Iron-stimulated changes in $^{13}$C fractionation and export by equatorial Pacific phytoplankton: Toward a paleogrowth rate proxy

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Abstract. We present $^{13}$C values for phytoplankton, which are capable of up to 7 per mil isotopic enrichment during the IronEx II iron fertilization experiment. We evaluate these data using a laboratory-derived $^{13}$C fractionation model and show this variability is largely the result of elevated growth rates. Isotopic enrichment and stimulation of growth rate were accompanied by a sevenfold increase in the export of particulate organic carbon as estimated from $^{234}$Th activities. This is the first direct evidence that enhanced productivity following iron enrichment can lead to both increased export of organic matter and an associated isotopic signal in an algal biomarker. On the basis of these results, we propose biomarker isotopic data be used in conjunction with paleo-CO$_2$ records to reconstruct paleogrowth rates. This approach provides a means to test for iron-stimulated changes in algal growth in sedimentary records.

1. Introduction

Martin [1990] hypothesized that new production rates in the modern Southern Ocean are limited by iron deficiency and that the low atmospheric CO$_2$ levels during the last glacial maximum (LGM) resulted from iron-stimulated increases in the efficiency of the biological pump. This “iron hypothesis” was also invoked to explain the high-nutrient, low-chlorophyll conditions in the equatorial Pacific and the Gulf of Alaska. Subsequently, unenclosed iron fertilization experiments performed in the equatorial Pacific have documented that the growth of phytoplankton in these waters is limited presently by iron availability [Martin et al., 1994; Coale et al., 1996a]. However, recent geological evidence from the equatorial Pacific and Southern Ocean suggests that iron did not stimulate productivity during glacial intervals and calls into question the iron hypothesis for controlling CO$_2$ levels during the LGM [Murray et al., 1995; François et al., 1997].

The stable carbon isotopic composition ($^{13}$C) of algal organic matter can provide important insights into the environmental conditions under which carbon fixation occurs. As such, the determination of $^{13}$C has been suggested as a valuable tool for reconstructing ancient biogeochemical processes [Hayes et al., 1990]. For example, various authors have related photosynthetic $^{13}$C fractionation ($\varepsilon_p$) to changes in primary productivity. Strictly speaking, however, for a given concentration of aqueous CO$_2$ ([CO$_2$]aq), $\varepsilon_p$ is inversely correlated with phytoplankton growth rate [Laws et al., 1995]. Phytoplankton growth ($\mu$, d$^{-1}$) is related to the rate of primary production (dC/dt, mg C m$^{-3}$ d$^{-1}$) according to the following equation [Popp et al., 1997]:

$$\mu = \frac{C}{C_{max}} \frac{dC}{dt}$$

where C is phytoplankton carbon biomass (mg C m$^{-3}$). This equation implies that equivalent production rates can be achieved under conditions of moderate algal biomass and low growth rate (e.g., postbloom waters) and low algal biomass and moderate growth rate (e.g., open oceanic waters). Coale et al. [1996b] have shown that subnanomolar increases in iron concentration can yield a threefold increase in the net growth rate of equatorial Pacific phytoplankton. Algal growth and primary production rates can be related only if the standing stock of phytoplankton carbon is known. Consequently, the development of a paleoproxy for $\mu$ would be potentially useful for detecting iron-stimulated changes in phytoplankton growth in the sedimentary record.

Recent laboratory-based chemostat studies have documented that [CO$_2$]aq, growth rate ($\mu$), cell geometry, and active dissolved inorganic carbon (DIC) transport are important factors controlling the $^{13}$C of marine phytoplankton [Laws et al., 1995, 1997; Bidigare et al., 1997a; Popp et al., 1998]. We participated in IronEx II to extend these chemostat studies and to establish predictive linkages between $\mu$, [CO$_2$]aq, $\varepsilon_p$, and the rate of export production in equatorial Pacific waters. On the basis of previous studies, we expected significant increases in $\mu$ and export production following iron addition [Martin et al., 1994; Coale et al., 1996b; Gordon et al., 1997; Landry et al., 1997]. Since marine particulate organic carbon (POC) is a complex mixture of autotrophs, heterotrophs, and detritus, biomarker distributions and their isotopic compositions were used to monitor changes in phytoplankton biomass, community structure, and isotopic composition during IronEx II.
Figure 1. Time series of biomarker and organic carbon parameters measured at 3 m depth during IronEx II: (a) POC:Chl weight ratio (w:w) and phytoplankton concentration (nM), (b) carotenoid composition (% total), and (c) δ13CPOC and δ13Cphytopl. (‰ versus PeeDee belemnite (PDB). Fucoxanthin (Fucox), 19'-hexanoyloxyfucoxanthin (H-Fucox), 19'-butanoyloxyfucoxanthin (B-Fucox), lutein, and zeaxanthin (Zeax) are taxon-specific biomarkers for estimating pigment biomass contributions by diatoms, haptophytes, pelagophytes, chlorophytes, and cyanobacteria, respectively. The curve describing time-dependent changes in δ13Cphytopl was fit by eye, whereas the line describing the δ13CPOC data corresponds to that predicted by least squares regression analysis. The three sequential infusions of FeSO4 on YD 149 (+2 nM), YD 152 (+1 nM), and YD 156 (+1 nM) are denoted as “+Fe” on the abscissa of Figure 1c.

