

Stable Carbon Isotopic Composition of the C_{37:2} Alkenone: A Proxy for CO₂(aq) Concentration in Oceanic Surface Waters?

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Abstract: We tested the applicability of the carbon isotopic composition of C_{37:2} alkenones ($\delta^{13}\text{C}_{37:2}$) as a proxy for dissolved carbon dioxide CO₂(aq) in oceanic surface waters. For this purpose we determined $\delta^{13}\text{C}_{37:2}$ in suspended particulate organic matter (POM) and surface sediments from the South Atlantic. In opposite of what would be expected from a diffusive CO₂ uptake model for marine algae we observed a positive correlation between 1/[CO₂(aq)] and the isotopic fractionation (ϵ_p) calculated from $\delta^{13}\text{C}_{37:2}$. This clearly demonstrates that CO₂(aq) is not the primary factor controlling ϵ_p at the sites studied. On the other hand we found a negative correlation between ϵ_p and the phosphate concentration in the surface waters (0-10 m) supporting the assumption of Bidigare et al. (1997) that ϵ_p is primarily related to nutrient-limited algal growth rather than to [CO₂(aq)]. Reconstructing past CO₂(aq) levels from $\delta^{13}\text{C}_{37:2}$ thus requires additional proxy information in order to correct for the influence of haptophyte growth on the isotopic fractionation. In the eastern Angola Basin, we previously used $\delta^{15}\text{N}$ of bulk organic matter as proxy for nutrient-limited growth rates. As an alternative the Sr/Ca ratio of coccoliths has been recently suggested as growth-rate proxy which should be tested in future studies.

Introduction

From air trapped in the Vostok ice core (Antarctica) it is well known that the concentration of atmospheric carbon dioxide (CO₂) varied during the past 420,000 years in concert with late Quaternary climatic cycles (Petit et al. 1999). CO₂ is one of the so-called greenhouse gases controlling the global heat budget and there is growing evidence that the increase in the atmospheric CO₂ level observed since the beginning of the 19th century is contributing to world wide warming (e.g. Crowley 2000). However, predictions of future changes of Earth's

climate are difficult since the relationship between atmospheric CO₂ and long-term climatic cycles is very complex and poorly understood (Stouffer et al. 1994).

Atmospheric CO₂ levels depend on the balance of CO₂ between the world's oceans and terrestrial ecosystems. To a first approximation, equatorial regions of the modern ocean are supersaturated in CO₂ with respect to the atmosphere while sub-polar regions approach air-sea equilibrium and polar regions are undersaturated (Feely et al. 2001). To

define better the mechanisms by which oceanic and atmospheric levels of CO₂ have changed over geological time scales, paleoceanic sources and sinks of carbon dioxide must be delineated. Therefore paleo-indicators (proxies) for past CO₂ concentrations in the surface oceans are required.

Empirical relationships between the carbon isotopic composition of suspended organic matter ($\delta^{13}\text{C}_{\text{org}}$) and the concentration of dissolved carbon dioxide ([CO₂(aq)]) in oceanic surface waters imply that $\delta^{13}\text{C}_{\text{org}}$ of marine phytoplankton varies as a function of ambient [CO₂(aq)] (Degens et al. 1968; Rau et al. 1989, 1992; Francois et al. 1993; Rau 1994; Fischer et al. 1997, 1998; Bentaleb et al. 1998). Based on these observations it has been suggested that the isotopic composition of sedimentary organic carbon can be used as proxy for [CO₂(aq)] in ancient surface waters. Respective paleoceanographic reconstructions of CO₂ used the isotopic composition of bulk sedimentary organic carbon (Arthur et al. 1985; Fontugne and Calvert 1992; Müller et al. 1994; Bentaleb et al. 1996) as well as of individual biomarker compounds such as geoporphyrins (Popp et al. 1989) and long-chain alkenones (e.g. Jasper et al. 1994; Andersen et al. 1999; Pagani et al. 1999).

However, recent laboratory and field experiments as well as theoretical considerations indicate that the isotopic fractionation (ϵ_p) of carbon during photosynthesis, and consequently also the sedimentary $\delta^{13}\text{C}$ of organic matter, could also be influenced by physiological processes and environmental factors such as active carbon uptake (e.g. Laws et al. 1997), direct bicarbonate utilisation (Burns and Beardall 1987; Keller and Morel 1999), cell geometry and membrane permeability (e.g. Popp et al. 1998; Burkhardt et al. 1999). Moreover, growth rate and the growth rate limiting resources (e.g. temperature, nutrient supply, irradiance) were recently identified as additional factors (e.g. Bidigare et al. 1997, 1999; Riebesell et al. 2000a; Laws et al. 2001; Gervais and Riebesell 2001; Benthien et al. 2002).

Popp et al. (1998) demonstrated that some of the above mentioned factors can be evaded by using the isotopic composition of C₃₇ alkenones. This biomarker is exclusive to haptophyte algae such as the coccolithophorid *Emiliania huxleyi* and species of the genus *Gephyrocapsa* (Volkman et al. 1989;

Volkman et al. 1995; Conte et al. 1995), which both have a limited range in cell size and geometry. Assuming that alkenone-producing algae assimilate CO₂ mainly by passive diffusion, the relation between ϵ_p and [CO₂(aq)] can be expressed as follows (Jasper et al. 1994):

$$\epsilon_p = \epsilon_f - \frac{b}{[\text{CO}_2(\text{aq})]} \quad (1)$$

where ϵ_f is the enzymatic fractionation during carbon fixation and b is an arbitrary, empirically derived parameter accounting for all physiological factors influencing the carbon isotope discrimination (e.g. Rau et al. 1996).

Some laboratory and field studies have focused on the isotopic fractionation in alkenone producing algae and the $\delta^{13}\text{C}$ signal of C₃₇ alkenones (e.g. Bidigare et al. 1997; 1999; Popp et al. 1999; Riebesell et al. 2000b; Gonzales et al. 2001; Benthien et al. 2002). The results of these studies indicate that the fractionation of the C_{37.2} alkenone depends not solely on ambient [CO₂(aq)] but on a variety of factors (for a recent review see Laws et al. 2001). Bidigare et al. (1997) invoked that most variations in ϵ_p result from variations in growth rate related to nutrient availability rather than to [CO₂(aq)]. In their laboratory experiments they used nitrate limited chemostat cultures with continuous light and temperature conditions. This finding is consistent with the results of Riebesell et al. (2000b) who demonstrated by using N-repleted, light controlled batch cultures, that the effect of [CO₂(aq)] on isotope fractionation in *E. huxleyi* is small compared to potential changes of ϵ_p due to growth rate variations and factors that affect the growth rate (μ). However, considerable discrepancies were found in absolute values of ϵ_p as well as in the slope of ϵ_p vs. $\mu/[\text{CO}_2(\text{aq})]$. Probably these discrepancies are an effect of differences in the phytoplankton culture conditions (for a detailed discussion about the influence of culture experiment design see Laws et al. 2001).

