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Balancing supply and demand: controls on carbon isotope fractionation in the Cariaco Basin (Venezuela) Younger Dryas to present

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Abstract

Carbon isotope fractionation associated with photosynthetic carbon fixation (ε_p) is known to be controlled by many factors. Among these factors are the availability and carbon isotopic composition of dissolved inorganic carbon (DIC), the form of DIC that is taken up (CO_2 vs. HCO_3^-), whether DIC is taken up via passive diffusion or active uptake, specific growth rates, nutrient availability (e.g. NO_3, PO_3, trace nutrients), cell size and geometry, and irradiance. An understanding of the oceanographic controls on these factors and how they influence the final ε_p signature preserved in organic matter is critical to accurate reconstructions of past environments based on carbon isotope data, including the potential to reconstruct paleo-pCO_2 values. We have investigated the sedimentary record of carbon isotope fractionation in the Cariaco Basin, spanning the past 12.6 ^{14}C ky utilizing both bulk and molecular carbon isotope analyses. Our results indicate that the carbon isotope composition of $CaCO_3$ is controlled predominantly by the supply of DIC, regardless of variations in primary production. Furthermore, ε_p remains low and constant throughout the interval of study, despite major variability in primary production and planktonic ecosystem structure, and is in fact lower than would be predicted based on empirical relationships between ε_p, $[CO_2]_{aq}$, and $[PO_4]$ developed for haptophyte algae. These results are consistent with active uptake of bicarbonate, rather than $[CO_2]_{aq}$ by haptophyte algae, followed by intracellular carbonic anhydrase-catalyzed conversion of HCO_3^- to CO_2 for cellular utilization.

Keywords: Supply; Demand; Carbon isotope fractionation; Cariaco Basin

1. Introduction

The carbon isotope composition of organic matter and biogenic carbonate ($\delta^{13}C_{org}$ and $\delta^{13}C_{CaCO_3}$, respectively) have long been utilized as proxies for variations in the supply of inorganic carbon and its

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utilization (demand) via primary production in aquatic environments (Anderson and Arthur, 1983; McKenzie, 1985; Berger and Vincent, 1986; Hayes et al., 1989; Hollander and McKenzie, 1991; Hollander et al., 1993a,b; Schelske and Hodell, 1995; Talbot and Laerdal, 2000; Murphy et al., 2000). Interpretation of the marine $\delta^{13}C_{CaCO_3}$ has typically been based on the assumption that the primary controls are (1) the availability of dissolved inorganic carbon (DIC), which is controlled by the reservoir size and the utilization of DIC by autotrophs (McKenzie, 1985; Mix, 1987), (2) the temperature dependent equilibrium fractionations in the DIC system (Mook et al., 1974), and (3) any vital effects associated with the incorporation of DIC (as CO_{2aq} or HCO_3^-) into shell carbonate (Charles and Fairbanks, 1990; Lynch-Stieglitz et al., 1994; Kohfeld et al., 2000; Russell and Spero, 2000). In lacustrine systems there is an additional complicating factor related to hydrological variations (Talbot, 1990). Thus, given that most vital effects are small (Charles and Fairbanks, 1990; Lynch-Stieglitz et al., 1994; Russell and Spero, 2000) and can be constrained by analyzing individual species (e.g., of foraminifera), and temperature dependent equilibrium variations can be calculated, the traditional interpretations of marine $\delta^{13}C_{CaCO_3}$ signatures have focused on the DIC reservoir size and the effects of supply and utilization on it (Berger and Vincent, 1986; Mix, 1987; Zachos et al., 1989; Hsu and McKenzie, 1990; Hollander et al., 1993a,b), though other factors have certainly been recognized in several studies (Arthur et al., 1985; Kump and Arthur, 1999; Ripperdan et al., 1998; Ripperdan, 2001).

The interpretation of $\delta^{13}C_{org}$ is more complicated than that of $\delta^{13}C_{CaCO_3}$. In addition to being affected by the quantity and isotopic composition of the inorganic carbon source, the $\delta^{13}C_{org}$ is affected by fractionations associated with carbon assimilation, metabolism and synthesis, and cellular carbon budgets (Hayes, 1993). These additional factors make it extremely difficult to make interpretations based on $\delta^{13}C_{org}$ measurements on bulk organic matter alone, however, a number of researchers have had success when combining such analyses with other biogeochemical proxy records (Hollander et al., 1993a,b; Murphy et al., 2000; Talbot and Laerdal, 2000; Werne et al., 2002). Some of the complexity inherent in bulk sedimentary records can be removed by utilizing carbon isotope analysis of specific organic biomarkers derived from known sources. In examining sedimentary stratigraphic trends of such compounds we can assume that any variations in fundamental metabolic and synthetic processes and cellular carbon budgets have not been significant, as the organisms producing a given biomarker are unlikely to have changed (Brassell et al., 1987; de Leeuw et al., 1995).

It is more informative, however, to consider the carbon isotope *fractionation* (that is, the difference between the inorganic carbon source and that of the biosynthesized organic compounds) associated with, in the case of eukaryotic algae, photosynthetic carbon fixation, ε_p. Controls on ε_p are similar to those on $\delta^{13}C_{org}$, but the measure is more informative because it assesses both the carbon source and product, allowing the investigator to constrain at least the $\delta^{13}C$ of the source DIC. Over the past ~30 years, significant research has been carried out seeking to understand the controls on ε_p, and relate it quantitatively to environmental and growth conditions (see Freeman, 2001 for a brief review). One of the driving forces behind this research was, and continues to be, the potential to utilize ε_p and its quantitative relationship with $[CO_2]_{aq}$ to reconstruct paleo-pCO_2 conditions (Dean et al., 1986; Popp et al., 1989; Jasper and Hayes, 1990; Rau et al., 1991; Rau, 1994; Hollander and McKenzie, 1991; Freeman and Hayes, 1992; Jasper et al., 1994; Goericke and Fry, 1994; Pagani et al., 1999, 2002; Kienast et al., 2001). In addition to attempts to calibrate ε_p to pCO_2, numerous theoretical, culture, and field studies have been carried out investigating the various contols on ε_p related to carbon uptake and growth rate (Hinga et al., 1994; Thompson and Calvert, 1994; Laws et al., 1995, 1998; Rau et al., 1996, 1997, 2001; Korb et al., 1996; Bidigare et al., 1997, 1999; Pancost et al., 1997, 1999; Tortell et al., 1997, 2000; Popp et al., 1998; Eek et al., 1999; Keller and Morel, 1999; Burkhardt et al., 1999, 2001; Riebesell et al., 2000; Gervais and Riebesell, 2001; Rost et al., 2002, 2003; Benthein et al., 2002; Woodworth et al., in press). We will briefly describe the controls on carbon isotope fractionation by algae, for further more detailed information we refer the interested reader to the above studies and numerous recent reviews of the subject (Goericke et al., 1994;

Fry, 1996; Johnston and Kennedy, 1998; Gonzalez et al., 2001; Laws et al., 2001; Hayes, 2001).