2. Materials and Methods

The IronEx II experiment was conducted during May-June 1995 and was initiated at 4°S, 105°W [Coale et al., 1996a]. For comparative purposes, we have also included results obtained during the U.S. Joint Global Ocean Flux Study (JGOFS) EqPac study [Murray et al., 1992]. FePac cruises TT007 and TT011 took place during February-March and August-September 1992, periods which coincided with El Niño and “normal” conditions, respectively [Landry et al., 1997]. Seawater and large-volume particulate samples were collected for the determination of pigment [Latasa et al., 1997] and lipid biomarker [Wakeham and Caneel, 1988] concentrations, phytoplankton growth rates [Landry and Hassett, 1982], carbonate system parameters [Steinberg et al., 1998], δ13C of ΣCO2 and POC [Laws et al., 1993], δ13C of algal biomarkers [Bidigare et al., 1991; Hanson, 1997; Pancost et al., 1999], and dissolved and particulate 234Th [Buesseler, 1998]. Fucoxanthin, 19'-hexanoyloxyfucoxanthin, 19'-butanoyloxyfucoxanthin, lutein, and zeaxanthin were used as taxon-specific biomarkers for estimating pigment biomass contributions by diatoms, haptophytes, pelagophytes, chlorophytes, and cyanobacteria (Prorocentrum spp. and
Synechococcus spp., respectively [Bidigare and Ondrusek, 1996]. The $\delta^{13}$C of phytoplankton ($\delta^{13}$C$_{phytopl}$) sampled during the EqPac and IronEx II expeditions was reconstructed from compound-specific isotopic analyses of chlorophyll $a$ ($\delta^{13}$C$_{chl}$). EqPac cruise TT007 [Laws et al., 1995] and phyto ($\delta^{13}$C$_{phy}$), IronEx II and EqPac cruises TT007/TT011 [Hanson, 1997; Pancost et al., 1999]). For the Chl-based $\delta^{13}$C$_{phytopl}$ reconstructions, phytoplankton were assumed to be enriched in $\delta^{13}$C by 1.1% relative to $\delta^{13}$C$_{chl}$. The latter value was calculated by mass balance, assuming that the chlorin ring (i.e., chlorophyllide $a$) and phytopl chain of Chl are enriched and depleted in $\delta^{13}$C by 0.5 and 4.0%, respectively, relative to plant biomass [Hayes et al., 1987; Bidigare et al., 1997b]. For the phyto-based $\delta^{13}$C$_{phytopl}$ reconstructions, phytoplankton were assumed to be enriched in $\delta^{13}$C by 4.0% relative to $\delta^{13}$C$_{phy}$ [Bidigare et al., 1997b]. The $\delta^{13}$C$_{phytopl}$ and $\delta^{13}$C$_{co2}$ values determined during EqPac and IronEx II were used to estimate $\epsilon_p$, the fractionation associated with photosynthetic carbon fixation [Freeman and Hayes, 1992]:

$$\epsilon_p = 1000 \left( [\delta^{13}C_{CO2} - \delta^{13}C_{phytopl}] / (1000 + \delta^{13}C_{phytopl}) \right)$$

The flux of POC ($F_{POC}$, mmol m$^{-2}$ d$^{-1}$) during IronEx II (Year Day (YD) 148-168) was calculated as follows:

$$F_{POC} = \frac{F_{Th}}{\Delta^{234}Th}$$

Th flux ($F_{Th}$, dpm m$^{-2}$ d$^{-1}$) is determined from the $\Delta^{234}$Th activity balance in the surface ocean.