In the present paper, we summarize isotopic results obtained from alkenones in the South Atlantic within the scope of the Collaborative Research Project 261 (Andersen et al. 1999; Benthien et al. 2002, and unpubl. data). In order to establish relationships between ϵ_p and environmental conditions

characteristic for the present surface ocean, we analysed suspended particulate organic matter (POM) and surface sediment samples for the isotopic composition of C_{37:2} alkenones and compared the results to CO₂ and phosphate concentrations in the overlying surface waters (0-10 m). In accordance with literature data, our results indicate only a weak effect of [(CO₂(aq))] on ε_p and δ¹³C_{alkenones} but a strong influence of nutrient-related growth rate. Finally, we compare late Quaternary paleo-PCO₂ reconstructions from the eastern Angola Basin based on the isotopic composition of total organic carbon (Müller et al. 1994) and C₃₇ alkenones (Andersen et al. 1999) and discuss them in the light of the new extended calibration results.

Material and Methods

Samples

Sediment samples were collected during several cruises of RV *Meteor*, RV *Sonne*, and R/V *Victor Hensen* (Andersen et al. 1999; Benthien et al. 2002; Fig. 1). Surface sediments were obtained using a giant box corer and a multiple corer (Tab. 1), except for site GeoB1016-3 where the surface sediment sample was taken from the top of the gravity corer. For the surface sediments a Holocene age was confirmed by the occurrence of the planktonic foraminifera *Globorotalia menardii* and/or by δ¹⁸O and ¹⁴C measurements on foraminifera (for details see Benthien et al. 2002 and references therein). The stratigraphy of gravity core GeoB1016-3 is based on foraminiferal δ¹⁸O (Schneider et al. 1995). After core recovery, subsamples from gravity and giant box cores were taken using plastic syringes (10 ml) and stored at 4°C until analysis. The gravity core was re-sampled 6 years after recovery for isotopic analyses on alkenones (Andersen et al. 1999). Sediments collected by the multiple corer were sectioned into 1 cm slices and frozen at -18°C until analysis.

Particulate organic matter was obtained by filtering 40 l of surface sea water through pre-combusted Whatman GF/F (nominal pore size 0.7µm) glass-fibre filters. Water for filtering was obtained aboard RV *Meteor* (cruise M46/3, Tab.

1) using a membrane pump situated at about 5 m water depth at the front of the vessel. The filters were stored at -18°C until analysis.

Alkenone Analysis

Detailed descriptions of analytical procedures can be found elsewhere (Schneider et al. 1995; Müller et al. 1998; Benthien and Müller 2000). Briefly, alkenones were extracted from freeze-dried and homogenised sediment with a UP 200H ultrasonic disrupter probe using three successively less polar mixtures of methanol and dichloromethane. For this purpose filters with POM were cut into small pieces after freeze drying. Thereafter the extracts were purified by passing them over a silica gel cartridge and then saponified to remove possibly interfering esters. Alkenone unsaturation ratios were determined by gas chromatography.

The carbon isotopic analysis of C_{37:2} alkenones was performed using a HP 5890 II gas chromatograph (GC) coupled via a combustion interface to a Finnigan MAT 252 mass spectrometer (for analytical details see Andersen et al. 1999 and Benthien et al. 2002). The isotopic composition of the C_{37:2}-alkenone was determined relative to PDB by comparison with co-injected *n*-alkanes (C₃₄, C₃₆, C₃₇, C₃₈) and a standard gas (CO₂) of known isotopic composition. Generally each sample was measured two to four times revealing an analytical precision better than 0.3‰.

Surface Water CO₂ and Nutrients

In contrast to other studies (e.g. Bidigare et al. 1997; Popp et al. 1999) we did not determine the concentrations of CO₂ and nutrients simultaneously with the sampling of POM. Instead we used integrated values of nutrients and CO₂ available from data collections or ocean atlases. Since core-top sediments in general represent at least a few hundred years a comparison with annually integrated values of surface water parameters is probably the best approach.

Unfortunately, for CO₂ no annually integrated values are available. We therefore estimated the partial pressure of CO₂ in the surface waters (PCO₂) from numerous expeditions carried out in the South Atlantic Ocean during different seasons

