Carbon isotopic fractionation (ε_p) of C_{37} alkenones in deep-sea sediments: Its potential as a paleonutrient proxy

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[1] We compared ocean atlas values of surface water [PO_4^{3-}] and [$CO_2(aq)$] against the carbon isotopic fractionation (ε_p) of alkenones obtained from surface sediments of the South Atlantic and the central Pacific (Pacific data are from *Pagani et al.* [2002]). We observed a positive correlation between ε_p and $1/[CO_2(aq)]$, which is opposite of what would be expected if the concentration of $CO_2(aq)$ were the major factor controlling the carbon isotopic fractionation of $C_{37:2}$ alkenones. Instead, we found inverse relationships between ε_p and [PO_4^{3-}] for the two ocean basins (for the Atlantic, $\varepsilon_p = -4.6*[PO_4^{3-}] + 15.1$, R = 0.76; for the Pacific, $\varepsilon_p = -4.1*[PO_4^{3-}] + 13.7$, R = 0.64), suggesting that ε_p is predominantly controlled by growth rate, which in turn is related to nutrient concentration. The similarity of the slopes implies that a general relationship between both parameters may exist. Using the relationship obtained from the South Atlantic, we estimated surface water nutrient concentrations for the past 200,000 years from a deep-sea sediment core recovered off Angola. Low ε_p values, indicating high nutrient concentrations, coincide with high contents of total organic carbon and C_{37} alkenones, low surface water temperatures, and decreased bulk $\delta^{15}N$ values, suggesting an increased upwelling of nutrient-rich cool subsurface waters as the main cause for the observed ε_p decrease. *INDEX TERMS:* 1050 Geochemistry: Marine geochemistry (4835, 4850); 1040 Geochemistry: Isotopic composition/chemistry; 1615 Global Change: Biogeochemical processes (4805); 1055 Geochemistry: Organic geochemistry; 1635 Global Change: Oceans (4203); *KEYWORDS:* alkenones, carbon isotopic composition, paleonutrient proxy, biomarker

1. Introduction

[2] Air trapped in the Vostok ice core (Antarctica) documents that the concentration of atmospheric carbon dioxide (CO_2) varied in concert with climatic cycles throughout the past 420,000 years [*Petit et al.*, 1999]. The decrease of 80–100 ppmv during glacial times cannot be explained solely by higher solubility of CO_2 in colder seawater [*Broecker*, 1982; *Sigman and Boyle*, 2000; *Archer et al.*, 2000]. Besides other causes a larger glacial ocean nutrient reservoir could have reduced the CO_2 partial pressure in the surface ocean and the atmosphere (*Broecker* [1982]; see *Sigman and Boyle* [2000] for a recent review). With more phosphate in the glacial ocean, the biological cycling was enhanced, increasing the extent to which surface waters were depleted in $\sum CO_2$ and thereby decreasing the atmospheric CO_2 content [*Broecker*, 1982; *Broecker and Peng*, 1987]. Hence the reconstruction of past surface water nutrient concentration is crucial to understand the processes responsible for the lower atmospheric CO_2 during glacials.

[3] Paleonutrient concentrations of ocean waters are commonly estimated from $\delta^{13}C$ and Cd/Ca in planktic and benthic foraminifera. The carbon isotope ratio in foraminiferal calcite, however, is controlled by a variety of factors such as the $\delta^{13}C_{\sum CO2}$, temperature, and pH of ambient seawater, or metabolic CO_2, which complicates its interpretation as nutrient proxy [*Lynch-Stieglitz et al.*, 1995; *Spero et al.*, 1997; *Bijma et al.*, 1999]. Similarly, the Cd/Ca elemental ratio in planktic foraminifera is highly temperature sensitive [*Rickaby and Elderfield*, 1999] and questionable as an alternative tracer of surface water nutrient concentration. Moreover, in ocean areas and water depths

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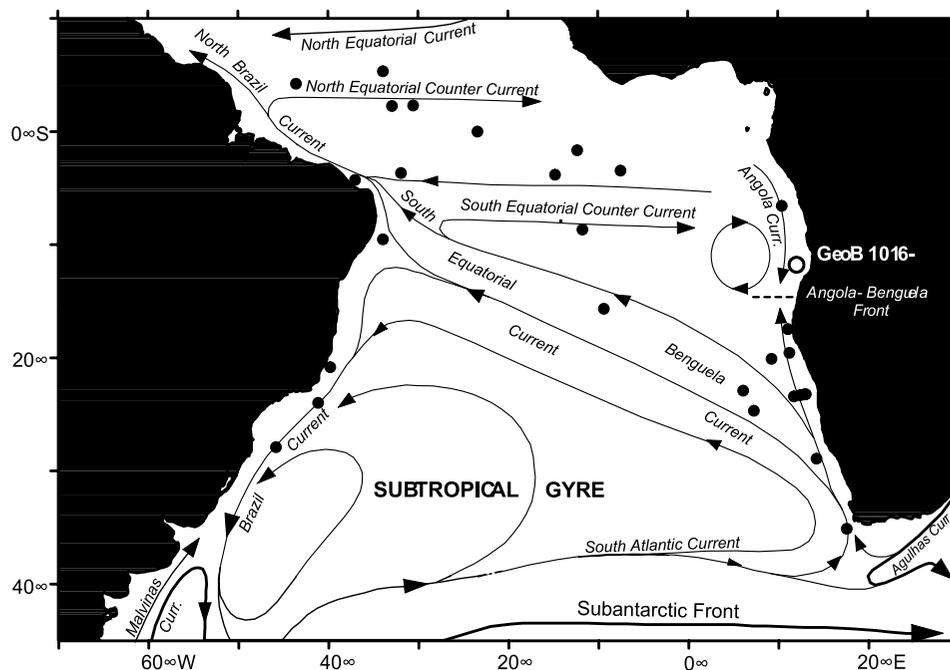
Figure 1. Map of the South Atlantic showing sample locations and main surface ocean currents.

where calcite dissolution occurs foraminiferal-based proxies are not applicable. Bulk sediment δ^{15}N, which is related to nutrient utilization, is not biased by dissolution [*Altabet and Francois*, 1994; *Holmes et al.*, 1999]. Other factors, however, influence the nitrogen cycle and may cause alterations of the δ^{15}N signal in the water column and sediments (e.g., nitrogen source, mineralization, nitrification, denitrification, diagenesis) [*Altabet et al.*, 1999].