To a first order approximation, ε_p is controlled by the balance between factors affecting the *supply* of inorganic carbon, and those affecting the *demand* (utilization) of inorganic carbon, i.e., growth. Supply-related factors controlling ε_p are essentially the same as those factors controlling $\delta^{13}C_{CaCO_3}$, and include the quantity and $\delta^{13}C$ of available DIC (Farquhar et al., 1982; Laws et al., 1995; Bidigare et al., 1997; Rau et al., 1997), whether the carbon utilized is in the form of CO_{2aq}, HCO_3^-, or a combination of both (Keller and Morel, 1999; Burkhardt et al., 1999), and the pH dependent ratio of $[CO_2]_{aq}$ to $[HCO_3^-]$ present in the system (Hinga et al., 1994). Demand-related factors are more numerous, and we break them down into carbon uptake related controls and growth related controls. Factors associated with carbon uptake include whether inorganic carbon uptake is diffusive or via active transport (Sharkey and Berry, 1985; Rau et al., 1996; Raven, 1997; Tortell et al., 2000), what type of carbon fixation pathway and specific enzyme is utilized (Preuß et al., 1989; Robinson and Cavanaugh, 1995; Schouten et al., 1998; van der Meer et al., 1998; Hayes, 2001), and the effects of cellular carbon budgets on the fraction of inorganic carbon fixed into different pools of organic matter (OM) and $CaCO_3$ relative to the fraction leaked back to the environment (Sharkey and Berry, 1985; Hayes, 1993, 2001; Rost et al., 2002). Among the factors associated with growth rate are cell size and geometry (Popp et al., 1998; Burkhardt et al., 1999), growth limitation by various nutrients such as NO_3, PO_4 or trace metals (Bidigare et al., 1997; Pancost et al., 1997, 1999; Eek et al., 1999; Laws et al., 2001; Gervais and Riebesell, 2001), light intensity (photon flux density) and light/dark cyclicity (Thompson and Calvert, 1994; Rost et al., 2002), and environmental growth conditions mimicking batch vs. continuous culture conditions (i.e., bloom vs. non-bloom production) (Riebesell et al., 2000; Rost et al., 2003). These factors are known to vary significantly between different algal species.

Despite the large uncertainty inherent in trying to balance all the myriad controls on ε_p, a certain consistency seems to be appearing in many studies. Based on theoretical, culture, and field studies of haptophyte algae (primarily *Emiliani huxleyi*), Bidigare et al. (1997) proposed the generalized relationship between ε_p, growth rate and inorganic carbon availability based a convention introduced by Rau et al. (1992) and Jasper et al. (1994)

$$\varepsilon_p = \varepsilon_f - b/[CO_2] \quad (1)$$

where ε_f is the fractionation associated with the enzyme-catalyzed carbon fixation step and b is a generic term proportional to all growth rate related effects. There is currently disagreement about what value should be utilized for ε_f, in terrestrial plants utilizing ribulose-1,5-bisphosphate carboxlase-oxygenase (Rubisco, form I) values as high as 29‰ have been observed (Roeske and O'Leary, 1985; Guy et al., 1993), while lower values are typically observed in eukaryotic algae utilizing Rubisco, ranging from 17‰ to 25‰ (Roeske and O'Leary, 1985; Guy et al., 1993; Laws et al., 2001).

Combined data from numerous field studies has allowed the identification of an empirical relationship between b and $[PO_4]$ of the form

$$b = 79 + 120[PO_4] \quad (2)$$

(Bidigare et al., 1997, 1999; Laws et al., 2001), though the authors suggest that this relationship results from actual growth limitation by some currently unknown trace nutrient that covaries with phosphate concentration (Bidigare et al., 1997). Thus, combining the two equations illustrates the relationship between ε_p, growth rate, and $[CO_2]$:

$$\varepsilon_p = \varepsilon_f - (79 + 120[PO_4])/[CO_2] \quad (3)$$

Critical assumptions in this model include (1) CO_2, not HCO_3^-, is utilized by phytoplankton, and (2) CO_2 is obtained via passive diffusion. These assumptions have come under significant attack in recent years due to culture and field based evidence for carbon concentrating mechanisms (CCM) leading to active uptake of CO_2 and/or HCO_3^- by various phytoplankton, including diatoms, dinoflagellates, and haptophytes (Sharkey and Berry, 1985; Burns and Beardall, 1987; Nimer et al., 1997; Raven, 1997; Tortell et al., 1997, 2000; Fielding et al., 1998; Keller and Morel, 1999; Kaplan and Reinhold, 1999; Rau et al., 2001; Rost et al., 2002, 2003).

These recent studies have advanced our knowledge of the controls on carbon isotope fractionation, but the overwhelming majority of the studies, particularly those suggesting CCM and/or bicarbonate uptake, are culture studies (Sharkey and Berry, 1985; Burns and Beardall, 1987; Nimer et al., 1997; Raven, 1997; Tortell et al., 1997, 2000; Fielding et al., 1998; Kaplan and Reinhold, 1999; Rost et al., 2002, 2003). While there are certainly many quality field-based studies of ε_p (Bidigare et al., 1997; Pancost et al., 1997, 1999; Rau et al., 2001; Woodworth et al., in press), there is still a shortage, particularly those that are based on the sedimentary record (Benthein et al., 2002). The present study is an investigation of the sedimentary carbon isotope record preserved in the Cariaco Basin over the last 12.6 ^{14}C ky. Based on recent advances in our understanding of the controls on carbon isotope fractionation, we interpret the δ^{13}C and ε_p signature of the Cariaco Basin sediments within the framework of known climate and environmental variations (Peterson et al., 1991; Hughen et al., 1996a,b; Lin and Peterson, 1997; Werne et al., 2000a,b). In order to minimize ambiguity in the bulk carbon isotopic record based on variability in cell size and geometry (Popp et al., 1998) and other metabolic factors between different phytoplankton species (Burkhardt et al., 1999), we have analyzed the δ^{13}C and ε_p of long-chain alkenones derived from haptophyte algae (Marlowe et al., 1984).

1.1. Regional setting and background of the Cariaco Basin

The Cariaco Basin (Fig. 1), the world's second largest anoxic marine basin after the Black Sea, is a pull-apart basin located on the northern continental shelf of Venezuela. Exchange with the Caribbean is restricted by sills located approximately 150 m below the present sea surface (Richards and Vaccaro, 1956; Heezen et al., 1959). These sills allow circulation between the upper water column of the Cariaco Basin and the Caribbean Sea, which provides a steady source of nutrients to stimulate productivity in the photic zone. Below the sills, however, circulation is restricted, thereby limiting the flux of oxygen needed to replenish that consumed by respiration of settling