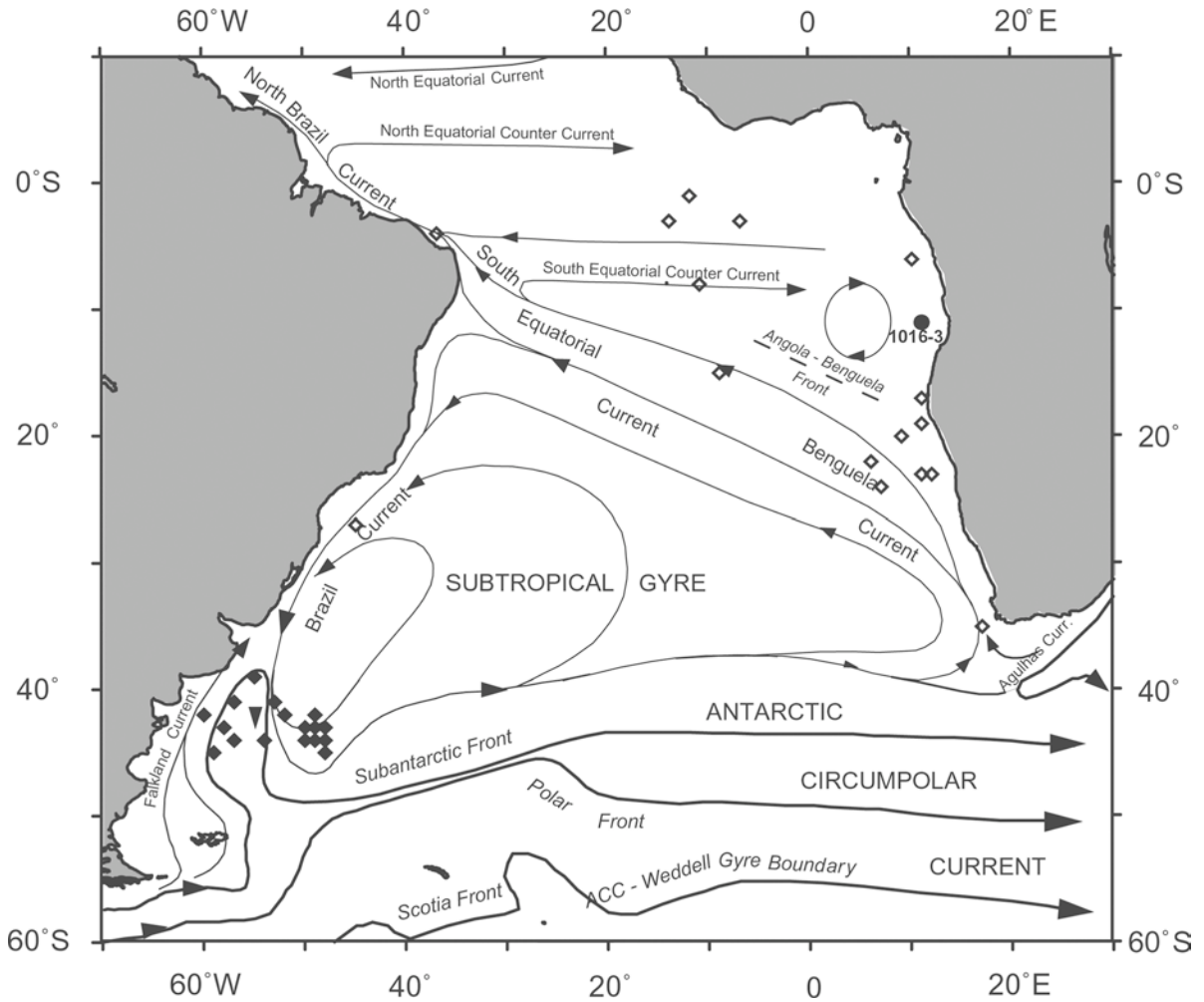


Fig. 1. Map of the South Atlantic Ocean showing sample locations and main surface currents: open diamonds represent locations of core top sediment, the black dot that of the gravity core GeoB1016-3 and filled diamonds those of particulate organic matter filtered from the water column.

and years (Weiss et al. 1992; Groupe CITHER 1, 1994; Johnson et al. 1995, 1998; extracted from the CDIAC (Carbon Dioxide Information Analysis Centre, web-page: <http://cdiac.esd.ornl.gov>) and converted the values into concentrations of dissolved carbon dioxide ($[\text{CO}_2(\text{aq})]$) applying Henry's Law (Fig. 2; Benthien et al. 2002). Pre-industrial $\text{CO}_2(\text{aq})$ concentrations were calculated in the same manner after subtracting the industrial increase of 70 ppmv (Takahashi et al. 1992). Such a correction is probably not appropriate for areas where strong upwelling of cold CO_2 -rich sub-surface waters results in a distinct sea-air imbalance

(e.g. Tans et al. 1990). Consequently the modern anthropogenic CO_2 increase has no significant influence on the surface water PCO_2 in such regions (Lee et al. 1997). Therefore, we did not correct the $\text{CO}_2(\text{aq})$ concentrations for the anthropogenic influence at core sites of the Angola and Benguela upwelling cells (Fig. 1). This problem was discussed in detail by Benthien et al. (2002). Finally, average $\text{CO}_2(\text{aq})$ concentrations were computed for each sample location (Fig. 2, Benthien et al. 2002) using the Kriging method (Davis 1986).

The annual mean concentration of phosphate in the surface water (0-10 m) at each location was

Core	Cruise	Lat.	Long.	SST [°C]	δ ¹³ C [‰]	ε _p [‰]	[CO ₂ (aq)] [μmol/L]	b-value [‰μmol/L]	[PO ₄] ³⁻ [μmol/L]
Sediment samples									
1016-3*	M6/6	11°46S	11°40E	24.7	-23.5	13.3	11.5	135	0.32
1008-6*	M6/6	6°34S	10°19E	25.5	-23.1	12.9	11.8	142	0.28
1028-4#	M6/6	20°06S	9°11E	20.6	-22.9	12.1	12.2	157	0.52
1032-2#	M6/6	22°54S	6°02E	19.8	-24.3	13.5	10.1	117	0.31
1041-1#	M6/6	3°28S	7°36W	26.1	-23.6	13.5	9.2	106	0.18
1105-3#	M9/4	1°39S	12°25W	25.7	-23.4	13.2	8.9	105	0.18
1117-3#	M9/4	3°48S	14°53W	26.2	-23.6	13.5	9.5	109	0.17
1214-2#	M12/1	24°41S	7°14E	20.6	-23.4	12.7	10	124	0.32
1413-1#	M16/1	15°40S	9°27W	24.8	-23.6	13.4	9	105	0.23
1501-1*	M16/2	3°40S	32°00W	26.2	-25.4	15.3	9.5	92	0.16
1503-2*	M16/2	2°18N	30°38W	26.7	-25	15	8.4	84	0.13
1505-3*	M16/2	2°16N	33°00W	26.3	-25.1	15.1	8.4	82	0.16
1508-1*	M16/2	5°20N	34°01W	27.1	-25.1	15.2	8.7	86	0.19
1515-2*	M16/2	4°14N	43°40W	26.6	-25	15	8	79	0.24
1703-5*	M20/2	17°27S	11°01E	19.6	-23.8	13	13.2	158	0.66
1706-1*	M20/2	19°33S	11°10E	18.1	-23.5	12.5	12.9	161	0.71
1710-2#	M20/2	23°25S	11°41E	18.9	-23	12.1	12.2	157	0.59
1711-5*	M20/2	23°18S	12°22E	18.3	-23.9	12.9	12.2	147	0.63
1712-2#	M20/2	23°15S	12°48E	18.2	-22.5	11.5	13.2	178	0.64
1713-6#	M20/2	23°13S	13°00E	17.9	-22.6	11.5	13.2	178	0.66
1719-5*	M20/2	28°55S	14°10E	17.5	-24.8	13.7	8.5	96	0.36
2102-1*	M23/2	23°59S	41°12W	24.7	-25.6	15.4	8.2	79	0.13
2109-3#	M23/2	27°54S	45°52W	23.9	-24	13.6	8.4	96	0.13
2125-2*	M23/2	20°49S	39°51W	25.2	-25.8	15.7	8.3	77	0.11
2215-8*	M23/3	0°00N	23°29W	26.7	-24.5	14.5	8.3	87	0.11
2204-1#	M23/3	8°31S	34°01W	26.5	-23.6	13.5	8.1	93	0.16
3603-1#	M34/1	35°07S	17°32E	19.9	-23.6	12.8	8.9	109	0.43
1903-1*	SO84	8°40S	11°50W	24.9	-25.7	15.6	8.7	82	0.19
3117-3#	JOPS II	4°17S	37°05W	27.5	-24.2	14.3	8.8	94	0.2
Particulate organic matter (POM)									
	M46/3	39°41S	55°82W	20.5	-29.7	15.8	13.9	128	0.75
	M46/3	41°85S	53°20W	19.9	-22.7	11	13.7	192	0.6
	M46/3	42°08S	52°70W	19.6	-25	11	13.7	194	0.53
	M46/3	42°84S	49°65W	18.5	-24.8	13.2	13.5	159	0.49
	M46/3	44°05S	48°68W	16.5	-24.9	13.2	13.3	157	0.55
	M46/3	45°58S	48°26W	15.7	-24.6	12.3	14.1	179	0.65
	M46/3	44°01S	49°94W	19.7	-25.9	13.8	13.6	152	0.52
	M46/3	44°38S	50°17W	19.8	-28.9	16.9	13.6	110	0.52
	M46/3	43°68S	49°68W	16.1	-25.1	13.3	13.6	159	0.52
	M46/3	43°80S	50°36W	18.8	-27.2	15.7	13.6	127	0.5
	M46/3	43°93S	48°95W	17.6	-25	12.8	13.3	161	0.59
	M46/3	44°23S	50°93W	18.7	-27.6	15.9	13.5	123	0.53
	M46/3	44°90S	54°45W	14.5	-22.7	10.5	13.6	197	0.66
	M46/3	45°20S	59°09W	12.3	-22.8	8.5	15.2	250	1.02
	M46/3	44°32S	57°50W	15.8	-22.7	10.1	14.4	215	0.9
	M46/3	44°34S	57°87W	15.9	-24.6	12.3	14.4	183	0.9
	M46/3	43°74S	58°99W	13.5	-21.8	9.6	15.2	234	0.95
	M46/3	42°30S	60°27W	19.2	-26.4	14	13.6	150	0.89
	M46/3	41°03S	57°53W	19.5	-23.6	9.4	14.8	232	0.85