[4] *Sigman and Boyle* [2000] pointed out that one of the major obstacles in the evaluation of hypotheses explaining the variations in atmospheric CO_2 concentration is the uncertainty in existing proxies for surface ocean nutrient levels. Of particular interest in the study of climate change is therefore the exploration of new nutrient proxies. The carbon isotopic fractionation (ε_p) in organic biomarkers, such as alkenones and phytol appears to be a promising candidate. The ε_p of phytol, for instance, has been proposed for the reconstruction of growth rates [*Bidigare et al.*, 1999a]. *Pagani et al.* [2000] applied the ε_p of C_{37} alkenones obtained from Miocene sediments to reconstruct changes in nutrient conditions, growth rates and ocean circulation.

[5] Besides other factors the growth rate significantly influences the carbon isotopic composition of marine phytoplankton [*Francois et al.*, 1993; *Bidigare et al.*, 1997, 1999b; *Popp et al.*, 1998a; *Riebesell et al.*, 2000]. Since the growth rate mainly depends on the availability of light and nutrients in the photic zone, the isotopic composition of organic compounds should provide information about the nutrient level at which the phytoplankton grew, especially in the tropical-subtropical ocean where sunlight is not a limiting factor. Cell geometry, enzymatic carbon fixation (ε_f), cell membrane permeability, cell surface area, and the ratio of active carbon uptake to carbon fixation are likely to cause systematic offsets on the isotopic fractionation of alkenones

[*Popp et al.*, 1998b] but are assumed to be relatively constant for alkenone producers. Therefore changes of the ε_p of C_{37} alkenones should predominantly reflect variations in growth rate and surface water nutrient concentration.

[6] In the present study we compare relationships between surface water concentrations of PO_4^{3-} and CO_2(aq) with the ε_p of the diunsaturated C_{37} alkenone extracted from core-top sediments of the South Atlantic [*Benthien et al.*, 2002] and the central Pacific [*Pagani et al.*, 2002]. In order to reconstruct nutrient levels for the last 200,000 years in the southeast Atlantic Ocean we applied our South Atlantic core-top calibration for [PO_4^{3-}] to sediment core GeoB1016-3 from the Angola Basin. Low values of carbon isotope fractionation (ε_p) of $C_{37:2}$ alkenones, indicating high nutrient concentrations, coincide with high contents of total organic carbon and C_{37} alkenones, low surface water temperatures, and decreased bulk δ^{15}N values, suggesting an increased upwelling of nutrient-rich, cool subsurface waters as the main cause for the decrease of ε_p.

2. Study Area

[7] The surface water circulation in the South Atlantic is dominated by a subtropical anticyclonic gyre (Figure 1). The eastern limb of this gyre is formed by the Benguela Current which is primarily fed by the South Atlantic Current and the Agulhas Current [*Peterson and Stramma*, 1991]. Near 30°S, the main part of the Benguela Current separates from the coast and forms the northwestward flowing Benguela Oceanic Current. Along the continental margin, the coastal branch of the Benguela Current transports cold and nutrient-rich water northward across the Walvis Ridge. At about 15°S, it converges with the southward flowing Angola Current, forming the Angola-Benguela Front. Surface water

is transported westward in the equatorial area with the South Equatorial Current (SEC) and the North Equatorial Current, while North and South Equatorial Counter Currents move surface water in the opposite direction. At about 10°S, off the coast of Brazil, the SEC splits into two branches, forming the southward flowing Brazil Current and the northward moving North Brazil Current which transport South Atlantic surface water across the equator into the Northern Hemisphere. The Brazil Current converges with the northward flowing Malvinas Current at about 35°S, is deflected to the east and feeds the South Atlantic Current, thereby closing the subtropical gyre circulation.

[8] Today, the northeastern Angola Basin is a region of high primary productivity [*Berger et al.*, 1989] due to oceanic upwelling which brings nutrients into the photic zone [*van Bennekom and Berger*, 1984; *Ravelo et al.*, 1990]. Wind-driven coastal upwelling does not significantly influence the region of core GeoB 1016-3 and is generally limited to latitudes south of about 15°S [*Shannon*, 1985; *Lutjeharms and Meeuwis*, 1987]. Nutrients are transported to the surface waters off Angola by the northward flowing coastal branch of the Benguela Current, which diverts to the subsurface in the Angola-Benguela frontal zone [*Shannon et al.*, 1987] and can be traced a far north as 5°S [*van Bennekom and Berger*, 1984].

3. Background Information on the Alkenone Signals

3.1. Seasonality and Living Depth of Haptophytes

[9] The interpretation of the δ¹³C signal of alkenones extracted from marine sediments requires knowledge about the living depth of the alkenone producers. Hapthophytes need sunlight for photosynthesis and thrive in the photic zone. Dependent on the concentration of suspended particles, the depth of the photic zone varies from ∼20 m in eutrophic to ∼120 m in oligotrophic regions [*Morel and Berthon*, 1989; *Longhurst*, 1993]. Since the discovery that the extent of unsaturation in alkenones changes with water (growth) temperature [*Marlowe*, 1984; *Brassell et al.*, 1986], several water column and core-top studies from various oceanic regions were performed to calibrate the alkenone temperature signal (for a recent review, see *Herbert* [2001]). In general, these studies indicate that the sedimentary $U_{37}^{K'}$ signal reflects the annual mean temperature of the oceanic surface mixed layer. Exceptions hereof were described for the eastern and central North Pacific Ocean, where the depth of alkenone production appears to occur mainly in thermocline waters, significantly deeper than the surface mixed layer [*Prahl et al.*, 1993; *Doose et al.*, 1997; *Ohkouchi et al.*, 1999]. Core-top calibrations encompassing various biogeographical coccolithophorid zones of the South Atlantic show that the best correlation between $U_{37}^{K'}$ and sea surface temperature (SST) is obtained when using modern atlas temperature from 0 to 10 m water depth [*Müller et al.*, 1998; *Benthien and Müller*, 2000]. The study of *Müller et al.* [1998] also indicates that the effect of seasonal changes in primary production on the sedimentary $U_{37}^{K'}$ signal is negligible in these regions. Recent sediment trap studies from the tropical-subtropical eastern Atlantic likewise suggest that $U_{37}^{K'}$ principally records the annual average of

mixed layer temperature [*Treppke et al.*, 1996; *Müller and Fischer*, 2001, 2004]. The isotopic composition of alkenones extracted from sediments represents a time-integrated signal that comprises several hundreds to thousands of years, depending on the size of the sample, the sediment accumulation rate, and the bioturbation intensity. We therefore compare core-top sediments with annual mean nutrient concentrations of the upper 10 m of the water column obtained from the World Ocean Atlas [*Conkright et al.*, 1994].