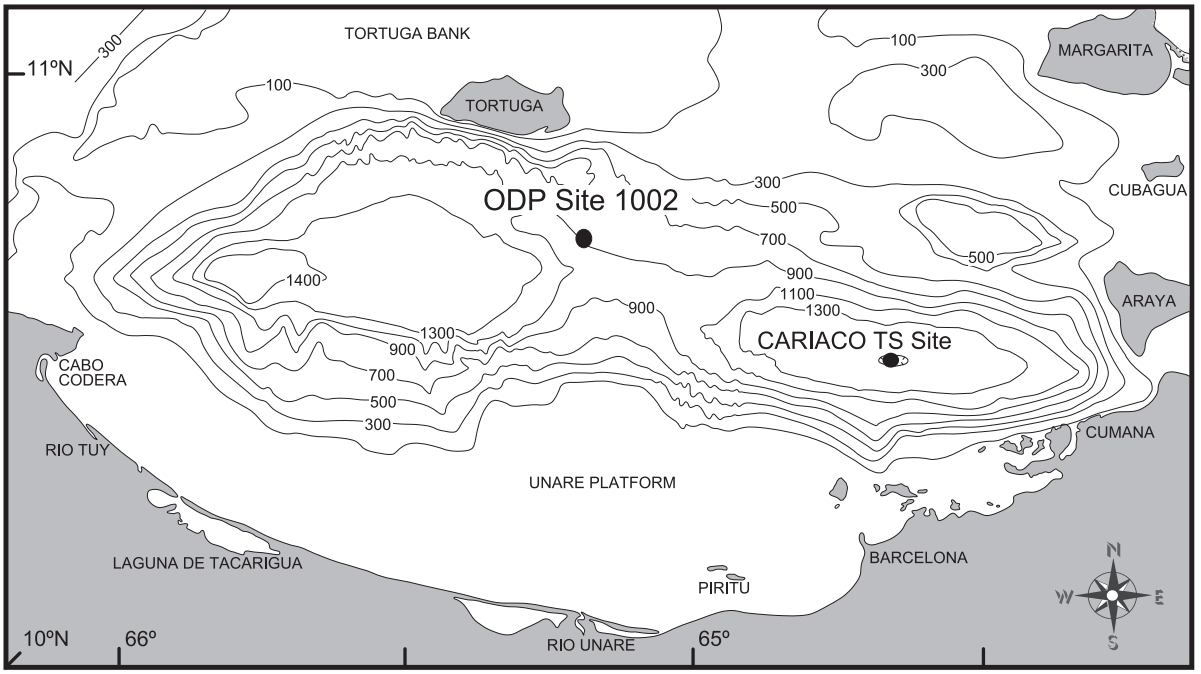

Fig. 1. Bathymetric map of Cariaco Basin showing location of ODP site 1002B (core location) and CARIACO Time Series site (water column and sediment trap sampling location).

organic matter in the deeper waters of the basin. As a result of this imbalance in the oxygen budget, the deep basin is anoxic (Peterson et al., 1991). Continuously laminated sediments in the basin suggest that anoxic conditions have persisted in the deeper basin continuously for the past 12.6 thousand ^{14}C years (Peterson et al., 1991), preventing any significant reworking by burrowing heterotrophs.

Currently, the waters of the Cariaco Basin are anoxic and sulfidic (euxinic) from approximately 300 m to the maximum water depth of about 1400 m (Fry et al., 1991; Wakeham, 1990; Scranton et al., 2001) and pore water sulfide reaches concentrations of more than 5 mM (Werne et al., 2002). Pore water sulfate concentration decreases systematically to less than 15% of seawater sulfate concentrations from the surface sediments to the base of the interval studied (Werne et al., 2002), suggesting that microbial sulfate reduction is proceeding at a steady rate, and is not concentrated in a single depth interval. Due in part to anoxia, and in part to high sedimentation rates (Shipboard Scientific Party, 1997), there has been minimal sedimentary degradation of organic matter in the upper 6 m of sediment in the Cariaco Basin (Wakeham and Ertel, 1988; Werne et al., 2000a,b).

Since 1995, there has been an ongoing cooperative US-Venezuelan time series study, the CARIACO program (CArbon Retention In A Colored Ocean; Walsh et al., 1999; Muller-Karger et al., 2000, 2001; Thunell et al., 2000; Taylor et al., 2001; Scranton et al., 2001) that has analyzed numerous hydrographic parameters (Walsh et al., 1999; Muller-Karger et al., 2000, 2001), as well as employing sediment traps to analyze the flux of particulate matter to the sea floor (Thunell et al., 2000), thereby providing a wealth of information with which to constrain sedimentary data. The Cariaco Basin region thus has an extremely well documented annual cycle, during which variations in the intensity of upwelling affect the supply of isotopically depleted dissolved inorganic carbon (DIC) and nutrients (NO_3), directly affecting the level of primary production in the basin (Ballester, 1969; Herrera and Febres-Ortega, 1975; Aparicio, 1986; Muller-Karger and Aparicio, 1994; Astor et al., 1997; Muller-Karger et al., 2000, 2001; Thunell et al., 2000). These changes in upwelling and production are directly related to the climate in the region of the Cariaco Basin, which is strongly influenced by seasonal migration of the intertropical convergence zone (ITCZ) and therefore undergoes significant variation from monsoonal to arid extremes. During the winter months, when the ITCZ is located at its southernmost position, strong tradewinds develop above the Cariaco Basin (Herrera and Febres-Ortega, 1975; Aparicio, 1986). These easterly tradewinds induce Ekman transport of surface waters northward away from the basin, which in turn induces strong upwelling (Herrera and Febres-Ortega, 1975; Aparicio, 1986). Upwelled waters bring a large supply of nutrients and dissolved inorganic carbon to the surface, which are then available for biological utilization and can support elevated productivity in the surface waters (Ballester, 1969; Muller-Karger and Aparicio, 1994; Astor et al., 1997; Walsh et al., 1999; Muller-Karger et al., 2000, 2001; Thunell et al., 2000). Conversely, the tradewinds are weaker during the summer months when the ITCZ assumes its northernmost position more nearly over the basin, which leads to less intense Ekman-induced upwelling and ultimately to reduced, though still comparatively high productivity (Muller-Karger and Aparicio, 1994; Astor et al., 1997).

The existence of pronounced productivity differences in the Cariaco Basin as a result of seasonal climate oscillations led Peterson et al. (1991) to propose an analogous model for longer-term changes in productivity and oceanographic conditions in the Cariaco region as a result of climate variability. They proposed that during cooler periods in Earth history (e.g., the Younger Dryas, YD) the overall climate pattern in the Cariaco Basin was similar to the present day winter climate with a more southerly position of the ITCZ causing increases in tradewind strength and upwelling intensity and a higher level of primary productivity. During warmer periods, the climate was generally more like present day summer, with a more northern locus of the ITCZ associated with weaker tradewinds, less intense upwelling, and a lower level of productivity. Recent studies have supported the hypothesis that during colder periods in Earth history the overall climate pattern in the Cariaco region appears to have been similar to present day winter conditions, with elevated upwelling intensity and primary productivity (Peterson et al., 1991; Hughen et al., 1996b; Lin and Peterson, 1997; Werne et al., 2000a), and during warmer

periods (e.g., most of the Holocene) the overall climate pattern seems to be similar to present day summer conditions. It is not known whether this pattern of similarity to winter climate during cold periods is due to more intense upwelling or simply upwelling for a greater proportion of the annual cycle, but both would give a similar signal in a time-averaged sedimentary study.

2. Materials and methods

Cariaco Basin sediments were acquired from Ocean Drilling Program (ODP) Leg 165, Site 1002 (Fig. 2). Samples were taken from core 1002B, which was a 6-m continuous core taken from ~900 m water depth for dedicated geochemical studies (Shipboard Scientific Party, 1997). Sampling, bulk organic carbon and carbonate concentrations and accumulation rate determinations are described in Werne et al. (2000a). Age control is provided by a suite of accelerator mass spectrometer (AMS) ^{14}C dates from core PL07-39PC with a standard reservoir correction of 420 years (Lin et al., 1997) correlated to core 1002B using high resolution records of magnetic susceptibility (Werne et al., 2000a). Ages are reported as reservoir-corrected radiocarbon years.

