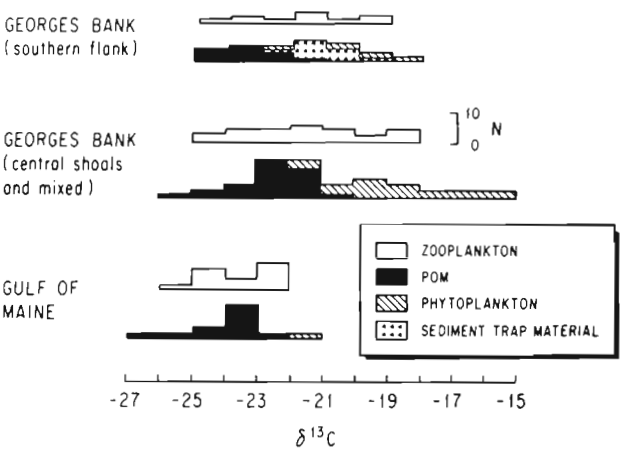

Fig. 6. Histogram of $\delta^{13}C$ values of zooplankton POM, net phytoplankton and sediment trap materials from different sectors of the Georges Bank ecosystem. Highest ^{13}C contents occur in the central shoals area of Georges Bank. Sediment trap samples were collected in 1982; all other samples were collected from 1988 to 1990

temperature, pH, and CO_2 (aq) concentration (Table 1).

We analyzed zooplankton to check whether ^{13}C-rich compositions of algae were transferred to higher trophic levels. Zooplankton from the Gulf of Maine had ^{13}C-depleted values in a relatively narrow −22.0 to −25.1‰ range (Fig. 6). Zooplankton samples from Georges Bank had an overlapping $\delta^{13}C$ range, with $\delta^{13}C$ values of half the samples falling in the same −22 to −25‰ range, and half the samples showing ^{13}C enrichment with values in the −18.5 to −22.0‰ range (Fig. 6). An additional component of ^{13}C-rich zooplankton was thus present on Georges Bank, but absent in the Gulf of Maine samples, consistent with a stronger transfer of ^{13}C-rich carbon from diatoms to consumers on Georges Bank. Average isotopic values were significantly different (*t*-test, $p < 0.05$) between Gulf of Maine

(−23.4 ± 0.5‰) and Georges Bank (−22.0 ± 0.6‰) zooplankton samples.

Additional analyses showed this average regional difference in zooplankton $\delta^{13}C$ was not due to feeding at different trophic levels or effects of lipid storage. Zooplankton from Georges Bank and the Gulf of Maine had similar trophic positions, as measured by $\delta^{15}N$ values (Fig. 7), suggesting that regional differences in

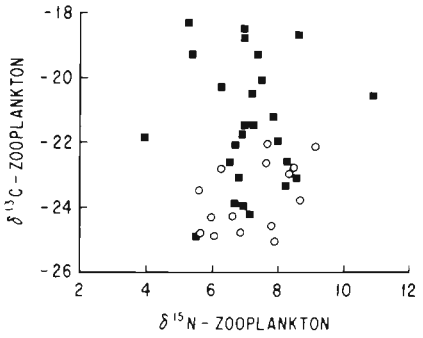

Fig. 7. Relationship between zooplankton $\delta^{13}C$ values and $\delta^{15}N$. Symbols denote region of collection, as in Fig. 1

$\delta^{13}C$ were not due to trophic level differences. Lipid storage also played a relatively minor role in the regional differences, since lipid extraction only slightly decreased observed differences. For example, 3.3‰ of a large 3.9‰ regional difference in $\delta^{13}C$ values of zooplankton that were collected in August 1988 persisted after lipid extraction. Before lipid extraction, seven August 1988 samples averaged −22.7 ± 0.5 and −18.8 ± 1.0‰ from the Gulf of Maine and the central shoals region of Georges Bank respectively, and after lipid extraction, −20.6 ± 0.6 and −17.3 ± 1.3‰.

Analyses of POM from other blooms in the North Atlantic, off the Mississippi River and off the northwestern US coast showed that relatively high values of −18.5 to −21.5‰ are common but not ubiquitous where diatoms are important (Fig. 8). Chlorophyll concentrations during blooms in these areas were 0.5 to 1.5, 20 to 40 and 1 to 8 μg l^{-1}, respectively (G. Harrison, E. Walser, and T. Bates pers. comm.). Surface water samples collected for $DI^{13}C$ measurement in the Mississippi and Washington studies averaged −1.7 ± 0.5‰ and +1.5 ± 0.3‰, respectively.