3.2. Factors Influencing εₚ of C₃₇ Alkenones

[10] Simple two step models assuming passive diffusion of CO_2 into the cell suggest that the photosynthetic carbon isotopic fractionation ε_p is a function of enzymatic carbon fixation ε_f (e.g., 29‰ for Rubisco; *Raven and Johnston* [1991]), the ambient $[CO_2(aq)]$ and the so-called b value, which is an arbitrary, empirically derived parameter accounting for all physiological factors (e.g., growth rate or cell size) influencing the carbon isotopic fractionation [*Jasper et al.*, 1994]:

$$\varepsilon_p = \varepsilon_f - \frac{b}{[CO_2(aq)]}. \tag{1}$$

[11] On the basis of models of carbon isotopic fractionation, *Rau et al.* [1996] and *Keller and Morel* [1999] showed that the ε_p of marine phytoplankton can vary as a function of growth rate, ε_f, cell membrane permeability, cell surface area, and the ratio of active carbon uptake to carbon fixation rate. Since alkenones are taxon-specific biomarkers, the effects of variations in cell size and membrane permeability are assumed to be small [*Bidigare et al.*, 1997; *Popp et al.*, 1998b].

[12] On the basis of laboratory experiments several authors suggested that marine phytoplankton may possess a CO_2-concentrating mechanism (CCM) and that inorganic carbon either as bicarbonate (HCO_3^-) or as CO_2 is actively transported into the cell [*Kerby and Raven*, 1985; *Burns and Beardall*, 1987; *Nimer et al.*, 1996; *Korb et al.*, 1997; *Laws et al.*, 1997]. Active transport, especially in case of bicarbonate uptake, can affect the δ¹³C of phytoplankton and therefore has important implications for the interpretation of isotope data. However, the discussion of this topic is still controversial (see *Benthien et al.* [2002] for more details).

[13] The isotopic fractionation in marine phytoplankton also varies as a function of growth rate [*Francois et al.*, 1993]. On the basis of theoretical considerations, *Rau et al.* [1996] suggested that ε_p should decrease with increasing growth rates. This finding was corroborated by *Benthien et al.* [2002], *Pagani* [2002], and *Pagani et al.* [2002] who recently demonstrated by core-top studies that the isotopic fractionation of C₃₇ alkenones is influenced by growth rate and/or growth rate influencing factors such as the surface water nutrient concentration.

4. Material and Methods

4.1. Samples

[14] The surface sediment samples from the South Atlantic were collected during several cruises of R/V *Meteor*, R/V

Table 1. Isotopic Composition and Fractionation Data (Both in ‰ Versus PDB) of $C_{37:2}$ Alkenones From South Atlantic Core-Top Sediments[a]

Core	Latitude	Longitude	SST	$\delta^{13}C_{37:2}$	ε_p	$[CO_{2(aq)}]$	b Values	$[PO_4^{3-}]$
1016-3[b]	11°46S	11°40E	24.7	−23.5	13.3	11.5	135	0.32
1008-6[b]	6°34S	10°19E	25.5	−23.1	12.9	11.8	142	0.28
1028-4[c]	20°06S	9°11E	20.6	−22.9	12.1	12.2	157	0.52
1032-2[c]	22°54S	6°02E	19.8	−24.3	13.5	10.1	117	0.31
1041-1[c]	3°28S	7°36W	26.1	−23.6	13.5	9.2	106	0.18
1105-3[c]	1°39S	12°25W	25.7	−23.4	13.2	8.9	105	0.18
1117-3[c]	3°48S	14°53W	26.2	−23.6	13.5	9.5	109	0.17
1214-2[c]	24°41S	7°14E	20.6	−23.4	12.7	10.0	124	0.32
1413-1[c]	15°40S	9°27W	24.8	−23.6	13.4	9.0	105	0.23
1501-1[b]	3°40S	32°00W	26.2	−25.4	15.3	9.5	92	0.16
1503-1[b]	2°18N	30°38W	26.7	−25.0	15.0	8.4	84	0.13
1505-3[b]	2°16N	33°00W	26.3	−25.1	15.1	8.4	82	0.16
1508-1[b]	5°20N	34°01W	27.1	−25.1	15.2	8.7	86	0.19
1515-2[b]	4°14N	43°40W	26.6	−25.0	15.0	8.0	79	0.24
1703-5[b]	17°28S	11°01E	19.6	−23.8	13.0	13.2	158	0.66
1706-1[b]	19°33S	11°10E	18.1	−23.5	12.5	12.9	161	0.71
1710-2[c]	23°25S	11°41E	18.9	−23.0	12.1	12.2	157	0.59
1711-5[b]	23°18S	12°22E	18.3	−23.9	12.9	12.2	147	0.63
1712-2[c]	23°15S	12°48E	18.2	−22.5	11.5	13.2	178	0.64
1713-6[c]	23°13S	13°00E	17.9	−22.6	11.5	13.2	178	0.66
1719-5[b]	28°55S	14°10E	17.5	−24.8	13.7	8.5	96	0.36
2102-1[b]	23°59S	41°12W	24.7	−25.6	15.4	8.2	79	0.13
2109-3[c]	27°54S	45°52W	23.9	−24.0	13.6	8.4	96	0.13
2125-2[b]	20°49S	39°51W	25.2	−25.8	15.7	8.3	77	0.11
2215-8[b]	0°00N	23°29W	26.7	−24.5	14.5	8.3	87	0.11
2204-1[b]	9°31S	34°01W	26.5	−23.6	13.5	8.1	93	0.16
3603-1[c]	35°07S	17°32E	19.9	−23.6	12.8	8.9	109	0.43
1903-1[b]	8°40S	11°50W	24.9	−25.7	15.6	8.7	82	0.19
3117-3[c]	4°17S	37°05W	27.5	−24.2	14.3	8.8	94	0.20

[a]Sea surface temperatures (in °C) derived from $U_{37}^{K'}$ [*Andersen et al.*, 1999; *Benthien et al.*, 2002] applying the calibration of *Prahl et al.* [1988]. Also given are the concentrations of surface water CO_2(aq) [*Benthien et al.*, 2002] and phosphate [*Conkright et al.*, 1994] (extracted from the Web site http://ferret.pmel.noaa.gov/NVODS/servlets/dataset/servlets/dataset).

[b]From *Benthien et al.* [2001].

[c]From *Andersen et al.* [1999].

Sonne and R/V *Victor Hensen* (Table 1, Figure 1) using a giant box corer (0−2 cm) and a multiple corer (0−1 cm). Only at site GeoB-1016-3 the surface sediment was sampled from the top of the gravity corer. A Holocene age of the sediments was confirmed by the occurrence of the planktic foraminifera *Globorotalia menardii* and/or by oxygen isotope stratigraphy and radiocarbon dating. Depending on sedimentation rates and bioturbation intensity, the surface samples cover several hundreds to thousands of years (for details, see *Benthien et al.* [2002] and references therein). Subsamples from the box and gravity corer were taken with plastic syringes (10 ml) and stored at 4°C until analysis at the University of Bremen. Sediments collected by the multiple corer were cut into 1 cm slices and frozen at −18°C until analysis.