2.1. Bulk isotopic analysis

Samples were acidified in 0.1 N HCl to remove carbonate for analysis of the stable isotopic composition of organic carbon ($\delta^{13}C_{org}$). Samples were then combusted using a Fisons NA 1500 Elemental Analyzer; the isotopic ratio of the resultant CO_2 gas was measured using a continuous flow inlet system on a VG Optima stable isotope ratio monitoring mass spectrometer (IRMS). For analysis of the isotopic composition of carbon in bulk carbonate ($\delta^{13}C_{CaCO_3}$), samples were heated to 350 °C under vacuum to remove organic matter. Samples were then acidified at 95 °C in concentrated phosphoric acid with a Fisons Isocarb unit, and the evolved CO_2 gas was analyzed using the same IRMS. All bulk organic isotopic analyses were run in triplicate; inorganic analyses were performed with standards interspersed with the samples. Carbon isotopic values are reported relative to the VPDB standard (using NBS-19 as a working

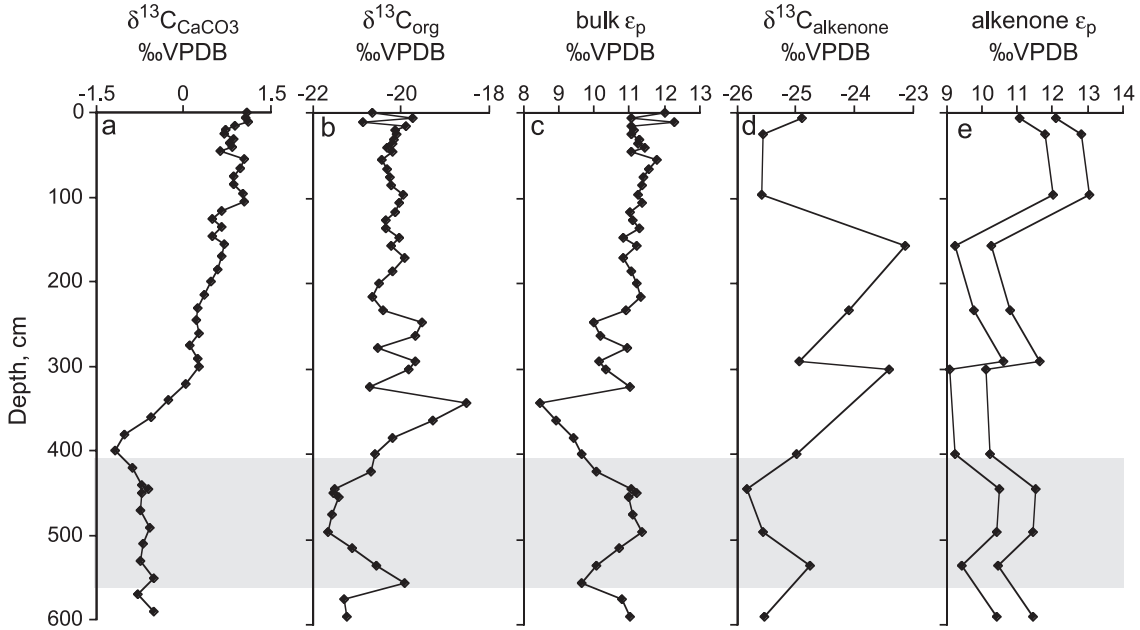

Fig. 2. Depth trends of sedimentary carbon isotope data. (a) $\delta^{13}C_{CaCO3}$; (b) $\delta^{13}C_{org}$; (c) ε_p calculated from $\delta^{13}C_{org}$; (d) $\delta^{13}C_{alkenone}$; (e) ε_p calculated from $\delta^{13}C_{alkenone}$. Shaded area is the Younger Dryas cold period.

standard) in conventional per mil (‰) notation. Standard deviation of the isotopic measurements was better than 0.1‰ for carbonate carbon and 0.2‰ for organic carbon.

2.2. Biomarker analysis

For this study, we analyzed a biomarker of haptophyte algae (coccolithophorids; heptatriaconta-15E,22E-trien-2-one, i.e. C_{37} alkenone), and a biomarker of bacteria, (hop-22(29)-ene; diploptene). Extraction, quantification, and identification procedures for the alkenone are described in Werne et al. (2000a), and those of diploptene are the same as those described in Werne et al. (2000b). Accumulation rate calculations for diploptene were made following Werne et al., 2000a).

2.3. Compound-specific isotopic analysis

Compound-specific isotopic measurements were made using a Hewlett-Packard 5890 Series II GC coupled to the same IRMS, and sample isotope values were calibrated against internal standards. Reported values are averages of duplicate analyses. Injection, column, flow, and oven temperature conditions were as described in Werne et al. (2000a). The temperature of the combustion furnace was 850 °C. Precision of compound specific carbon isotopic measurements was better than ± 0.7‰.

2.4. Calculations of carbon isotope fractionation

Determinations of ε_p are carried out following the general equations outlined in Jasper et al. (1994) modified with recent data from Laws et al. (2001), and require calculations for $\delta^{13}C_{CO_2}$ (dissolved CO_2 in the water column) and $\delta^{13}C_{pp}$ (primary photosynthate). We calculate ε_p according to Eq. (4):

$$\varepsilon_p = \left\{\left[\left(1000 + \delta^{13}C_{CO_2}\right)/\left(1000 + \delta^{13}C_{pp}\right)\right] - 1\right\}*1000 \quad (4)$$

$\delta^{13}C_{CO_2}$ in this study is calculated based on the temperature-dependent equilibrium isotopic offset between mineral calcite and dissolved CO_2 (Δ_{md}) using equations outlined in Mook et al. (1974) and Morse and Mackenzie (1990) and the isotopic difference between equilibrated mineral calcite and foraminiferal calcite (Δ_{mf}) (Jasper et al., 1994).

$$\delta^{13}C_{CO_2} = \delta^{13}C_{CaCO_3} + \Delta_{md} + \Delta_{mf} \quad (5)$$

This equation assumes no diagenetic alteration or post-depositional contributions to sedimentary carbonate, which is an accurate assumption in the Cariaco Basin sediments (Hastings and Emerson, 1988). Sea surface temperature was estimated using the $U_{37}^{k'}$ alkenone unsaturation index which suggests that surface waters where haptophytes were living was 23 °C throughout the interval of study (data not shown, calculations described in Prahl and Wakeham, 1987; Prahl et al., 1988).

In our study we have utilized isotopic measurements of bulk sedimentary carbonate rather than individual foraminifera, therefore we must make some significant assumptions. First, it is assumed that the bulk $CaCO_3$ isotopic value represents an "average" of the contributing organisms. In the Cariaco sediments, the primary contributions of $CaCO_3$ during the period of this study are derived from planktonic foramifera and coccoliths. Coccolith $CaCO_3$ is less than 10% of the total $CaCO_3$ during the YD, increasing gradually to almost 20% at 6 ka, then decreasing again through the later Holocene (Lynn, 1998). Coccolith carbonate is typically slightly ^{13}C enriched relative to foraminiferal carbonate (Ennyu et al., 2002), however, the trends in the relative percent of $CaCO_3$ that is coccolith derived cannot explain the observed variability in $\delta^{13}C_{CaCO_3}$ in the Cariaco Basin sediments. Thus, we believe that the sedimentary $\delta^{13}C_{CaCO_3}$ signal is dominated by foraminiferal $CaCO_3$. Comparison of the $\delta^{18}O$ of bulk sedimentary carbonate (this study, data not shown) with that of individual foraminifera in the sediments (Lin and Peterson, 1997) demonstrates that the bulk signal is nearly identical to that of *Neogloboquadrina dutertrei* (inhabits the chlorophyll maximum; Woodworth et al., in press), but slightly offset towards the lighter values observed for *Globigerina bulloides* (surface water dweller) (cf. Lin and Peterson, 1997). Furthermore, comparison of our bulk $\delta^{13}C_{CaCO_3}$ data with the $\delta^{13}C_{CaCO_3}$ data measured on *N. dutertrei* by Woodworth et al. (in press) shows that during the Holocene, bulk $\delta^{13}C_{CaCO_3}$ values are very similar to those of *N.*

dutertrei in the modern water column. The depths of these foraminifera, which apparently dominate the bulk $\delta^{13}C_{CaCO_3}$ signal, are similar to those of haptophyte algae (i.e., near surface).