$$\Delta^{234}Th = (\Delta^{234}U - \Delta^{234}Th)\lambda - F_{Th} + V$$

where $\Delta^{234}$U and $\Delta^{234}$Th are the measured activities, $\lambda$ is the $\Delta^{234}$Th decay rate (0.0288 d$^{-1}$), $F_{Th}$ is the net loss rate on sinking particles, and $V$ is the sum of physical transport processes. If integrated for a given depth horizon (here 25 m was used), this equation allows one to calculate the $\Delta^{234}$Th export flux on sinking particles (dpm m$^{-2}$ d$^{-1}$). For this application in IronEx II, the average measured total $\Delta^{234}$Th activities at YD 151, 156, and 163 was used to calculate $\Delta^{234}Th$. $V$ has been shown to be insignificant in most open ocean settings [Buesseler, 1998]. A source of $\Delta^{234}$Th was added owing to the deepening of the mixed layer between YD 151-156 (mixed layer depth increased from 35 to 50 m by YD 156 and remained constant, and $\Delta^{234}$Th fluxes increased from 700 to 1400 dpm m$^{-2}$ d$^{-1}$, depending upon mixed layer depth assumptions). If a simple steadystate model had been used ($\Delta^{234}Th = 0$ and $V = 0$), calculated fluxes would have been similar, except during YD 156-163, when the increase in $F_{POC}$ would be smaller, peaking at 17 mmol C m$^{-2}$ d$^{-1}$. Measured POC/$\Delta^{234}$Th ratios were taken from samples collected on 53 mm-mesh screens, and values of 10, 14, and 17 mmol dpm$^{-1}$ were used in the $F_{POC}$ calculations.

### Table 1. Variations in Pigment-Specific Isotope Ratios During EqPac Cruise TT007

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Depth, m</th>
<th>$\delta^{13}$C$_{phy}$</th>
<th>$\delta^{13}$C$_{chl}$</th>
<th>$\delta^{13}$C$_{chl}$</th>
<th>$\delta^{13}$C$_{chl-phy}$</th>
<th>Phy</th>
<th>Chl</th>
<th>$\Delta^{13}$C</th>
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<tbody>
<tr>
<td>5°N</td>
<td>78</td>
<td>-26.4</td>
<td>-23.6</td>
<td>-22.0</td>
<td>+4.4</td>
<td>-22.4</td>
<td>-22.5</td>
<td>+0.1</td>
</tr>
<tr>
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<td>20</td>
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<td>-23.6</td>
<td>-22.0</td>
<td>+4.4</td>
<td>-22.4</td>
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<td>+0.1</td>
</tr>
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<td>-23.6</td>
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<td>-22.0</td>
<td>-21.2</td>
<td>-0.8</td>
</tr>
<tr>
<td>1°N</td>
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<td>-23.6</td>
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<td>+5.8</td>
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<td>-21.2</td>
<td>-0.8</td>
</tr>
<tr>
<td>1°N</td>
<td>44</td>
<td>-25.4</td>
<td>-23.6</td>
<td>-22.9</td>
<td>+2.5</td>
<td>-21.4</td>
<td>-22.7</td>
<td>+1.3</td>
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<td>-26.7</td>
<td>-23.6</td>
<td>-22.9</td>
<td>+2.5</td>
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<td>+1.3</td>
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<td>-23.6</td>
<td>-21.7</td>
<td>+3.5</td>
<td>-21.2</td>
<td>-21.9</td>
<td>+0.7</td>
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</table>

Ratios are in % versus Pee Dee belemnite (PDB). TT007 Stations were occupied along 140°W during February-March 1992. The isotopic composition of chlorophyllide $a$ ($\delta^{13}$C$_{chl-phy}$) was calculated from $\delta^{13}$C$_{phy}$ and $\delta^{13}$C$_{chl}$ by mass balance.
Table 2. Variations in isotope parameters, $[\text{CO}_2]_{\text{aq}}$ (μmol kg$^{-1}$), and $\mu$ (d$^{-1}$) in the equatorial Pacific