[15] Core GeoB 1016-3 was recovered from the continental margin off Angola (11°46′ S/11°40′E, 3411 m water depth, Figure 1) [*Wefer et al.*, 1988]. The stratigraphy of the core is based on δ^{18}O variations measured on the planktic foraminifera *Globigerinoides ruber* (pink) [*Schneider et al.*, 1995]. For δ^{13}C analyses on alkenones the gravity core was resampled six years after recovery [*Andersen et al.*, 1999].

4.2. Alkenone Analysis

[16] Analytical procedures are described in detail in the work of *Benthien et al.* [2002]. In brief, alkenones were extracted from freeze-dried and homogenized sediment sam-

ples with an UP 200H ultrasonic disrupter probe using three successively less polar mixtures of methanol and dichloromethane. Thereafter, the extracts where purified by passing them over a silica gel cartridge and then saponified to remove possibly interfering esters. Alkenone unsaturation ratios and concentrations were determined by gas chromatography.

[17] The carbon isotope analyses of the $C_{37:2}$ alkenone were made with a HP 5890 II gas chromatograph (GC) coupled via a combustion interface to a Finnigan MAT 252 mass spectrometer. The isotopic composition of the $C_{37:2}$ alkenone was determined relative to PDB by comparison with coinjected *n*-alkanes (C_{34}, C_{36}, C_{37}, C_{38}) and a standard gas (CO_2) of known isotopic composition. Each sample was measured 2−4 times revealing an analytical precision better than 0.3‰.

4.3. Surface Water CO_2 and Nutrients

[18] In contrast to the study of *Pagani et al.* [2002] we used integrated values of nutrient and CO_2 available from data collections and ocean atlases because the core-top sediments cover a time span of at least several hundreds of years. Therefore the comparison with time-integrated values of surface water properties is a suitable approach. Annual mean concentrations of phosphate (0−10 m) for each location were extracted from the World Ocean Atlas (*Conkright et al.* [1994]; http://ferret.pmel.noaa.gov/NVODS/servlets/dataset/servlets/dataset; Table 1).

Table 2. Isotopic Composition and Fractionation Data (Both in ‰ Versus PDB) of $C_{37:2}$ Alkenones From Central Pacific Core-Top Sediments [*Pagani et al.*, 2002][a]

Site	Latitude	Longitude	SST	$\delta^{13}C_{37:2}$	ε_p	$[CO_{2(aq)}]$	b Value	$[PO_4^{3-}]$
NB75	40.00°N	177E	13.9	−22.90	11.61	11.58	155.06	0.51
NB74	37.50°N	177E	14.80	−23.20	11.92	10.31	134.85	0.26
NB72	33.00°N	177E	16.70	−23.90	12.99	9.68	116.35	0.14
NB70	27.07°N	177E	18.10	−23.10	12.48	10.01	125.35	0.10
NB69	24.00°N	177E	21.50	−23.50	12.47	9.53	119.46	0.11
NB68	21.82°N	177E	21.82	−23.90	13.61	9.19	104.77	0.13
NMC1	19.00°N	177E	24.30	−21.30	11.22	8.83	121.69	0.14
NB67	15.00°N	177E	26.60	−23.10	13.75	9.37	105.43	0.14
NB66	12.90°N	177E	26.80	−22.70	14.07	8.44	92.27	0.15
NB65	09.98°N	177E	27.30	−22.70	13.29	8.02	93.94	0.17
NB62	03.00°N	177E	28.30	−22.60	12.75	10.59	129.68	0.25
NB61	00.00°	177E	27.90	−22.50	13.21	9.93	117.14	0.33
NGC43	02.00°S	177E	28.30	−22.30	11.92	10.44	136.51	0.35
NB60	05.00°S	177E	27.00	−22.10	11.96	11.85	154.52	0.33
NB59	07.00°S	177E	26.60	−22.40	12.35	12.20	154.35	0.32

[a]Isotopic fractionation represents the mean value calculated from the seasonal data given in the work of *Pagani et al.* [2002]. Sea surface temperatures (in °C) are derived from alkenone analyses [*Pagani et al.*, 2002]. Also given are the concentrations of preindustrial surface water $CO_2(aq)$ calculated form the observed modern $CO_2(aq)$ concentrations [*Pagani et al.*, 2002] and phosphate (annual mean; 0–10 m; *Conkright et al.* [1994]; extracted from the Web site http://ferret.pmel.noaa.gov/NVODS/servlets/dataset/servlets/dataset).

[19] Since annually integrated values for the partial pressure of CO_2 in the surface water (*PCO₂*) are not available, we gathered *PCO₂* data from several expeditions carried out in the South Atlantic Ocean [*Weiss et al.*, 1992; *Groupe CITHER 1*, 1994; *Johnson et al.*, 1995, 1998] (data are provided by the Carbon Dioxide Information Analysis Centre's Web page at http://cdiac.esd.ornl.gov) and converted the *PCO₂* values into concentrations of dissolved carbon dioxide ($[CO_2(aq)]$) applying Henry's Law [*Benthien et al.*, 2002, Table 1]. Finally, the $CO_2(aq)$ concentrations were computed for each sample location [*Benthien et al.*, 2002] using the Kriging method [*Davis*, 1986].

[20] The alkenones extracted from core-top sediments were predominantly biosynthesized and deposited under preindustrial conditions. Consequently, preindustrial $CO_2(aq)$ concentrations were calculated after subtracting the industrial increase of 70 ppmv [*Takahashi et al.*, 1992]. However, such a correction seems not to be appropriate for areas where strong upwelling of cold subsurface waters with high CO_2 concentrations causes a distinct sea-air imbalance [*Tans et al.*, 1990]. We therefore have not corrected the $CO_2(aq)$ concentrations at the core sites in the Angola and Benguela upwelling cells.