Table 1. Isotopic composition and fractionation data (both in ‰) of the C_{37:2} alkenone determined in South Atlantic particulate organic matter (POM) and core top sediments. Data marked with * are from Andersen et al. (1999) and data marked with # are from Benthien et al. (2002). Data for POM are from this study. Sea-surface temperature (in °C) for the core tops are derived from alkenone analyses [U_{37}^K , Müller et al. 1998; Benthien and Müller 2000] applying the calibration of Prahl et al. 1988. Sea-surface temperature of POM samples are measured at sample station. Also given are the calculated concentrations of surface water carbon dioxide (Benthien et al. 2002) as well as the surface water concentration of phosphate (Conkright et al. 1994 extracted from the web site: http://ferret.wrc.noaa.gov/fbin/climate_server).

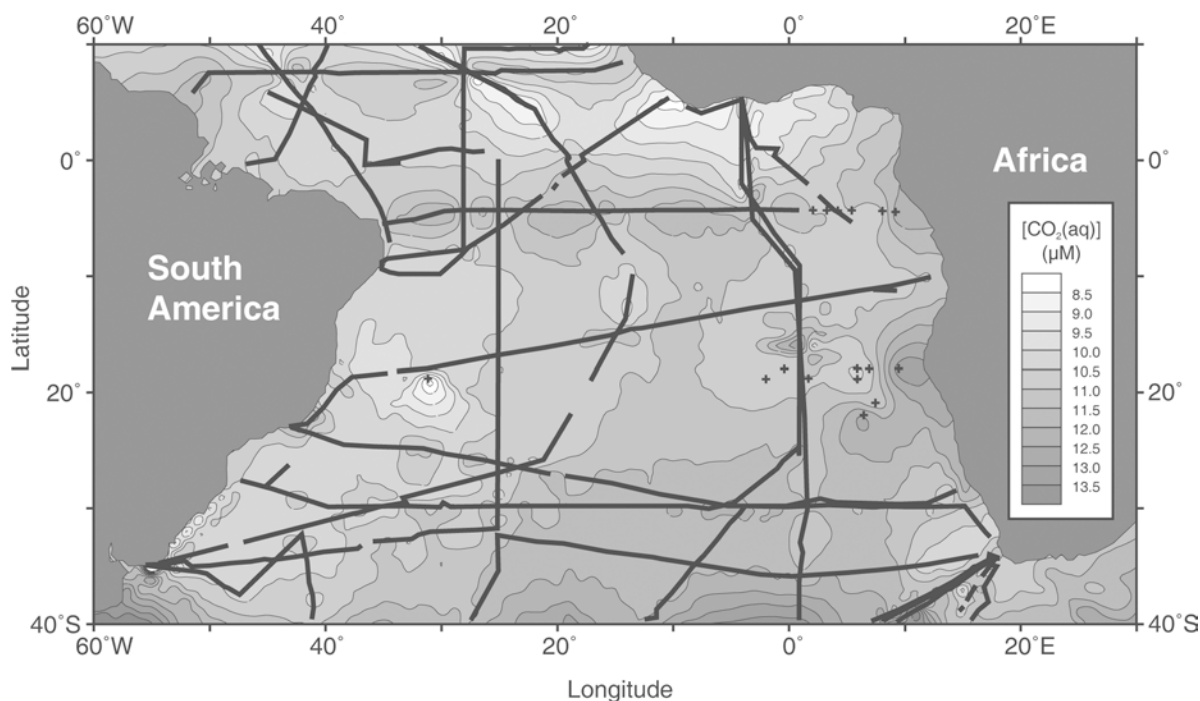


Fig. 2. Modern surface-water concentration of $\text{CO}_2(\text{aq})$ in the equatorial and South Atlantic Ocean. Concentrations were calculated from surface water partial pressure of carbon dioxide measured continuously during several expeditions (Weiss et al. 1992, Groupe CITHER 1 1994; Johnson et al. 1995, 1998). The tracks of this expeditions are indicated as solid thick lines. Single locations of measurements are shown as crosses. $[\text{CO}_2(\text{aq})]$ isolines were created with the Kridging method (redrawn from Benthien et al. 2002).

obtained from the World Ocean Atlas 1994 (http://ferret.wrc.noaa.gov/fbin/climate_server; Conkright et al. 1994).