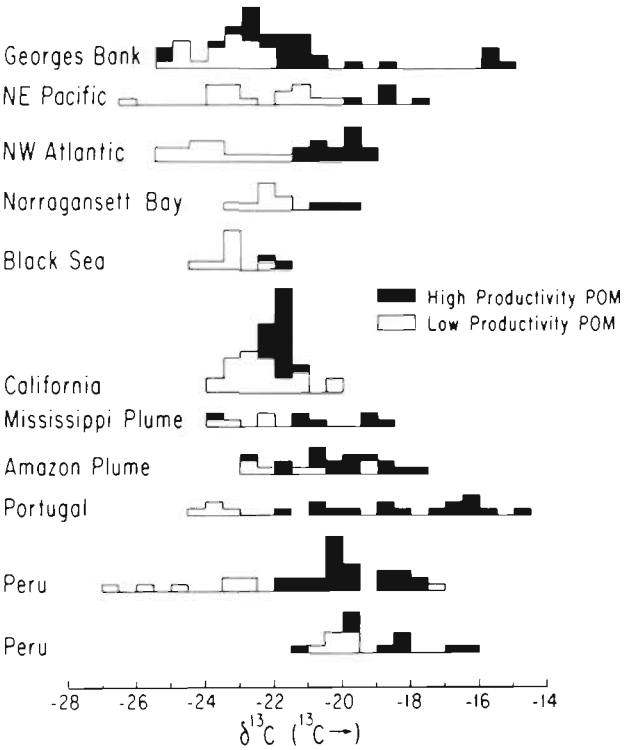

Fig. 8. $\delta^{13}C$ values of particulate organic matter (POM) from marine ecosystems. Samples from high-productivity (> 1 μg l^{-1} chlorophyll) regions (upwelling zones, blooms) are generally enriched in ^{13}C vs samples from more oligotrophic areas that are stratified and have chlorophyll *a* contents < 1 μg l^{-1}. Sources include: present study for Georges Bank, NE Pacific, Mississippi Plume and spring bloom in the NW Atlantic; Dickson (1986) for lower-productivity NW Atlantic off Newfoundland; Gearing et al. (1984), Narragansett Bay; Deuser (1970), Black Sea; Rau et al. (unpubl.), California; Cai et al. (1988), Amazon plume; Descolas-Gros (1983), Portugal; Libes (1983), Peru (upper); Degens et al. (1968a), Peru (lower) (samples include mixed phytoplankton and zooplankton)

DISCUSSION

Algal growth rate and isotopic fractionation

Growth rate was the best predictor of isotopic fractionation and algal $\delta^{13}C$ in this study (Fig. 5), in agreement with recent studies of corals and macroalgae that also show increased ^{13}C content at high growth rates (Wefer & Killingley 1986, Fischer 1989, Muscatine et al. 1989). Unfortunately, the precise physiological basis of ^{13}C enrichment in fast-growing diatoms and other algae is not yet fully understood. Correlation analysis (Rau et al. 1989) has indicated that the concentration of free CO_2 dissolved in seawater, CO_2 (aq), could be an important control of isotopic fractionation in marine phytoplankton. However, in our experimental culture work, we did not find a strong influence of CO_2 (aq) concentration on isotopic fractionation (Table 1).

Through their interactions with growth rate, temperature and nutrient supply may be more important controls of isotopic fractionation in diatoms. Previous culture work with diatoms growing at 10 to 30 °C has shown a trend towards lower $\delta^{13}C$ values at lower temperatures (Degens et al. 1968b, Wong & Sackett 1978) where growth rate may have been slower. In qualitative agreement with those studies, we found the lowest (−21 to −22‰) values for net diatoms on

Georges Bank in 4 °C waters at the end of the winter and beginning of the spring bloom (Fig. 3), and the highest (−15.5 ‰) values for *Coscinodiscus* sp. in 20 °C summer waters. Nutrient uptake may also influence diatom $\delta^{13}C$. Fixation of ^{13}C-rich bicarbonate by C_4 enzymes has been suggested as a possible source of ^{13}C enrichment in phytoplankton (Descolas-Gros & Fontugne 1985, Falkowski 1991), and Guy et al. (1989) have recently shown that rapid N assimilation in algae increases uptake of bicarbonate via PEP carboxylase. Diatoms are known for their ability to rapidly incorporate nitrogen (Wilkerson & Dugdale 1987, Zimmerman et al. 1987), and accompanying increases in bicarbonate uptake could generally account for ^{13}C-rich values of diatoms in nutrient-rich waters (Fig. 8).

While the precise physiological basis of isotopic distributions in marine POM remains somewhat speculative, a growth-rate-based model of isotopic fractionation could account for the wide $\delta^{13}C$ range reported for marine diatoms. For example, while this study shows that diatoms can have ^{13}C-rich values of −15.5 ‰ in offshore waters, previous field studies show that diatoms can also have ^{13}C-depleted values of −26 to −32 ‰, especially in Antarctic waters (Sackett et al. 1965, Rau et al. 1982, Wada et al. 1987). These low values are not inconsistent with a model that states that isotopic fractionation is inversely related to growth rate, since Antarctic diatoms are known to have low growth rates (Sommer 1989) and fractionate strongly during photosynthetic carbon uptake (Fischer 1989). Higher growth rates of Georges Bank diatoms could explain their ^{13}C-rich values.

High lipid content of Antarctic diatoms could also potentially contribute to the ^{13}C-depleted values of the Antarctic flora. Lipid content of diatoms averages near 25 % (Shifrin & Chisholm 1981), with most carbon fixation routed to lipid synthesis in cold, < 0 °C Antarctic waters (Smith & Morris 1980). However, ^{13}C-depleted values of −27 to −28 ‰ are still calculated for Antarctic phytoplankton after lipid removal (Sackett et al. 1965), suggesting that ^{13}C depletion is not solely a function of lipid storage. Measuring isotopic compositions of lipids such as fucoxanthin, a common diatom pigment, may be helpful in future studies of diatom $\delta^{13}C$ variation in different systems.