4.4. Calculation of ε_p and b Values

[21] We calculated the isotopic fractionation (ε_p) associated with the photosynthetic fixation of carbon using equation (2) [*Freeman and Hayes*, 1992], where δ_d is the isotopic composition of carbon in $CO_2(aq)$ and δ_p is the isotopic composition of photosynthate carbon:

$$\varepsilon_p = \left(\frac{\delta_d + 1000}{\delta_p + 1000} - 1\right)1000. \tag{2}$$

δ_p was derived from the isotopic composition of the $C_{37:2}$ alkenone corrected for the compound-specific fractionation ($\varepsilon_{alkenone}$) between the $C_{37:2}$ alkenone and the biomass of the alkenon-producing organisms. According to *Popp et al.* [1998a] we applied 4.2‰ for $\varepsilon_{alkenone}$:

$$\delta_p = \delta_{C37:2} + \varepsilon_{alkenone}\left(1 + \frac{\delta c_{37:2}}{1000}\right). \tag{3}$$

δ_d was calculated from $\delta_{\Sigma CO2}$ according to *Rau et al.* [1996] based on *Mook et al.* [1974]:

$$\delta_d = \delta_{\sum CO_2} + 23.644 - \frac{9701.5}{T}, \tag{4}$$

where T is the temperature in Kelvin. Temperatures were obtained from the alkenone unsaturation index ($U_{37}^{K'}$) using the calibration of *Prahl et al.* [1988]. Foraminiferal $\delta^{13}C$ values for the estimation of the preindustrial $\delta^{13}C$ of $CO_2(aq)$ in surface waters are not available for each surface sediment sample. We therefore assumed a constant preindustrial $\delta^{13}C_{\Sigma CO2}$ value of 2.5‰ for all samples [*Kroopnick*, 1985]. In core GeoB 1016-3 we estimated $\delta_{\Sigma CO2}$ from the $\delta^{13}C$ record of the surface-dwelling planktic foraminifera *G. ruber* (pink) [*Andersen et al.*, 1999]. The tests of *G. ruber* are depleted in ¹³C relative to the isotopic composition of total dissolved CO_2. To account for this offset we added 0.5‰ to the $\delta^{13}C$ values [*Fairbanks et al.*, 1982; *Curry and Crowley*, 1987]. The b value was calculated by rearranging equation (1) to:

$$b = \left(\varepsilon_f - \varepsilon_p\right)[CO_2(aq)]. \tag{5}$$

For the maximum isotope fractionation associated with the enzymes Rubisco and β-carboxylase we adopted $\varepsilon_f = 25‰$ as found by *Bidigare et al.* [1997] in chemostat experiments with two strains of *E. huxleyi*. This value is
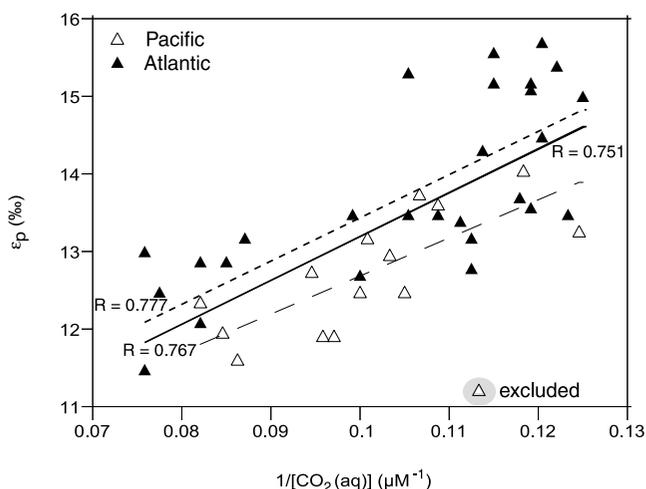
Figure 2. Relationships between isotopic fractionation (ε_p) of $C_{37:2}$ alkenones extracted from surface sediments against $1/[CO_2(aq)]$ of surface water in the South Atlantic (solid triangles) [*Benthien et al.*, 2002] and the central Pacific (open triangles) [*Pagani et al.*, 2002]. The outlier was excluded from the regression. Stippled lines represent the regressions for the Atlantic and Pacific data sets. The solid line denotes the regression for the complete data set.

Figure 3. Relationships between isotopic fractionation (ε_p) of $C_{37:2}$ alkenones extracted from surface sediments against surface water $[PO_4^{3-}]$ in the South Atlantic (solid triangles) [*Benthien et al.*, 2002; *Conkright et al.*, 1994] and the central Pacific (open triangles) [*Pagani et al.*, 2002]. The outlier was excluded from the regression. Stippled lines represent the regressions for the Atlantic and Pacific data sets. The solid line denotes the regression of the complete data set.

close to the range of 25.4–28.3‰ determined for eukaryotic algae [*Goericke et al.*, 1994].

5. Results and Discussion

5.1. Isotopic Fractionation (ε_p) in Core-Top Sediments

[22] To ascertain the main factor controlling the carbon isotope ratio of alkenones we analyzed core-top sediments from the South Atlantic Ocean for the isotopic composition of the $C_{37:2}$ alkenone, calculated their b and ε_p values, and compared the latter to surface water carbon dioxide and phosphate concentrations.

[23] The δ¹³C values of the $C_{37:2}$ alkenone in the South Atlantic core tops range from −25.8‰ to −22.5‰ and the corresponding ε_p values (calculated according to equation (2)) range from 11.5‰ to 15.5‰ (Table 1) [*Benthien et al.*, 2002]. These values are similar to the data recently determined by *Pagani et al.* [2002] on surface sediments samples from the central Pacific (−23.5‰ to −19.2‰ and 10.5‰ to 14.1‰, respectively; Table 2). In contrast to our study, *Pagani et al.* [2002] calculated the ε_p values from the δ¹³C of the $C_{37:2}$ alkenone for two different seasons (spring and autumn). Furthermore, they used seasonal depth-temperature profiles collected within the scope of the Northwest Pacific Carbon Cycle Study (NOPACCS) to constrain $[PO_4^{3-}]$ and calculated carbon dioxide concentration from NOPACCS water column measurements (for details, see *Pagani et al.* [2002]).

[24] To allow for a better comparison between the Pacific data of *Pagani et al.* [2002] and our Atlantic data set we determined an average annual ε_p from the spring and autumn values given in the work of *Pagani et al.* [2002]. For consistency we did not use the NOPACCS $[CO_2(aq)]$ and $[PO_4^{3-}]$ values reported by *Pagani et al.* [2002] but
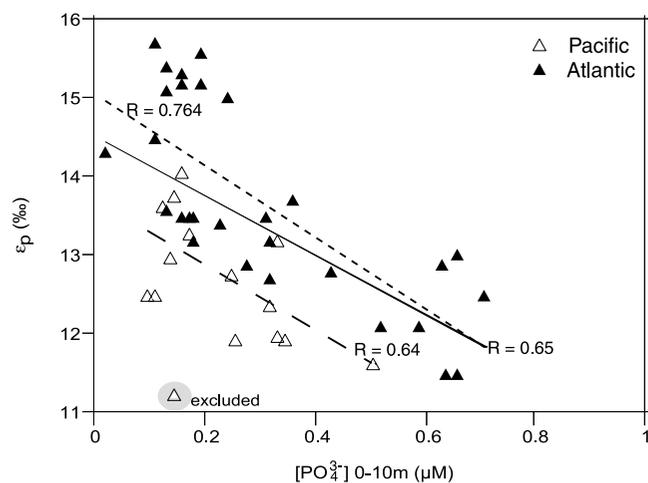
extracted the surface water $[PO_4^{3-}]$ (0–10 m) from the World Ocean Atlas [*Conkright et al.*, 1994]. Furthermore, we reduced the CO_2 concentrations listed in the work of *Pagani et al.* [2002, Table 2] for the anthropogenic CO_2 increase (equivalent to 70 ppmv) to obtain preindustrial values (Table 2). The relationships between ε_p, $[CO_2(aq)]$, and $[PO_4^{3-}]$ for the Pacific data set generally agree with each other when using either the original data from *Pagani et al.* [2002] or the recalculated annual mean values; the
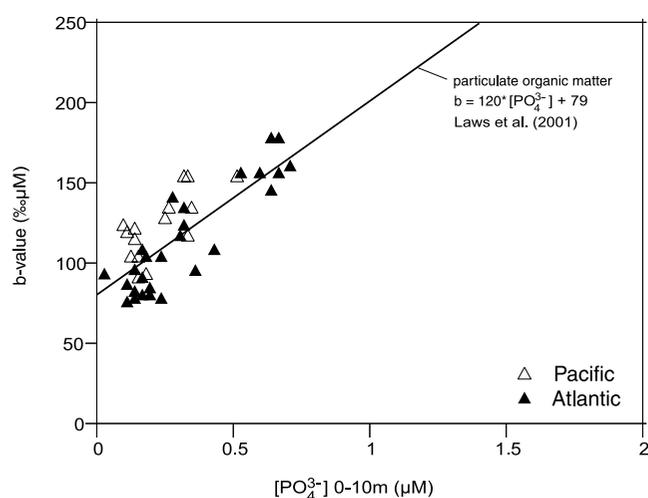