Calculation of ϵ_p

The isotopic fractionation ϵ_p of alkenones associated with photosynthetic fixation of carbon was calculated using the following equation (Freeman and Hayes 1992), where δ_d is the isotopic composition of dissolved carbon in $\text{CO}_2(\text{aq})$ and δ_p that of photosynthate carbon:

$$\epsilon_p = \left(\frac{\delta_d + 1000}{\delta_p + 1000} - 1 \right) 1000 \quad (2)$$

δ_p was derived from the isotopic composition of $\text{C}_{37:2}$ alkenones and corrected for the compound-specific fractionation $\epsilon_{\text{alkenone}}$ between the $\text{C}_{37:2}$ alkenones and the biomass of alkenone-producing organisms. We adopted 4.2‰ as the value for $\epsilon_{\text{alkenone}}$ (Popp et al. 1998):

$$\delta_p = \delta_{\text{C}_{37:2}} + \epsilon_{\text{alkenone}} \left(1 + \frac{\delta_{\text{C}_{37:2}}}{1000} \right) \quad (3)$$

δ_d was calculated from $\delta_{\Sigma\text{CO}_2}$ following the equation of Rau et al. (1996) based on Mook et al. (1974):

$$\delta_d = \delta_{\Sigma\text{CO}_2} + 23.644 - \frac{9701.5}{T} \quad (4)$$

where T is the temperature in Kelvin. Temperatures for sediment samples were obtained from the alkenone unsaturation index (U_{37}^K) using the calibration of Prahl et al. (1988). For POM samples directly measured temperatures were available. For both sample types we assumed a constant pre-industrial $\delta_{\Sigma\text{CO}_2}$ -value of 2.5‰ (Kroopnick 1985). In core GeoB1016-3 $\delta_{\Sigma\text{CO}_2}$ was calculated from the $\delta^{13}\text{C}$ record of the surface-dwelling planktonic foraminifer *Globigerinoides ruber* (pink) (Andersen et al. 1999). The tests of *G. ruber* are depleted in ^{13}C relative to the isotopic composition

of total dissolved CO₂. To consider this we assumed an offset of 0.5‰ (Fairbanks et al. 1982; Curry and Crowley 1987). Based on propagating error calculations Andersen et al. (1999) determined an absolute error of +/-0.42‰ for the calculation of ϵ_p .

Results and Discussion

Modern Situation (Attempt of Calibration)

Since laboratory data cannot perfectly mimic natural environments, which undergo changes in physical (e.g. temperature, mixing), chemical (e.g. major and trace nutrients) and biological (e.g. grazing pressures, species competition) processes, extrapolation to the field must be done with caution (Laws et al. 2001). In addition, laboratory and water column studies cannot completely imitate the sum of environmental conditions and physiological processes which may influence the sedimentary isotopic signal of alkenones. Therefore it is necessary to test hypotheses like the potential of an influence of CO₂(aq) concentrations on the fractionation of C_{37:2} alkenones also by sediment-based studies.

Such a calibration requires knowledge of the water depth where the $\delta^{13}\text{C}$ signal of alkenones ($\delta^{13}\text{C}_{37:2}$) was produced. Hapthophytes use sunlight for photosynthesis and thus live in the photic zone. Dependent on suspended particles in the water column, the photic zone depth varies from about 20 m in eutrophic to about 120 m in oligotrophic regions (Morel and Berthon 1989; Longhurst 1993). Our core-top studies in the South Atlantic showed that for most hydrographic regions the best correlation between the sedimentary U_{37}^K signal and sea-surface temperature (SST) is obtained when modern atlas values from 0-10 m water depth are used (Müller et al. 1998; Benthien and Müller 2000). It was further demonstrated that seasonal changes in primary production had only a negligible effect on the sedimentary U_{37}^K signal in this region (Müller et al. 1998). Recent sediment trap studies from the tropical-subtropical eastern Atlantic also suggest that U_{37}^K principally records the annual average of mixed-layer temperature in this region (e.g. Müller and Fischer 2001; PJ Müller unpubl. data). We therefore used surface water

properties (upper 10 m) to "calibrate" the alkenone $\delta^{13}\text{C}$ signal in POM and surface sediments.

In the low to mid latitude South Atlantic $\delta^{13}\text{C}_{37:2}$ values for the POM range from -29.7‰ to -21.8‰ and for surface sediments from -25.8‰ to -22.5‰. The corresponding ϵ_p -values (calculated from equation 1) range from 8.5‰ to 15.8‰ and 11.5‰ to 15.7‰, respectively (Tab. 1). Figure 3a shows the relationship between ϵ_p of the C_{37:2}-alkenone and the reciprocal of [CO₂(aq)]. If the concentration of [CO₂(aq)] was the major factor controlling the carbon isotopic fractionation of the C_{37:2} alkenone, a negative correlation between ϵ_p and the 1/[CO₂(aq)] would be expected (e.g. Rau et al. 1992, Eq. 1). Instead, a positive, but not identical relationship is observed for both, the POM and core top sediments (Fig. 3a; R = 0.72 and R = 0.77, respectively). This result is in accordance with the relationship between ϵ_p of alkenones and 1/[CO₂(aq)] found by Popp et al. (1999) in POM of the Southern Ocean and indicates that isotopic fractionation in alkenones is influenced by factors other than [CO₂(aq)].

In spite of these regionally observed correlations between ϵ_p and 1/[CO₂(aq)] (this study; Popp et al. 1999), no general relationship between both parameters is apparent if additional literature data are considered (Fig. 3b, Laws et al. 2001). This also implies that factors other than [CO₂(aq)] influence the isotopic fractionation.

In the case of taxon-specific biomarkers such as alkenones the effects of variation in cell size and membrane permeability are accounted to be relatively small (e.g. Bidigare et al. 1997; Popp et al. 1998), especially for core-top sediments which typically represent at least a few hundred years. A constant value for the maximum fractionation ϵ_f attributed to enzymatic carbon fixation can also be assumed, since it is likely to be species-dependent (Bidigare et al. 1997) and thus not a problem for taxon-specific biomarkers. We adopted a value of 25‰ which was reported from culture experiments of two different strains of *E. huxleyi* (Bidigare et al. 1997). In addition, variations of growth rate and the growth rate influencing factors (e.g. Riebesell et al. 2000a; Gervais and Riebesell 2001) as well as different carbon acquisition mechanisms and inorganic carbon sources (i.e. CO₂ and HCO₃⁻)