Second, we assume that there is a negligible vital effect between dissolved CO_2 and this average $CaCO_3$ value. Although it is unlikely that the average $\delta^{13}C_{CaCO_3}$ value is in perfect isotopic equilibrium with dissolved CO_2 (Spero and Williams, 1989; Spero et al., 1991), we feel that this approximation is valid, given the similarities between the isotopic signals in bulk $CaCO_3$ and individual foraminifera. Woodworth et al. (in press) applied a vital effect correction of 0.7‰ to their calculations using *N. dutertrei*, which is in the same range as many other foraminiferal vital effects (typically ~1‰; Charles and Fairbanks, 1990; Lynch-Stieglitz et al., 1994; Russell and Spero, 2000, though values ranging up to 4‰ have been suggested (Kohfeld et al., 2000). However, they also show a variation through the annual cycle of nearly 1‰. Furthermore, if we include a 0.7‰ vital effect, our ε_p values change by ~0.5‰, and these values fall within the range already indicated on Fig. 2e by utilizing two different biosynthetic fractionations (see below for calculations of primary photosynthate). Thus, given the spread in the observed data from sediment trap studies of individual planktonic foraminifera (Woodworth et al., in press), and the small effect of foraminiferal vital effects on the ε_p signal, we feel that neglecting these vital effects for our downcore studies (which are averaging many years of deposition, as well as many carbonate producing organisms) is an appropriate approximation.

Third, it is assumed that the offset in isotopic fractionation during carbonate precipitation by carbonate producing plankton (dominantly coccolithophorids and foraminifera) is consistent throughout the interval studied, which may not be strictly accurate (Spero et al., 1991), but given the condition that we are measuring averaged isotopic values over many years, the deviations from consistent fractionation are believed to be of minor importance.

To calculate the isotopic value of the primary photosynthate, we employed two approaches. First, we utilized the bulk $\delta^{13}C_{org}$ record as an approximation of photosynthate. Clearly, however, bulk OM is not all composed of primary photosynthate, and in addition to inputs from zooplankton, there may be inputs from terrestrial OM (though terrestrial inputs are thought to be minor, Werne et al., 2000a,b). In order to remove such effects related to zooplankton and terrestrial inputs, we also measured the carbon-isotopic composition of C_{37} diunsaturated alkenones, biomarkers for haptophyte algae ($\delta^{13}C_{alk}$). Culture studies have identified an isotopic shift ($\Delta\delta_{pp\text{-}alk}$) ranging from 3.1‰ to 5.3‰ between primary photosynthate and alkenone biomarkers (Degens et al., 1968; Jasper and Hayes, 1990; Hayes, 1993; Bidigare et al., 1997; Popp et al., 1998). The average ($\Delta\delta_{pp\text{-}alk}$ based on a number of studies is 3.9‰ for continuous cultures and 4.9‰ for batch cultures (Laws et al., 2001; Bidigare et al., 1997; Popp et al., 1998; Riebesell et al., 2000). We have therefore calculated the $\delta^{13}C_{pp}$ based on both of these values to give the range we might expect to see in nature according to the equation

$$\delta^{13}C_{pp} = \delta^{13}C_{biomarker} + \Delta\delta(3.9 - 4.9‰) \quad (6)$$

thereby putting upper and lower bounds on what we would expect based on the different culture studies.

3. Results

3.1. Bulk carbon isotopic composition

$\delta^{13}C_{CaCO_3}$ values range from a minimum of −1‰ just after the Younger Dryas to more than +1‰ in the later Holocene (Fig. 2). Values are very constant at approximately −0.7‰ during the YD, and increase gradually throughout the Holocene to a maximum of +1.1‰ in surface sediments. $\delta^{13}C_{org}$ values range from a minimum of almost −22‰ during the YD to a maximum of about −18.5‰ during the early Holocene (Fig. 2). After an initial decrease from −20‰ to almost −22‰ at the beginning of the YD, values remain about −22‰ for the remainder of the YD. Again it should be noted that during the YD, a period of maximum production, the carbon isotope composition of organic matter was most depleted. At the YD–Holocene transition an abrupt increase occurs to almost −18‰, followed by a period of oscillation between −20‰ and −21‰ during the middle Holocene. In the later Holocene, $\delta^{13}C_{org}$ values reach a steady state around −20.3‰.

3.2. Bulk carbon isotopic fractionation

Bulk ε_p values are generally low, with a maximum of 12‰ in the latest Holocene (Fig. 2). During the Younger Dryas and earliest Holocene, values are more variable, ranging from a low of ~8‰ up to values between 10‰ and 11‰, followed by a general trend toward heavier values through the middle to late Holocene (Fig. 2). The most notable excursions are the increase during the middle of the YD, and the significant decrease immediately following the YD.

3.3. Alkenone carbon isotopic composition

Bulk OM is typically a mixture derived from many sources. Therefore, the carbon-isotopic compositions of biomarker compounds indicative of haptophyte algae were measured to ascertain whether bulk $\delta^{13}C_{org}$ accurately reflected the conditions of the phytoplanktonic community over the past 12 ky in the Cariaco Basin, rather than a terrestrial signal. The carbon isotopic composition of the C_{37} alkenone ($\delta^{13}C_{alk}$) displays a trend towards more depleted isotopic values during the YD, however, during the early to middle Holocene the $\delta^{13}C_{alk}$ trends more positive, followed by a significant shift in the later Holocene to more negative values. The magnitude of the $\delta^{13}C_{alk}$ variability is very low, ranging from −23‰ to almost −27‰ (Fig. 2).

3.4. Alkenone carbon isotope fractionation

The carbon isotopic fractionation associated with photosynthetic carbon fixation (ε_p) was calculated using $\delta^{13}C_{CaCO_3}$ (from bulk carbonate) and $\delta^{13}C_{alk}$ from the sediments of the Cariaco Basin. ε_p values fall in the range of ~9–13‰ throughout the YD and Holocene (Fig. 2). This range includes ε_p values calculated based on offsets from planktonic biomass ($\Delta\delta_{pp\text{-}alk}$) of 3.9‰ and 4.9‰, which are the values identified in continuous and batch culture studies, respectively. ε_p values calculated using a given $\Delta\delta$ had a narrower range of 2–3‰. This range of ε_p values is smaller than that reported for haptophytes from the Peru upwelling zone (Bidigare et al., 1997).