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Phytopl</th>
<th>$\delta^{13}$C, %</th>
<th>$\mu$</th>
<th>$\text{CO}_2$</th>
<th>aq</th>
<th>Ep (%)</th>
<th>$[\text{CO}<em>2]</em>{\text{aq}}$</th>
<th>$\mu$</th>
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<tbody>
<tr>
<td>TTO07 (3°N-3°S)</td>
<td>-22.0</td>
<td>-6.67</td>
<td>15.6</td>
<td>10.99</td>
<td>0.45</td>
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<tr>
<td>Error</td>
<td>±0.6</td>
<td>±0.07</td>
<td>±0.6</td>
<td>±0.32</td>
<td>±0.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n</td>
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<td>13</td>
<td>13</td>
<td>13</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TT011 (3°N-3°S)</td>
<td>-23.4</td>
<td>-7.24</td>
<td>16.6</td>
<td>13.22</td>
<td>0.76</td>
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<tr>
<td>Error</td>
<td>±1.0</td>
<td>±0.06</td>
<td>±1.0</td>
<td>±0.56</td>
<td>±0.39</td>
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<td>n</td>
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<table>
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<th>Cruise</th>
<th>Phytopl</th>
<th>$\delta^{13}$C, %</th>
<th>$\mu$</th>
<th>$\text{CO}_2$</th>
<th>aq</th>
<th>Ep (%)</th>
<th>$[\text{CO}<em>2]</em>{\text{aq}}$</th>
<th>$\mu$</th>
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<tr>
<td>Controls</td>
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<td>-7.33</td>
<td>17.6</td>
<td>15.36</td>
<td>0.62</td>
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<tr>
<td>Error</td>
<td>±0.8</td>
<td>±0.08</td>
<td>±0.9</td>
<td>±0.28</td>
<td>±0.12</td>
<td></td>
<td></td>
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<tr>
<td>n</td>
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<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YD 150-152</td>
<td>-23.6</td>
<td>-7.24</td>
<td>16.8</td>
<td>15.16</td>
<td>0.64</td>
<td></td>
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<tr>
<td>Error</td>
<td>±0.5</td>
<td>±0.01</td>
<td>±0.5</td>
<td>±0.15</td>
<td>±0.06</td>
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<tr>
<td>n</td>
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<td>2</td>
<td>2</td>
<td>2</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>YD 155-158</td>
<td>-18.5</td>
<td>-7.10</td>
<td>11.6</td>
<td>13.76</td>
<td>1.28</td>
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<tr>
<td>Error</td>
<td>±0.4</td>
<td>±0.02</td>
<td>±0.4</td>
<td>±0.20</td>
<td>±0.46</td>
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<tr>
<td>YD 163</td>
<td>-17.5</td>
<td>-7.06</td>
<td>10.7</td>
<td>13.18</td>
<td>1.14</td>
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</table>

$[\text{CO}_2]_{\text{aq}}$ values are in μmol kg$^{-1}$, and $\mu$ values are in d$^{-1}$. Errors are the standard deviation or the range of duplicate determinations, and n is the number of determinations.
The mean $\delta^{13}$C$_{\text{phytopl}}$ value for TTO07 was calculated using the data given in Table 1. Samples collected during TTO01 and IronEx II for the determination of $\delta^{13}$C$_{\text{phytopl}}$ were acquired at depths of 15-40 and 3 m, respectively. For IronEx II, $\mu$ was determined for samples collected from the surface mixed layer. For EqPac cruises TTO07 and TT011 (3°N-3°S, along 140°W), mean growth rates were calculated from measurements performed at depths of 10-20, 45-50, and 70-80 m [Latasa et al., 1997].

The $\delta^{13}$C of phytoplankton sampled during EqPac was reconstructed from compound-specific isotopic analyses of both Chl and phytol. During TTO07, $\delta^{13}$C$_{\text{Chl}}$ and $\delta^{13}$C$_{\text{phytol}}$ were analyzed together in four samples, and results were used to compute the isotopic composition of chlorophyllide α ($\delta^{13}$C$_{\text{Chl}}$). The difference in $\delta^{13}$C between chlorophyllide α and phytol ranged from +2.5 to +5.8% (Table 1). These results are in good agreement with the range of values determined for sedimentary geoporphyrins and polysisoprenoids (+3.8 to +5.5% [Hayes et al., 1990]).

The difference in $\delta^{13}$C$_{\text{phytopl}}$ (Δ$\delta^{13}$C) calculated for these four paired samples ranged from –0.8 to +1.5%, implying that the carbon isotopic reconstructions reported here are accurate to within ±1%.