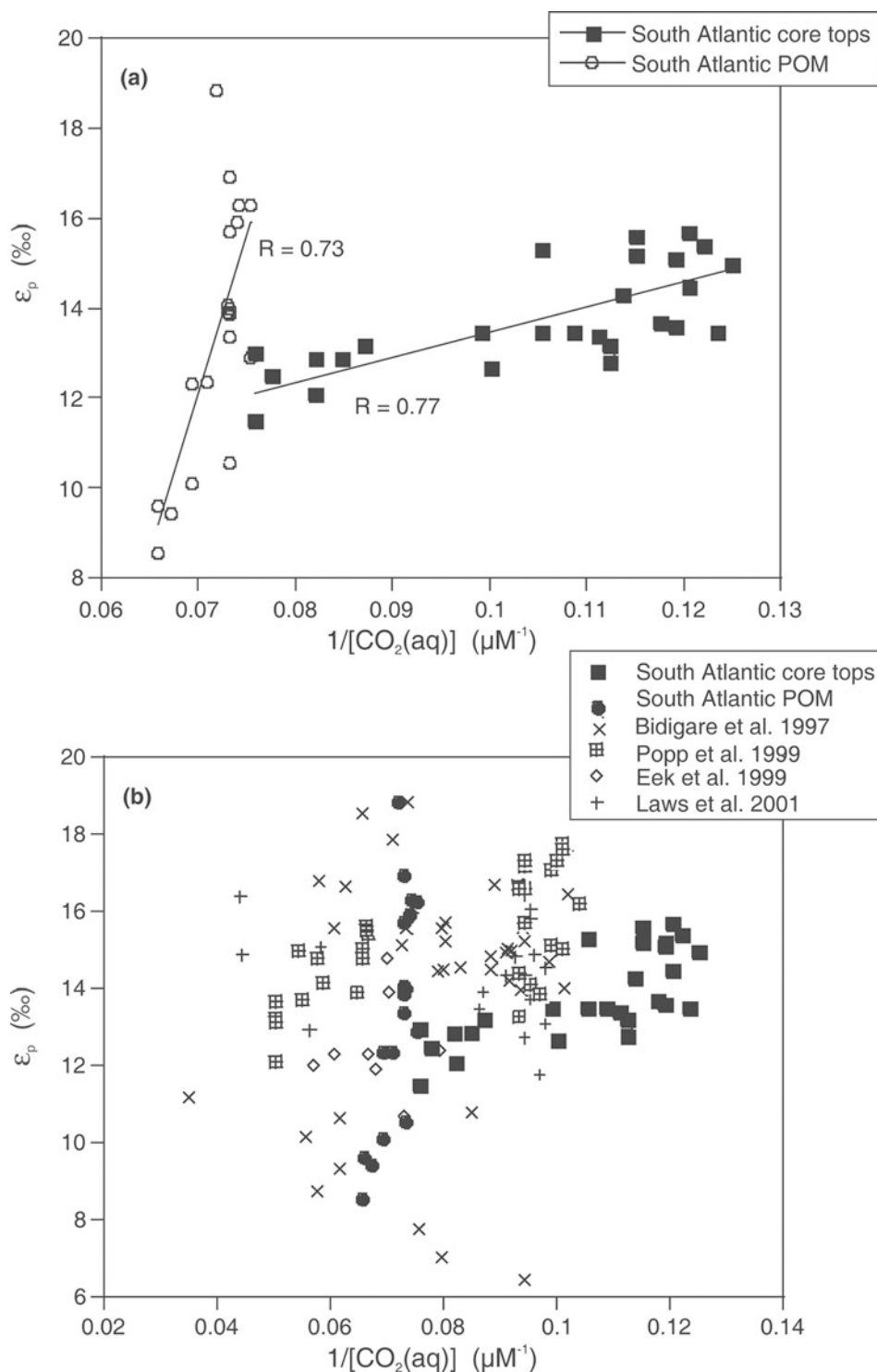


Fig. 3. a) Carbon isotopic fractionation (ϵ_p) of the $\text{C}_{37.2}$ alkenone determined in particulate organic matter (POM; open circles) and core top sediments (filled squares) from the South Atlantic in relation to $1/[\text{CO}_2(\text{aq})]$. **b)** Relationship between ϵ_p and $1/[\text{CO}_2(\text{aq})]$ in POM (this study and literature data (Laws et al. 2001)) and core top sediments (this study). Linear regression of all data ($n = 145$) yields no significant correlation ($R = 0.12$).

may further influence the isotopic fractionation of alkenones (Rau et al. 1996; Keller and Morel 1999; Gonzales et al. 2001; Benthien et al. 2002).

The ϵ_p values of C_{37:2} alkenones in POM and surface sediments of the South Atlantic correlate well with ambient surface water concentrations of phosphate which is in accordance with results of Popp et al. (1999) and Andersen et al. (1999). Both POM and surface sediments exhibit a negative relationship between ϵ_p and surface water phosphate, but the correlations have different intercepts and slopes (Fig 4a). A compilation of all currently published ϵ_p values of C_{37:2} alkenones from POM together with the data of the present study reveals only a weak negative correlation ($R = 0.46$) between ϵ_p and the surface water phosphate concentration (Fig. 4b). Bidigare et al. (1997) pointed out that for environments with non-zero concentrations of phosphate the growth rate of alkenone-producing algae is linearly related to $[\text{PO}_4^{3-}]$. Based on a predictive model, Rau et al. (1996) proposed, that ϵ_p decreases with increasing growth rates. Apparently, the variations of ϵ_p observed in Figure 4b are related to variations in growth rate. When the growth rate increases, the diffusive CO₂ flux through the cell membrane decreases relative to carbon fixation. At first, due to the discrimination against ¹³C, more ¹²C is consumed. This subsequently leads to an enrichment of the internal carbon pool in ¹³C, which is then consumed by carbon fixation. As a result of this mechanism, $\delta^{13}\text{C}_{37:2}$ values increase while those for ϵ_p decrease (Keller and Morel 1999).

The influence of growth rate on the isotopic fractionation in alkenones is further supported by a significant correlation between the calculated b -values and phosphate concentrations (Fig 5a, $R = 0.88$). We added our results to the compilation of Laws et al. (2001) and got a nearly identical relationship (Fig. 5a). It was reasoned by Bidigare et al. (1997) that this correlation may be caused by growth-rate limiting concentrations of micronutrients (e.g. Fe, Zn, Co) rather than by phosphate concentrations since *E. huxleyi* has a low phosphorus requirement. This interpretation is supported by the fact that the phosphate concentrations in the studied areas are much higher than the half-saturation constant for growth determined for *E.*

huxleyi (Riegman et al. 2000). In addition, if growth rate would be limited by phosphate it should follow Michaelis-Menten saturation kinetics rather than a linear relationship (Fig. 5a). Consequently, it seems more reasonable that micronutrients such as iron, zinc and cobalt are the growth-rate limiting factors and that the phosphate concentration is closely related to that of micronutrients (see Bidigare et al. 1997 for a detailed discussion).