Figure 4. Relationship between the b value (calculated according to equation (5)) and surface water phosphate concentration. Filled triangles indicate Atlantic data [*Benthien et al.*, 2002; *Conkright et al.*, 1994], and open triangles denote Pacific data [*Pagani et al.*, 2002].
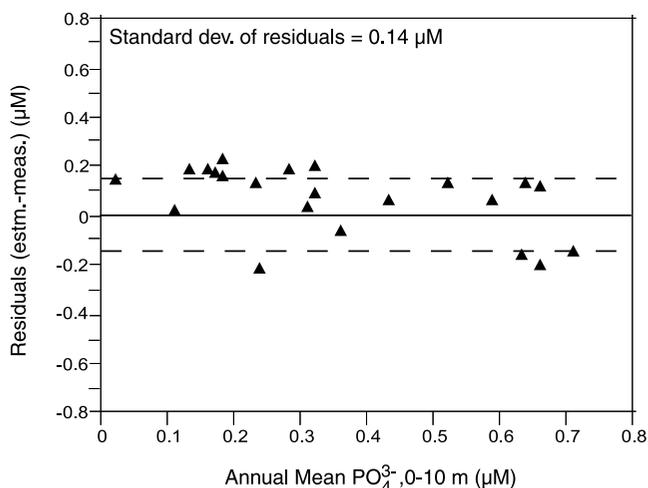
Figure 5. Annual mean phosphate concentration of surface water [*Conkright et al.*, 1994] against residual phosphate concentration estimated from the South Atlantic data set. Dashed lines denote the standard deviation of the residuals.

correlation coefficients, however, are higher for the annual mean values. For comparison we include both relationships in the following sections.

[25] If the concentration of $CO_2(aq)$ were the major factor controlling the carbon isotope fractionation of $C_{37:2}$ alkenones, a negative correlation between ε_p and the reciprocal of $CO_2(aq)$ would be expected [*Rau et al.*, 1992] (cf. equation (1)). In contrast, we observe positive linear relationships for both the Atlantic and the Pacific data sets (Figure 2). The correlations for the core-top sediments are similar for the two ocean basins (Figure 2; Atlantic: $\varepsilon_p = 55.7*[1/CO_2(aq)] + 7.9$, R = 0.78; Pacific $\varepsilon_p = 48.6*[1/CO_2(aq)] + 7.9$, R = 0.77; original autumn data: $\varepsilon_p = 58.7*[1/CO_2(aq)] + 7.2$, R = 0.66 [*Pagani et al.*, 2002]) suggesting that a general relationship exists between ε_p and $1/[CO_2(aq)]$, denoted by the solid line in Figure 2 ($\varepsilon_p = 56.5*[1/CO_2(aq)] + 7.6$, R = 0.75). However, the fact that the correlation between ε_p and $1/[CO_2(aq)]$ is opposite of what would be expected, strongly implies that factors other

than $[CO_2(aq)]$ control the isotopic fractionation, as recently discussed by *Laws et al.* [2001], *Benthien et al.* [2002], *Pagani et al.* [2002], and *Schulte et al.* [2004]. A possible explanation for the positive relationship between ε_p and $1/[CO_2(aq)]$ is that the isotopic fractionation of the $C_{37:2}$ alkenone reflects surface water properties covarying with the $CO_2(aq)$ concentration, such as the availability of nutrients.

[26] A dependence of ε_p on nutrient concentration is suggested by the negative correlation between ε_p and surface water phosphate concentration in the South Atlantic and the central Pacific (Figure 3). The slopes in the equations for the two ocean basins are similar (Atlantic: $\varepsilon_p = -4.6*[PO_4^{3-}] + 15.1$, R = 0.76; Pacific: $\varepsilon_p = -4.1*[PO_4^{3-}] + 13.7$, R = 0.64; original autumn data: $\varepsilon_p = -2.1*[PO_4^{3-}] + 13.05$, R = 0.59), indicating that a general relationship between ε_p in surface sediments and surface water $[PO_4^{3-}]$ may exist. Combining the Pacific and Atlantic data sets yields $\varepsilon_p = -3.8*[PO_4^{3-}] + 14.5$, R = 0.65 (n = 44) for the annual mean values. The different intercept values in the equations for the Atlantic and the Pacific Ocean might result from the fact that the surface samples of the two data sets represent different time spans. The Atlantic core-top samples comprise several hundreds up to a few thousands of years [*Benthien et al.*, 2002] whereas the Pacific samples originate from areas with sedimentation rates of about 0.2 to 0.4 cm kyr^{-1} [*Pagani et al.*, 2002], corresponding to time intervals of at least 2500 to 5000 years for the uppermost centimeter. Further core-top studies from other oceanographic settings are required to check whether a global relationship between ε_p and surface water $[PO_4^{3-}]$ exists.