Chemical and biological measurements from the patch 1 experiment were grouped into categories on the basis of bloom sequence: prerelease/control, prebloom (YD 150-152), bloom (YD 155-158), and postbloom (YD 163). Unfortunately, data are not available during YD 153-154 and 159-162 because of survey activities and the time required to deploy and sample the patch 2 (SF6 control) and patch 3 (+0.3 mM FeSO$_4$) experiments [Coale et al., 1996a]. Grouping the data in this manner minimizes lag effects associated with progressive changes in environmental ($[\text{CO}_2]_{\text{aq}}$ and nutrient concentrations), biological ($\mu$ and species composition), and carbon isotopic ($\delta^{13}$C$_{\text{CO}_2}$ and $\delta^{13}$C$_{\text{phytol}}$) parameters. The phytoplankton growth rate for the prerelease and control group averaged 0.62 d$^{-1}$, a value which falls between the mean rates of 0.45 and 0.76 d$^{-1}$ determined for TTO07 and TT011, respectively (Table 2). Highest values of $\mu$ were observed at the peak of the diatom bloom during YD 155-158 (1.28 ± 0.46 d$^{-1}$). These iron-enhanced growth rates yielded significant increases in algal biomass (Figure 1a), which in turn depleted the concentration of nitrate [Coale et al., 1996a]. In addition, the diatom bloom drew down $[\text{CO}_2]_{\text{aq}}$ by 2.2 μmol kg$^{-1}$. Values of $\delta^{13}$C$_{\text{phytol}}$ increased by 7 (Figure 1c and Table 2). An enrichment of only 2% in $\delta^{13}$C$_{\text{POC}}$ was observed during the same period, which documents that bulk POC is not representative of phytoplankton biomass at this study site.

Values of Ep determined for the prerelease and control group during the initial phase of the diatom bloom averaged 17.6 and 16.8%, respectively, and were similar to those measured during EqPac (Table 2). As the bloom progressed, Ep decreased to a minimum value of 10.7% on YD 163. Recently, Laws et al. [1997] have shown that fractionation of $^{13}$C by the pennate diatom, Phaeodactylum tricornutum, can be described by a theoretical model that assumes this alga regulates its cytoplasmic $[\text{CO}_2]_{\text{aq}}$ to minimize the energy required to concentrate $\text{CO}_2$ at the carboxylation site. This model was used to investigate Ep variations during EqPac and IronEx II by assuming that $\varepsilon_{\text{max}}$ for
Figure 2. Relationship between $\mu/[\text{CO}_2]_{aq}$ and $E_P$ for phytoplankton assemblages investigated during the EPAC and IronEx II cruises. The error bars correspond to the variability of $\mu$ and $E_P$ given in Table 2. The curved line (model) corresponds to the equation $\mu/[\text{CO}_2]_{aq} = 0.065 \times [(26.80 \times E_P)/(E_P - 1.28)] \text{kg \, \mu mol}^{-1} \text{d}^{-1}$ (see text for details).

The naturally occurring radionuclide thorium-234 (234Th, half-life = 24.1 days) was used as a tracer of upper ocean particle export during IronEx II. Sorption of 234Th on sinking particles results in a net deficiency, relative to its 238Th source, in its concentration in the surface ocean. For IronEx II, seven surface samples were collected during YD 148-163 for the determination of concentrations of dissolved and particulate 234Th and POC (Figure 3a). These showed that activities of total 234Th were essentially constant during YD 150-158 and that both particulate 234Th and POC increased during the bloom, presumably as the available surface area and biomass increased (Figure 3b). The total activity of 234Th decreased after YD 158. This change was coincident with the large decrease in diatoms, documented by flow cytometry [Cavender-Bares et al., 1999], and with decreases in phytoplankton concentrations (Figures 1a, 1b, and 3). On the basis of benthic observations made during EqPac [Smith et al., 1997] and IronEx II, [CO2]aq and $E_P$ averaged 14.44 $\mu$mol kg$^{-1}$ and 0.85 d$^{-1}$, and individual determinations ranged from 13.18 to 15.64 $\mu$mol kg$^{-1}$ and from 0.52 to 1.81 d$^{-1}$, respectively. These data and the model in Figure 2 were used to assess the relative importance of $\mu$ and [CO2]aq in modifying $E_P$ and the sensitivity analysis revealed that $\mu$ was 7 times more important than [CO2]aq in causing $E_P$ variations during IronEx II.