A positive relationship between the b -value and phosphate concentration could also be simply the result from a correlation between phosphate and dissolved CO₂ as pointed out by Bidigare et al. (1997). Indeed, a high correlation is observed between these two parameters ($R = 0.89$; Fig. 5b). Popp et al. (1999) examined the effect of $[\text{PO}_4^{3-}]$ on ϵ_p at relatively constant concentrations of dissolved CO₂ and found a significant correlation. By contrast, no correlation between $[\text{CO}_2(\text{aq})]$ and ϵ_p was observed. They thus concluded that the correlation between the b -value and $[\text{PO}_4^{3-}]$ is not caused by the relationship between $[\text{CO}_2(\text{aq})]$ and $[\text{PO}_4^{3-}]$ in surface waters. This is further supported by the positive correlation observed here between ϵ_p and $1/[\text{CO}_2(\text{aq})]$ in POM and core top sediment from the South Atlantic (Fig 3a) as well as in POM from the subantarctic Southern Ocean (Popp et al. 1999). As mentioned above such a correlation is opposite of what is expected from a $[\text{CO}_2(\text{aq})]$ controlled, diffusive uptake model. This strongly suggests, that the isotopic fractionation in haptophyte algae is more sensitive to variations of growth rate and/or growth rate limiting factors (e.g. Riebesell et al. 2000a; Rost et al. 2002) and micronutrient availability (Bidigare et al. 1997) than to varying concentration of $[\text{CO}_2(\text{aq})]$.

Paleo-PCO₂ Estimates in the Angola Current

In this section we briefly summarize the results of earlier paleo-PCO₂ reconstructions in the South Atlantic (Müller et al. 1994; Andersen et al. 1999) and evaluate them in the light of the above results. These studies are based on a late Quaternary sediment core (GeoB1016-3) from the eastern Angola Basin covering the last 200,000 years (Fig. 6). In the first study, we used the isotopic composition of bulk sedimentary organic carbon ($\delta^{13}\text{C}_{\text{org}}$), pub-

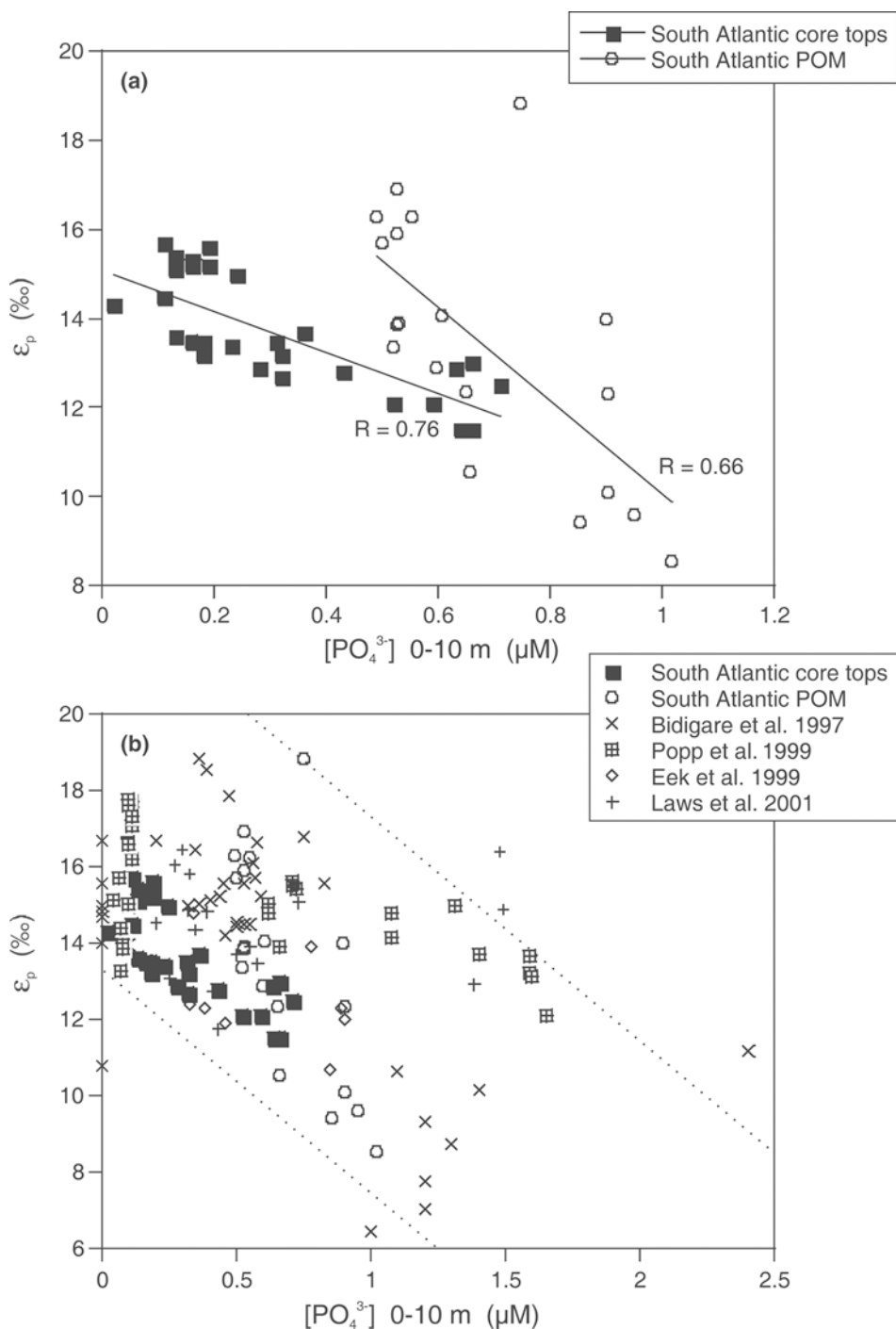


Fig. 4. a) Relationship between the isotopic fractionation (ϵ_p) of the $\text{C}_{37:2}$ alkenone measured in POM (open circles) and core top sediments (filled squares), and the annual mean surface water concentration of phosphate (0-10 m) in the South Atlantic. The lines represent the linear correlation between the two parameters. **b)** Relationship between ϵ_p and phosphate. Compilation of literature data for POM and data obtained in the present study (POM and sediments). Stippled lines are for better visualization of the weak correlation observed between ϵ_p and phosphate ($R = 0.46$; all data $n = 145$).