Diatom contributions to food webs

While it is frustrating that diatoms most often cannot be isolated for direct isotopic analyses, evidence accumulated from net phytoplankton and POM collections (Fig. 8) and from culture work (Fig. 4) indicates that diatoms are often a source of ^{13}C-rich carbon in marine ecosystems. A ^{13}C-rich composition for diatoms is most closely associated with the end of blooms or rapid diatom growth in well-mixed and frontal waters (Cifuentes et al. 1988, present study). Occurrence of a $\delta^{13}C$ distinction between rapidly growing diatoms and other slower-growing algae can provide an important tracer for food web studies.

On Georges Bank, diatoms are known to be an important and productive part of the phytoplankton through most of the year (Bigelow 1926, Cura 1987), and ^{13}C enrichment in scallops (Fry 1988) and zooplankton (Fig. 6) over central Georges Bank is consistent with an increased role of ^{13}C-rich diatoms in this food web. Filamentous cyanobacteria that could potentially be an alternative source of ^{13}C-rich carbon are not common on Georges Bank (Cura 1987).

The observed ^{13}C depletion for zooplankton in the Gulf of Maine relative to zooplankton on Georges Bank points to a decreased importance of fast-growing diatoms in the food web of the Gulf of Maine. This seems reasonable when evidence from phytoplankton studies is considered. These studies show that annual primary productivity in the Gulf of Maine is 270 g C m^{-2}, 58 % of that over central Georges Bank, and that dinoflagellates rather than diatoms dominate cell counts in this system (Bigelow 1926, Marshall 1984).

An initial estimate of diatom contributions to zooplankton diets can be made by assuming a −16 ‰ value for zooplankton feeding in a food web based on fast-growing diatoms and a −24 ‰ value for zooplankton feeding in a system where other, slower-growing algae dominate. The −24 ‰ value represents zooplankton values from the Gulf of Maine where dinoflagellates dominate cell counts (Marshall 1984), and the −16 ‰ value represents expected $\delta^{13}C$ values of zooplankton grazing on ^{13}C-rich diatoms. (Average values for ^{13}C-rich diatoms in this study ranged from −19.4 ‰ at the end of the spring bloom to −15.5 ‰ for *Coscinodiscus* sp. collected in August.) Given these −24 and −16 ‰ end members, fast-growing diatoms contribute between 0 and 25 % to the carbon necessary for zooplankton growth in the Gulf of Maine, and contribute an average of ca 40 % to the nutrition of zooplankton on Georges Bank (estimated from Fig. 6). For zooplankton collected off the nearby shelf of Nova Scotia, estimated importance of ^{13}C-rich diatoms is 20 to 30 % given zooplankton $\delta^{13}C$ values of −23.5 to −20.4 ‰ (Mills et al. 1984).

We note that these calculations are highly sensitive to selection of end-member values. For example, the 40 % estimates made with −24 and −16 ‰ end-member values are probably minimum estimates, because the diatom importance would increase if the −16 ‰ diatom end-member value were shifted towards the −18.5 to −20.5 ‰ values characteristic of diatoms at the end of the spring bloom (Fig. 3).

The present study shows that diatoms can be important sources of ^{13}C-rich carbon in marine food webs. The extent to which other phytoplankton groups are also rich in ^{13}C is not yet fully known, although other taxa, especially filamentous cyanobacteria, can also have ^{13}C-rich values in the −10 to −20‰ range (Craig 1953, Fry & Parker 1979, E. Wada pers. comm.). Because of this possible overlap in $\delta^{13}C$ values between fast-growing diatoms and other algal groups, isotopic data will have to be combined with other observations of phytoplankton species composition and abundance before reaching final conclusions about the importance of diatoms per se in marine food webs. Sites most favorable for use of $\delta^{13}C$ as a tracer of diatom carbon probably include upwelling systems where diatom blooms are persistent and other systems where sedimentation of diatoms from the end of the spring bloom is an important source of nutrition for benthic consumers.

Acknowledgements. We thank Tom Azarowitz, Tim Bates, Glenn Harrison, Ellen Johnson, Bill Michaels, John Nielson, Ian Perry, Nancy Rabalais, John and Gail Sibunka, Ed Walser, Christine Zetlin and the staff of US and Canadian RVs 'Acadia', 'Delaware II' and 'Hudson' for their assistance in collecting samples. Bruce Keafer and Quay Dortch assisted in phytoplankton identifications, Greg Rau provided previously unpublished data from the California upwelling system, and Ralf Goericke, George Kling, and Susan Saupe commented on early versions of this manuscript. This research was supported by NSF grants OCE-8800101 and BSR-8704738.

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This article was presented by D. A. Caron, Woods Hole, Massachusetts, USA

Manuscript first received: March 3, 1991
Revised version accepted: July 26, 1991