3.5. Predicted C-isotope fractionation

We have calculated theoretical ε_p values for the water column based on [CO_2] and [PO_4] data from the CARIACO time series (Muller-Karger et al., 2000, 2001; Y. Astor, F. Muller-Karger and R. Bohrer, unpublished data) using Eq. (3). Predicted values vary over the annual cycle, but are generally

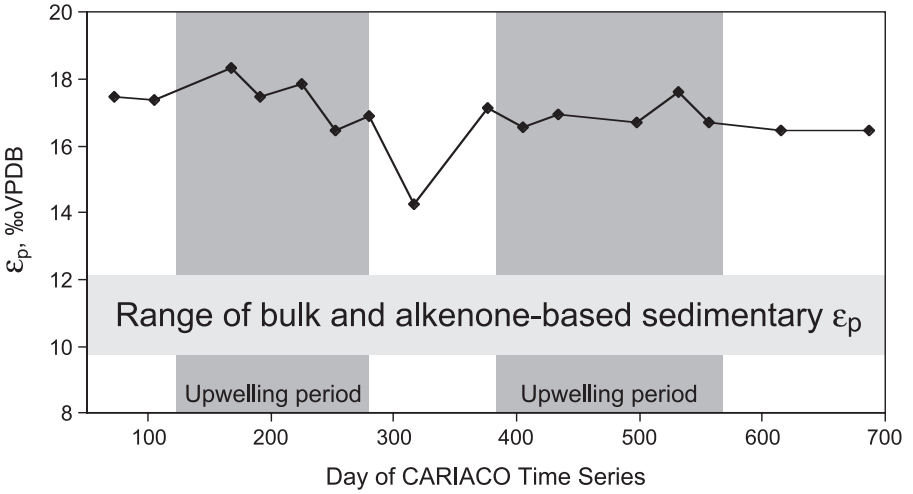

Fig. 3. Predicted ε_p over the annual cycle calculated based on water column $[CO_2]_{aq}$ and [PO_4] data (averaged over the upper 35 m where most of the primary production occurs, cf. Muller-Karger et al., 2001) from CARIACO Time Series Study using Eq. (3) (data courtesy of Y. Astor, R. Bohrer, and F. Muller-Karger). Lightly shaded area is average range of bulk and alkenone-based ε_p values, and darker shaded areas are spring upwelling periods. CARIACO Time Series data in this plot starts November 8, 1995.

between 16‰ and 18‰ (averaged over the upper 35 m of the water column, Fig. 3). These predicted ε_p values are greater than the values determined in the sedimentary record (see below), as well as values of ε_p calculated for sediment trap materials (Woodworth et al., in press).

4. Discussion

Several patterns in the sedimentary carbon isotope data emerge. First, $\delta^{13}C_{CaCO_3}$ values are consistently light during the YD followed by a trend of gradual ^{13}C enrichment through the Holocene. The $\delta^{13}C_{org}$ values, in contrast, display lightest values during the YD (though with more variability than the $\delta^{13}C_{CaCO_3}$ data), but during the Holocene simply remain near the same value with a general trend of decreasing variability. Third, both the bulk and molecular (alkenone) signals of fractionation (ε_p) display very low values compared to what is expected based on diffusive CO_2 uptake and C-fixation via the Rubisco enzyme (~25‰, Laws et al., 2001; Fig. 3). It is particularly interesting that both the bulk and molecular ε_p values are so low in comparison with the values calculated based on the present-day $[CO_2]_{aq}$ and $[PO_4]$ relationships utilizing the empirical relationship of Bidigare et al. (1997) and Laws et al., (2001). Finally, while the molecular ε_p trend is nearly invariant, that of the bulk OM shows significant variability, particularly in the early Holocene.

These trends are particularly intriguing because the YD was a period of significantly enhanced primary production in the Cariaco Basin, resulting in enhanced delivery of biogenic opal (Peterson et al., 1995) $CaCO_3$ (Hughen et al., 1996a,b; Werne et al., 2000a,b) and bulk and molecular OM (Werne et al., 2000a,b) to the sediments. Thus, at a time of maximum export productivity, the sedimentary record shows most ^{13}C depleted $\delta^{13}C_{org}$ and $\delta^{13}C_{CaCO_3}$ records, as well as low (near minimum) fractionation. These observations do not agree with models relating productivity to carbon isotope systematics under assumptions of plentiful inorganic carbon supply (i.e., higher productivity leads to ^{13}C enrichment due to depletion of the DIC pool in the lighter isotope; McKenzie, 1985). It is also curious that ε_p values, particularly those of the alkenone biomarkers, are low and constant, despite 3-fold variations in their accumulation rate (Werne et al., 2000a,b), which can be directly related to production in the absence of preservational artifacts.

4.1. Balancing supply and demand

During the YD, the Cariaco Basin is believed to have been characterized by more intense and/or longer periods of upwelling (Peterson et al., 1991; Hughen et al., 1996a,b; Werne et al., 2000a,b). In the modern day Cariaco Basin, upwelling is thought to bring Subtropical Underwater (SUW) to the surface, which is characterized by high DIC concentrations (Muller-Karger et al., 2001). Indeed, DIC concentrations are so high in the modern Cariaco that despite high levels of export productivity, the basin remains a source of CO_2 to the atmosphere (Muller-Karger et al., 2001). While the source of upwelling water to the Cariaco may have been different during the YD based on changes in physical oceanographic conditions (Broecker et al., 1985; Boyle and Keigwin, 1987; Hughen et al., 1998), the sedimentary bulk carbon isotope data suggest that ample DIC was available for production. Indeed, it appears that during the YD upwelling intensity brought such a large supply of DIC to the surface waters that, despite elevated levels of primary production, the supply was great enough to maintain a sufficient pool of ^{12}C. Thus, the $\delta^{13}C_{CaCO_3}$ and $\delta^{13}C_{org}$ values are lighter during the YD than during the Holocene, when upwelling was less intense.

It is clear, however, that there is greater variability in the $\delta^{13}C_{org}$ data than in the $\delta^{13}C_{CaCO_3}$ data, suggesting that additional factors are exerting control on the carbon isotope signals preserved in OM, that is, those factors related to photosynthetic carbon uptake. Interestingly, the bulk ε_p signal shows a trend of increasing fractionation in the Holocene very similar to the trend of increasing $\delta^{13}C_{CaCO_3}$, while the $\delta^{13}C_{org}$ and the alkenone ε_p do not. This observation suggests that there is an aspect of the carbon isotope fractionation systematics in the Cariaco basin that is more closely related to the supply of DIC (which we interpret to be the dominant control on $\delta^{13}C_{CaCO_3}$) than it is to any growth related controlling factors. These competing "growth" and "carbon supply" factors are discussed further below.

4.2. Autochthonous inputs, chemoautotrophy and phytoplanktonic community variations

One of the dangers inherent in the use of bulk OM is the fact that it is composed of a mixture of many different sources. Thus, the enhanced variability of the bulk records relative to the alkenone record (and the $CaCO_3$ record) may simply reflect the changing ratios of various components of the bulk OM, rather than any change in fractionation. For example, it is possible that some of the variability is due to enhanced inputs of terrestrial OM during the YD (or Holocene). We do not believe that this is a significant factor, however, because terrestrial inputs appear to be minimal in sediment trap materials (Goñi et al., 2003) and molecular studies show virtually no variation in the inputs of terrestrial biomarkers throughout the study interval (Werne et al., 2000a,b).