[27] However, at least in the Atlantic and Pacific regions of the present study, ε_p derived from the $C_{37:2}$ alkenone in core-top sediments appears to depend on the surface water phosphate concentration (Figure 3) [*Benthien et al.*, 2002; *Pagani et al.*, 2002]. This interpretation is supported by the good correlation between the *b* value and $[PO_4^{3-}]$ (Figure 4; $b = 121.5*[PO_4^{3-}] + 80.5$; R = 0.85, n = 44). The relationship resulting from our core tops is nearly identical with a compilation of data on marine suspended matter (*Laws et al.* [2001]; $b = 120 * [PO_4^{3-}] + 79$, R = 0.88, n = 145), indicated by the solid line in Figure 4. *Bidigare et al.* [1997] argued that the positive relationship between the *b*

Table 3. Error Propagation for the Paleo-$[PO_4^{3-}]$ Reconstruction[a]

Parameter	Initial Value	Absolute Error	Unit	Relative Error, %	Impact on ε_p
T	298	1	°K	0.34	+0.11
$\delta_{\Sigma CO2}$	2.5	0.1[b]	‰	4	+0.099
$\delta_{C37:2}$	−22	0.3[c]	‰	1.4	+0.308
$\varepsilon_{alkenone}$	4.2	0.2[d]	‰	4.8	−0.21
δ_p	−17.89	0.5	‰	2.8	+0.51
δ_d	−6.41	0.103	‰	1.6	−0.102
ε_p	11.69	0.51	‰	4.4	
PO_4^{3-}(atlas)	0.5	0.03[e]	μmol/l	6	
PO_4^{3-}(estimated)	0.74	0.077	μmol/l	10.4	

[a]As initial values we used values typical for the respective parameters. δ_p, δ_d and ε_p result from calculations (see equations (2), (3), and (4)) using the initial values.
[b]From *Kroopnick* [1985].
[c]From *Popp et al.* [1998a].
[d]From *Andersen et al.* [1999].
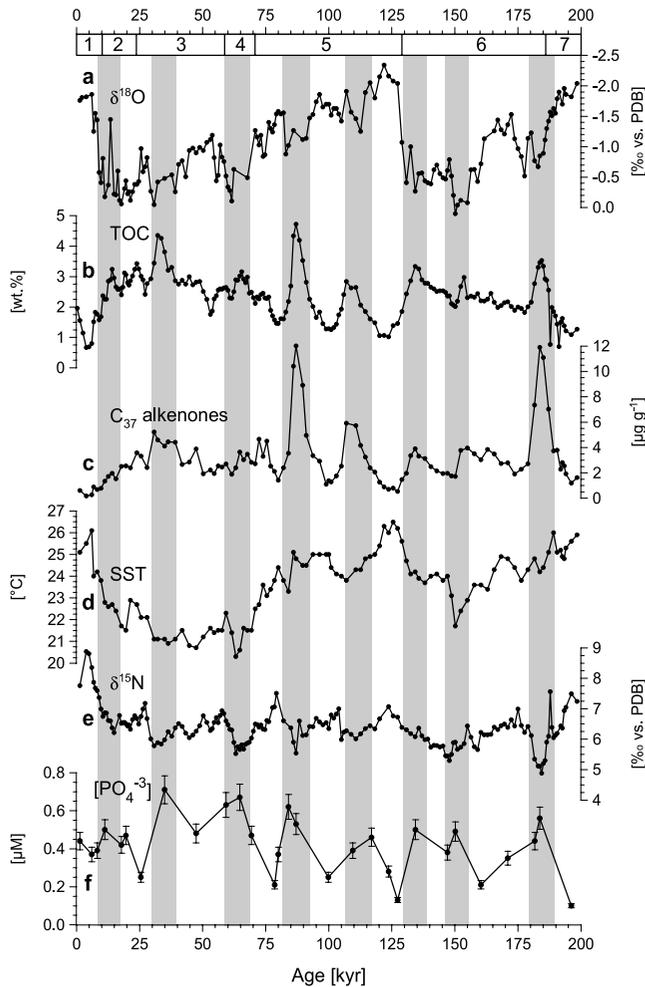[e]Typical error for atlas phosphate data extracted from the NOOA Web page (www.nooa.gov).

Figure 6. Time series of sediment core GeoB 1016-3. (a) Stable oxygen isotopes of *Globigerinoides ruber* (pink) [*Schneider et al.*, 1995], (b) total organic carbon concentrations [*Schneider et al.*, 1996], (c) C_{37} alkenone concentrations, (d) sea surface temperatures derived from $U_{37}^{K'}$ [*Schneider et al.*, 1995], (e) stable nitrogen isotopes of bulk sediment [*Holmes et al.*, 1999], and (f) estimated phosphate concentrations applying the relationship of ε_p versus $[PO_4^{3-}]$ obtained for the South Atlantic core tops (cf. Figure 3). The age model is based on $\delta^{18}O$ stratigraphy and is taken from *Schneider et al.* [1995]. Head bar denotes SPECMAP oxygen isotope stages.

value and phosphate concentration could simply be the result of the correlation between $[PO_4^{3-}]$ and $[CO_2(aq)]$. *Popp et al.* [1999b], however, examined the effect of $[PO_4^{3-}]$ on ε_p in marine suspended matter at relatively constant concentrations of $CO_2(aq)$ and found a poor relationship between $CO_2(aq)$ and ε_p but a significant correlation between $[PO_4^{3-}]$ and ε_p.

[28] Laboratory experiments, field studies, and theoretical considerations have established that b predominantly reflects the intracellular carbon demand which depends on microalgae growth, cell size and geometry, and membrane permeability [*Rau et al.*, 1996; *Popp et al.*, 1999b]. Because

variations in cell size, shape, and membrane properties are presumably small in haptophytes, their effects on the carbon isotope composition of the $C_{37:2}$ alkenone are considered to be minor [*Popp et al.*, 1998b, 1999a]. Consequently, we conclude that the correlation between $[PO_4^{3-}]$ and the b value reflects a dependency of haptophyte growth on surface water phosphate concentration. This assumption is consistent with the results of *Bidigare et al.* [1997] who observed a linear correlation between b and $[PO_4^{3-}]$ in oceanic environments with nonzero concentrations of phosphate. In a more recent study *Bidigare et al.* [1999a] used a sensitivity analysis to show that the effect of growth rate on variations in ε_p of marine phytoplankton is seven times higher than that of $[CO_2(aq)]$. *Riebesell et al.* [2000] likewise demonstrated that growth rate is far more important for the ε_p value than other factors. An influence of growth rate on the isotopic fractionation ε_p is also consistent with model results [*Rau et al.*, 1996]. With increasing growth rates the diffusive CO_2 flux through the cell membrane decreases relative to carbon fixation. The preferential uptake of ^{12}C leads to a ^{13}C increase of the internal carbon pool, which is then consumed by carbon fixation. As a result of this mechanism $\delta^{13}C_{37:2}$ values increase and those for ε_p decrease [*Keller and Morel*, 1999].

[29] In summary, the relationships between the isotopic fractionation of $C_{37:2}$ alkenones extracted from core-top sediments and surface water parameters suggest that ε_p is mainly influenced by growth rate and growth rate influencing factors, such as surface water phosphate concentration. We therefore propose that ε_p is a suitable proxy for the reconstruction of surface water nutrient concentrations.