As can be seen from Figure 4, the proposed scheme for the paleo-reconstruction of [CO2]aq and $E_P$, [CO2]aq is reconstructed with knowledge of the Emiliania huxleyi growth rate factor ($b_{[234Th]}$) and the stable carbon isotopic compositions of $\delta^{13}C_C$, alkaidene ($\delta^{13}C_{al}$) and calcium carbonate ($\delta^{13}C_{calc}$) [Jaques et al., 1994, Bideau et al., 1997a]. For surface waters in the vicinity of the equatorial Pacific (EqPac, IronEx II, and Peru upwelling system), Bideau et al. [1997a] found that $b_{[234Th]}$ was highly correlated with [PO4] (reduced major axis regression analysis: $b_{[234Th]} = 158 [\text{PO}_4] + 41$, $r = 0.98$, $n = 33$). Alternatively, if sedimentary aspenones are below the limit of quantification, [CO2]aq can be reconstructed from ice core pCO2 records. Values of $\mu$ are estimated via the stable carbon isotopic composition of phytoplankton ($\delta^{13}C_{ph}$), [CO2]aq, and the relationship shown in Figure 2.
al., 1996], it is likely that the diatoms facilitated the export of photosynthetic nanoplankton during IronEx II. The calculated POC flux at 25 m prior to enrichment was 7 mmol m⁻² d⁻¹. The flux roughly doubled to 15 mmol m⁻² d⁻¹ between YD 151 and 156 and peaked at values approaching 50 mmol m⁻² d⁻¹ between YD 156 and 163 (Figure 3c). These are the first data to show directly that particulate fluxes increase following addition of iron to HNLC regions. In turn, this export indicates that the associated decrease in Cp (Figure 3c) will be transferred to the sedimentary record. While it is tempting to establish a predictable relationship between POC flux and C, additional data are required to determine if this correlation exists for other marine environments.

4. Conclusions

The reconstruction of paleo-productivity patterns, as inferred from changes in bulk parameters in the sedimentary record (e.g., total organic carbon [TOC], δ¹³C-TOC, and δ¹⁵N), is confounded by variable preservation efficiencies, sediment focusing, changes in sedimentation rate, and the diagenetic alteration of isotopic signals. In addition, it has been shown that the Si:N and Si:P uptake ratios for diatoms increase under iron-deplete conditions, calling into question the use of opal accumulation rates for estimating paleo-productivity [Boyle, 1998; Hutchins and Bruland, 1998; Takeda, 1998]. Furthermore, Bidle and Azam [1999] have recently demonstrated that bacteria play a major role in the dissolution of diatom frustules, which may, in turn, alter isotopic signals recorded in diatom frustules. If sufficient quantities of phytoplankton are present in the sedimentary record for determining C, then it should be possible to estimate paleogrowth rates for the equatorial Pacific given knowledge of the paleo-CO₂ record (Figure 4). Recent studies indicate that the latter can be deduced from measurements of δ¹³Calkalike (Figure 4) [Jasper et al., 1994; Bidigare et al., 1997a]. Phytoplankton concentrations determined for equatorial Pacific sediments (5⁰N-5⁰S, 140⁰W) range from 37 to 300 ng g⁻¹d⁻¹ (0-5 cm interval) and from 2 to 5 ng g⁻¹d⁻¹ (10-12 cm interval), respectively [S. G. Wakeham, unpublished data, 1999]. If phytoplankton concentrations at the LGM interval (~35 cm [Jasper et al., 1994; Murray et al., 1995]) are similar to the latter, then 35-85 cm³ sediment would be required for determination of δ¹³Cp. These volumes of sediment would yield ≤100 ng phytoplankton, enough material for three 25 ng injections onto a isotopic-ratio-monitoring gas chromatograph/mass spectrometer (irmGC/MS) system. The use of compound-specific isotopic analyses (CSIA) to infer changes in paleogrowth rate is expected to be largely unbiased by selective preservation, sediment focusing, and diagenetic alteration since it is based on an intrinsic property (δ¹³C) determined for a molecular fossil [Hayes et al., 1990]. The results presented here indicate that CSIA may be useful for detecting variations in algal growth rate in the geologic record and evaluating the role of iron in past climate fluctuations.

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