A second possible complicating factor in the bulk isotopic signal is the contribution from chemoautotrophic biomass. Chemoautotrophy has been identified in the redox transition zone of the Cariaco Basin, and it has been proposed that this biomass is a significant source of organic carbon production (Taylor et al., 2001). As chemoautotrophic biomass tends to be ^{13}C depleted relative to photoautotrophic biomass due to differences in biosynthesis (Preuß et al., 1989; Schouten et al., 1998), a change in the contribution of chemoautotrophic biomass could have an effect on the $\delta^{13}C_{org}$, as well as calculations of ε_p based on bulk OM. In order to constrain possible chemoautotrophic microbial inputs, we assessed the inputs of chemoautotrophic biomass as reflected in the accumulation rate of diploptene (hop-22(29)-ene), a common hopanoid biomarker that has been attributed to a variety of different bacteria (Rohmer and Bouvier-Nave, 1984; Ourisson and Rohmer, 1992). The accumulation rate of diploptene increases significantly (nearly 5-fold) during the YD relative to either before or after (Fig. 4). It should be noted that this increase is only demonstrated in a single data point, but given the increases in the same depth interval in other biomarkers such as sterols (Werne et al., 2000a), we feel that the diploptene accumulation rate is real. The $\delta^{13}C$ of diploptene in Cariaco sediments ranges from −35‰ to −41‰, significantly lighter than photoautotrophic biomass (data not shown). Thus, contributions of chemoautotrophic biomass may contribute to the ^{13}C depleted $\delta^{13}C_{org}$ values observed during the YD.

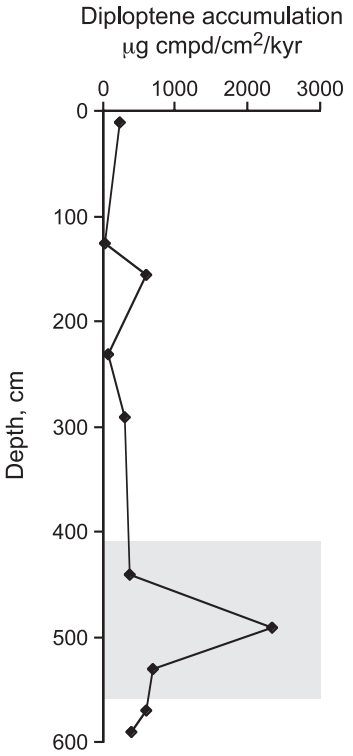

Fig. 4. Accumulation rate of diploptene through the study interval, showing maximum accumulation in YD (shaded).

It is also certainly true that eukaryotic algae other than haptophytes are contributing to the sedimentary $\delta^{13}C_{org}$ and bulk ε_p records. Werne et al. (2000a,b) and Dahl et al. (2004) have both documented significant changes in the planktonic ecosystem of the Cariaco Basin during this time interval, with significant inputs from diatoms and dinoflagellates as well as haptophytes. Biomarkers of both algal groups (sterols) show different isotopic trends from those of the haptophytes (Werne, unpublished data), which contributes to the bulk sedimentary isotopic signal. A full discussion of the isotopic trends of other biomarkers is beyond the scope of this paper, however, and will be the subject of another manuscript.

4.3. Diagenesis

In any study of sedimentary geochemical proxies, we must establish that diagenesis is not altering the

materials investigated. In this case, it is particularly important, because the sedimentary ε_p values are so much lower than the ε_p values calculated based on water column $[CO_2]_{aq}$ and $[PO_4]$ data and the empirical relationship developed by Bidigare et al. (1997) and Laws et al., (2001) for haptophyte algae (10–12‰ vs. 16–18‰, Figs. 2 and 3). Previous studies have suggested that biogenic materials, including OM, in the Cariaco Basin sediments are fairly well preserved (Wakeham and Ertel, 1988; Werne et al., 2000a,b; Dahl et al., 2004). Furthermore, the sediments are very similar in composition, and accumulation rate, to materials found in sediment traps (Werne et al., 2000a,b; Goñi et al., 2003). Indeed, the bulk and molecular $\delta^{13}C$ and ε_p values that we have determined for the sediments are in the same range as ε_p values (determined using specific foraminiferal tests and particulate organic carbon, POC) from sediment traps (Woodworth et al., in press). Thus, diagenetic alteration does not explain the low values of sedimentary ε_p compared with values predicted based on water column chemistry.

4.4. Rates, timing, and conditions of growth

Many studies have identified a relationship between growth rate and ε_p (Laws et al., 1995; Bidigare et al., 1997; Burkhardt et al., 1999; Laws et al., 2001). At first glance it may seem perplexing that the alkenone ε_p record in the Cariaco sediments remains low and constant despite significant changes in export productivity; however, we must recall that measures of primary production such as export productivity, biomass standing stock, and chlorophyll *a* are not the same as measures such as specific growth rate, and it is specific growth rate that has a relationship with ε_p, not export production. In the Cariaco Basin, specific growth rates (biomass specific carbon uptake rates, P^B), while variable, are near the physiological maximum throughout the annual cycle (Muller-Karger et al., 2001). These P^B rates show an inverse relationship with biomass and a direct relationship with nutrients, and are attributed to an annual succession that favors organisms with higher specific growth rates during periods of lower nutrient availability (Muller-Karger et al., 2001). These observations have two implications for the sedimentary ε_p record. First, very high growth rates would tend to minimize any growth related fractionation effects. Second, while there are minor variations in specific growth rate, rates are near maximum throughout the year, indicating that there is no nutrient limitation in the Cariaco Basin, even during the high productivity upwelling periods (Muller-Karger et al., 2001). Thus, effects such as those cited by Eek et al. (1999) related to nitrate limitation appear to be unlikely factors in controlling carbon isotope fractionation in this system.

Two other aspects of growth are likely to affect the carbon isotopic signature of the Cariaco Basin. First, the timing of production in the annual cycle has been documented to occur predominantly during the nutrient and $[CO_2]_{aq}$ replete upwelling season based on chlorophyll *a* (Muller-Karger et al., 2001) and sediment trap particle fluxes (Goñi et al., 2003). Thus, the majority of the sedimenting OM is produced during a particular time of year, and the sedimentary record is biased towards that period in the annual cycle characterized by the largest supply of DIC. Second, the depth of growth has implications for carbon isotope fractionation. Primary production in the Cariaco is concentrated in the upper water column, dominantly between 7 and 25 m water depth (Muller-Karger et al., 2001). This is due in part to the fact that the dominant phytoplankton taxa are bloom-forming algae, including haptophytes, diatoms, and dinoflagellates. The near surface blooms create light limitation on growth at depths greater than ~25 m. As will be discussed below, both the presence of bloom-forming phytoplankton and light limitation are likely to affect carbon isotope fractionation (Rost et al., 2002, 2003).

4.5. Inorganic carbon uptake

As discussed earlier, critical assumptions required for the empirical relationship between ε_p, growth rate, and $[CO_2]_{aq}$ (Eq. (3), Laws et al., 2001) include (1) $[CO_2]_{aq}$ is the form of inorganic carbon taken up by the cell, and (2) $[CO_2]_{aq}$ is taken up via passive diffusion. Recent studies, however, have increasingly demonstrated that many eukaryotic algae contain a carbon concentrating mechanism (CCM) that is capable of active uptake of CO_2 or HCO_3^-, which can have significant impact on carbon isotopic fractionation (Sharkey and Berry, 1985; Burns and

Beardall, 1987; Nimer et al., 1997; Raven, 1997; Tortell et al., 1997, 2000; Fielding et al., 1998; Keller and Morel, 1999; Kaplan and Reinhold, 1999; Rau et al., 2001; Rost et al., 2002, 2003). The active uptake of bicarbonate can occur via two different mechanisms. In the first, bicarbonate is actively transported directly into the cell where it is converted (intracellularly) into CO_2 by carbonic anhydrase (CA) and/or carboxylation reactions (Goericke et al., 1994; Korb et al., 1996; Raven, 1997). The CO_2 thus produced is utilized by the cell to produce biomass (except for some unknown portion that may "leak" out of the cell). As the $\delta^{13}C$ of bicarbonate is typically ~10‰ enriched in ^{13}C relative to $[CO_2]_{aq}$, such a mechanism would significantly alter the observed $\delta^{13}C$ and ε_p (as calculated with the assumptions of $[CO_2]_{aq}$ utilization), effectively reducing ε_p by ~10‰ if there was no leakage. It is possible, however, that HCO_3^- could be taken up in excess, converted intracellularly to CO_2, and allowed to equilibrate with ambient CO_2 either diffusing or being pumped into the cell. Under such a process, the 10‰ enrichment in ε_p would not likely be expressed due to equilibration with CO_2. It is thought, however, that organisms expending the energy to pump HCO_3^- into the cell would be unlikely to allow it to equilibrate with ambient CO_2. Rather, it seems that if an organism is actively pumping HCO_3^- into the cell, it is because the intracellular pool is finite, thus the resulting CO_2 would be nearly completely utilized with a minimum of leakage.