5.2. Example of Use for ε_p as Paleonutrient Proxy

[30] The use of ε_p of the $C_{37:2}$ alkenone as a proxy for surface water nutrient levels requires knowledge about the reliability of the obtained phosphate concentrations. To demonstrate the degree of accordance between measured and estimated values, we used the relationship shown in Figure 3 to calculate $[PO_4^{3-}]$ for each of our core-top sites and compared these values to the annual mean $[PO_4^{3-}]$ taken from the World Ocean Atlas [*Conkright et al.*, 1994]. Figure 5 shows the residuals (estimated - measured $[PO_4^{3-}]$) as a function of annual mean phosphate concentrations. The standard deviation, indicated by the dashed lines, is ± 0.14 μM. There is no significant trend of the residuals as a function of measured $[PO_4^{3-}]$ attesting the linearity of the relationship.

[31] According to a propagation of errors, all calculation steps listed in Table 3 result in a relative error of the estimated $[PO_4^{3-}]$ of 10.4%. This includes also a propagation of errors for the calculation of ε_p. To determine the impact of each variable, ε_p was calculated by adding an absolute error to each variable and keeping the other parameters constant. From Table 3 it is evident that the greatest error is introduced by δ_p, which is the sum of the errors of $\delta^{13}C_{37:2}$ and $\varepsilon_{alkenone}$ (cf. equation (3)). Thus a higher precision in the measurement of the isotopic composition of alkenones would reduce the error of the nutrient estimation.

[32] To give an example of use for ε_p as proxy for surface water nutrient concentrations we chose core GeoB 1016-3

Table 4. Estimated Surface Water Phosphate Concentrations (in μM) for the Past 200 kyr at the Location of Core GeoB1016-3[a]

Age, kyr	ε_p	$[PO_4^{3-}]$ (Estimated)
1.3	13	0.44
6	13.4	0.37
8.2	13.3	0.39
11.2	12.8	0.50
17.8	13.2	0.42
19.6	12.9	0.47
25.5	13.9	0.25
34.9	11.8	0.71
47.4	12.8	0.48
59.2	12.2	0.63
64.7	12	0.67
69.3	12.9	0.47
78.5	14.1	0.21
80	13.4	0.37
84	12.2	0.62
87	12.7	0.53
99.8	13.9	0.25
109.5	13.3	0.39
117	13	0.46
123.8	13.8	0.28
127.3	14.5	0.13
134.4	12.8	0.50
147.1	13.3	0.38
150.2	12.8	0.49
160.3	14.1	0.21
171	13.5	0.35
181.7	13.1	0.44
183.7	12.5	0.56
196.2	14.6	0.10

[a]The age model is based on $\delta^{18}O$ of *G. ruber* (pink) [*Schneider et al.*, 1995]. The ε_p values are from *Andersen et al.* [1999]. Modern annual mean phosphate concentration at this location is 0.32 μM [*Conkright et al.*, 1994].

which has already been examined for surface water PCO_2 inferred from the $\delta^{13}C$ of organic carbon and $C_{37:2}$ alkenones [*Müller et al.*, 1994; *Andersen et al.*, 1999], sea surface temperature determined by the alkenone method [*Schneider et al.*, 1995], paleoproductivity estimated from changes in total organic carbon (TOC) [*Schneider et al.*, 1995], and nutrient utilization derived from bulk $\delta^{15}N$ [*Holmes et al.*, 1999]. We estimated surface water phosphate concentrations for the past 200,000 years by rearranging the equation derived from the South Atlantic surface sediments:

$$\left[PO_4^{3-}\right] = \left(15.1 - \varepsilon_p\right)/4.6. \qquad (6)$$

[33] Reconstructed phosphate concentrations vary between 0.1 and 0.7 μM (Figure 6f; Table 4) which is within the range observed for the modern ocean (0.009–2.6 μM; *Conkright et al.* [1994]). The core-top value of 0.44 μM compares well to the modern value (0.32 μM) obtained from the World Ocean Atlas [*Conkright et al.*, 1994]. Despite differences in the temporal resolution of the time series shown in Figure 6, it is apparent that high phosphate levels occur during oxygen isotope maxima of *G. ruber* and coincide with high concentrations of TOC and C_{37} alkenones, low surface water temperatures, and decreased

bulk $\delta^{15}N$ values suggesting an increased upwelling of nutrient-rich cool subsurface waters as the main cause for the $[PO_4^{3-}]$ maxima. These variations in upwelling intensity and productivity off Angola are driven by changes in the strength of the West African Monsoon and the position of the subtropical high pressure cell over the South Atlantic at 23- and 100-kyr periodicities [*Schneider et al.*, 1996]. As the mixed layer in upwelling areas is characterized by high carbon dioxide concentrations, an influence of $[CO_2(aq)]$ on the isotopic fractionation of the $C_{37:2}$ alkenone cannot be excluded. Changes in $[CO_2(aq)]$ and in nutrient-controlled phytoplankton growth affect ε_p in opposite directions. High concentrations of aquatic carbon dioxide lead to higher values of ε_p whereas enhanced growth rates cause lower ε_p values. Therefore our reconstruction of $[PO_4^{3-}]$ most probably underestimates the true values. At the moment there is no established proxy to separate the effects of $[CO_2(aq)]$ and nutrient-controlled growth on ε_p [*Popp et al.*, 1999b]. However, despite these limitations, our approach of using the isotopic fractionation of the $C_{37:2}$ alkenone as proxy for past nutrient levels results in realistic values of surface water phosphate concentration.

6. Conclusion

[34] The isotopic fractionation (ε_p) of the diunsaturated C_{37} alkenone in surface sediments is closely related to the surface water phosphate concentration in the South Atlantic [*Benthien et al.*, 2002] and the central Pacific [*Pagani et al.*, 2002]. Both data sets yield equations with similar slopes implying that a general relationship between both parameters may exist. The relationship between ε_p and $[PO_4^{3-}]$ is most probably mediated by the phytoplankton growth rate or the growth rate influencing factors as the good correlation between the b value and surface water phosphate concentration suggests.

[35] We used the regression of ε_p of alkenones in core-top sediments against surface water $[PO_4^{3-}]$ for the South Atlantic to estimate surface water phosphate concentrations for the past 200,000 at site GeoB 1016 in the Angola Basin. The coincidence of phosphate maxima with stable nitrogen isotope minima and high TOC and alkenone concentrations as indicators of nutrient level and paleoproductivity suggests that changes in upwelling intensity caused the variations in ε_p and that the carbon isotopic fractionation of alkenones provides a useful tool for the reconstruction of surface water nutrient concentrations.

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