In the second bicarbonate uptake mechanism, CA is excreted and the conversion of HCO_3^- to CO_2 takes place extracellularly, followed either by active uptake or passive diffusion of $[CO_2]_{aq}$ (Goericke et al., 1994; Korb et al., 1996; Raven, 1997). This mechanism would not change the $\delta^{13}C$ or apparent ε_p as much (if at all), because the isotopic fractionation associated with the CA-catalyzed conversion of HCO_3^- to $[CO_2]_{aq}$ is ~10‰, the same as the temperature dependent equilibrium offset (at 15°; Riebesell and Wolf-Gladrow, 1995). Furthermore, isotopic equilibration with the ambient DIC pool is expected to be rapid, masking any CA-related carbon isotope fractionation. (The fractionation associated with CA-catalyzed conversion of HCO_3^- to CO_{2aq} would likely not be expressed in the first mechanism because all HCO_3^- taken up would be converted). Thus, anomalously low ε_p values would only be expected in the case of active bicarbonate uptake followed by intracellular conversion via CA to CO_2.

We suggest that the Cariaco Basin sedimentary isotopic record is best explained by invoking active uptake of bicarbonate by haptophyte algae, in conjunction with consistently high specific growth rates and export production predominantly during the spring upwelling season. ε_p values are low and constant despite significant changes in productivity regime and nutrient and $[CO_2]_{aq}$ availability. These values are lower than predicted based on the diffusion-based model of Bidigare et al. (2001) by approximately 6‰, which is less than the theoretical 10‰ discussed above. However, in a recent pair of studies, Rost et al. (2002, 2003) observed simultaneous uptake of HCO_3^- and $[CO_2]_{aq}$ by *E. huxleyi*. Furthermore, Rost et al. (2003) found that under light limited conditions such as would be found under bloom conditions, active uptake of carbon by *E. huxleyi* best explained their results.

Our findings in the Cariaco contrast with those of Benthein et al. (2002), who found that variations in alkenone based ε_p in numerous Atlantic Ocean sites appeared to be linked to variations in nutrient concentrations rather than $[CO_2]_{aq}$. Rau et al. (2001), however, found very similar results in a study of the upwelling zone of Monterey Bay. Consistently low ε_p values were observed in a low latitude upwelling system with high and variable $[CO_2]_{aq}$ were interpreted as indicative of active transport of bicarbonate into the cell, though it should be noted that the Monterey Bay phytoplankton community is dominated by diatoms, and the study utilized bulk measurements of particulate organic carbon (Rau et al., 2001). Our interpretations are also in agreement with earlier work of Pancost et al. (1997, 1999), who suggested that active transport may play a role in the carbon isotope fractionations by diatoms and dinoflagellates observed in the Peru upwelling margin. Furthermore, our data agree with sediment trap data from the Cariaco Basin, which also seem to indicate the operation of a CCM in Cariaco Basin phytoplankton (Woodworth et al., in press). Clearly, more research is required to elucidate which factors are dominating carbon isotope fractionation processes, and how spatially and temporally variable such controls may be.

5. Conclusions

The sedimentary record of carbon isotope fractionation in the Cariaco Basin reflects multiple oceanographic and physiological controls. The $\delta^{13}C_{CaCO_3}$ record is controlled primarily by DIC supply, likely due to the high concentrations of DIC provided to surface waters via upwelling of the SUW. In contrast, the $\delta^{13}C_{org}$ and bulk ε_p records appear to be in part controlled by DIC supply, but with significant additional controls imposed by growth rates, inorganic carbon uptake, and species-specific metabolic variations.

The molecular fractionation record removes any influences related to variations in species composition, and reflects only the ε_p related to photosynthetic carbon uptake by haptophyte algae. The low and constant ε_p values, despite significant variations in primary production and planktonic community structure, result from (1) specific growth rates near the physiological maximum throughout the annual cycle of growth; (2) the occurrence of growth (biomass production) primarily during the spring upwelling period, when nutrients and DIC are in highest concentration; and (3) active uptake of bicarbonate in addition to $[CO_2]_{aq}$, followed by intracellular conversion of HCO_3^- to CO_2 via carbonic anhydrase enzyme catalysis. The proportion of HCO_3^- utilized by haptophytes in the Cariaco Basin is likely controlled to some extent by the existence of bloom conditions and the potential for light limitations at depth as a consequence. It is not presently possible for us to estimate the relative influences these different factors on the ε_p signal in the Cariaco Basin sediments. Indeed, it is possible that only one or two of these factors are in fact controlling the carbon isotope fractionation systematics in the Cariaco Basin.

These results and interpretations are in agreement with sediment trap based fractionation studies in the Cariaco Basin by Woodworth et al. (in press), as well as studies in Monterey Bay (Rau et al., 2001), and have significant implications for the interpretation of carbon isotopic fractionation data in paleo studies. Many models of carbon isotopic fractionation make the assumption that $[CO_2]_{aq}$ is taken up into the cell via passive diffusion, and therefore must be in equilibrium with the surrounding waters. Such a diffusive mechanism would allow the estimation of paleo-$[CO_2]_{aq}$ (and pCO_2) concentrations from sedimentary carbon isotopic data, and has been applied in certain environments, seemingly successfully (cf. Pagani et al., 1999, 2002). The increasingly frequent recognition of active carbon uptake in general, and active uptake of bicarbonate in particular, in culture and field studies raises questions as to our ability to interpret fractionation data in the context of passive diffusion, and indicates that we should carefully evaluate the potential effects of active uptake on such diffusion-based models.

Active uptake has now been utilized to explain carbon isotopic fractionation values in high $[CO_2]_{aq}$ upwelling systems (Cariaco, this study; Monterey Bay, Rau et al., 2001; Peru Margin, Pancost et al., 1997, 1999) as well as low $[CO_2]_{aq}$ systems (coastal Pacific, Tortell et al., 2000). Other studies continue to find a lack of evidence for active carbon uptake, however, but rather seem to find the dominant controls on fractionation are imposed by growth rates and nutrient status (cf. Laws et al., 2001; Benthein et al., 2002). Clearly, additional research is required if we are to understand the many processes contributing to carbon isotopic systematics in natural aquatic systems. Future research efforts should focus on field studies that are investigating both the potential mechanisms of inorganic carbon uptake and the effects related to growth rate and nutrient conditions in natural systems characterized by different nutrient, [DIC], and productivity regimes.

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