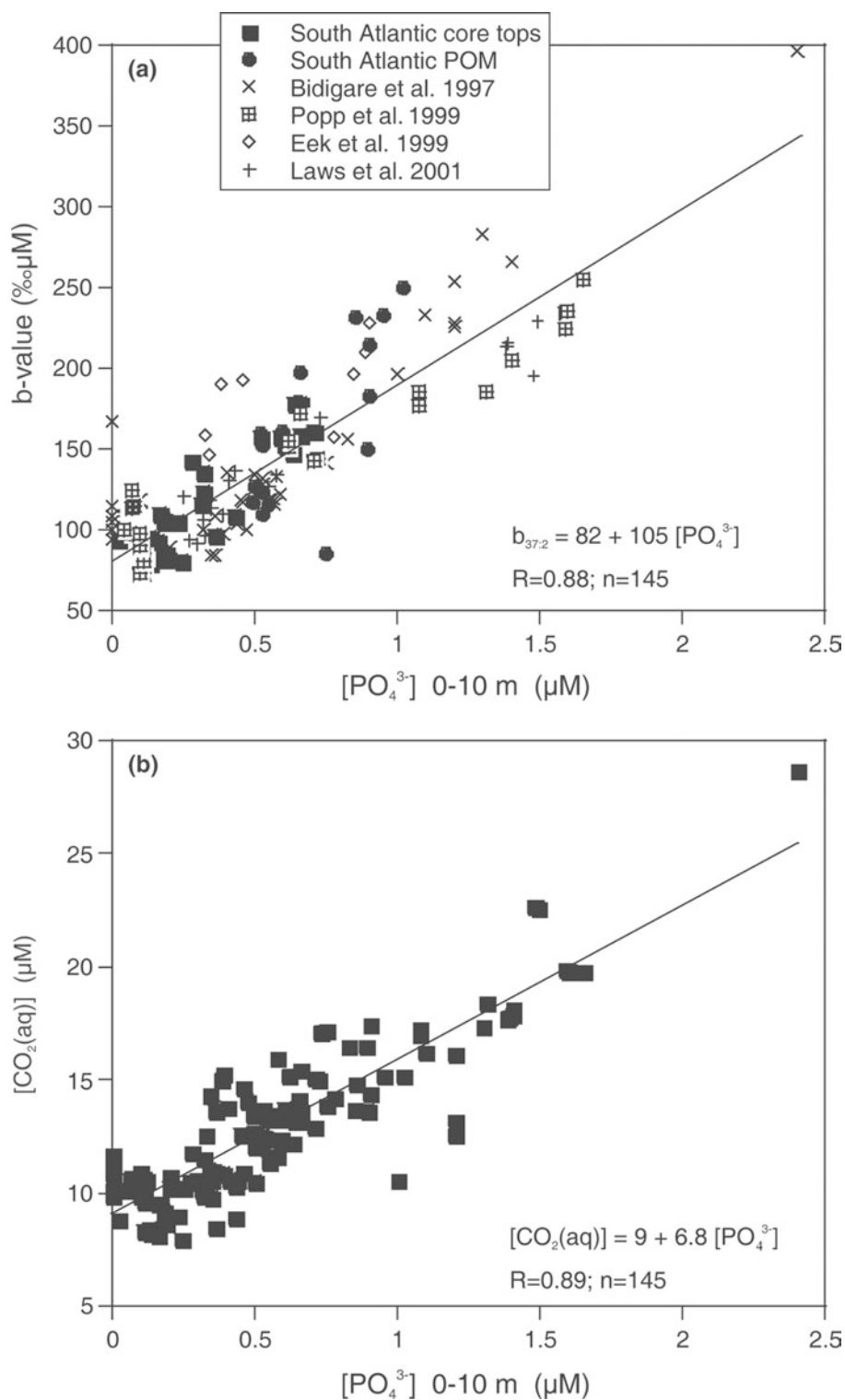


Fig. 5. a) Relationship between b-value and phosphate concentration of data of the present study plus literature data (Laws et al. 2001). The relationship found is nearly identical with that reported by Laws et al. (2001): $b_{(37.2)} = 79 + 120[\text{PO}_4^{3-}]$. **b)** Relationship between dissolved CO₂ and surface water phosphate concentration for the whole data set (present study plus data published in Laws et al. 2001).

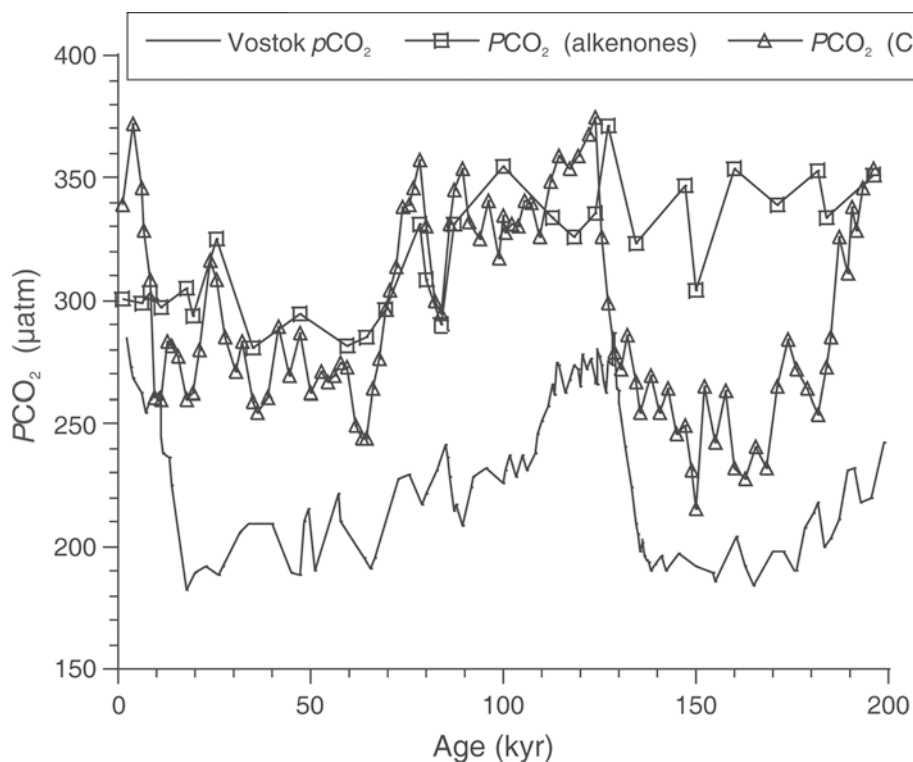


Fig. 6. Reconstructions of paleo- PCO_2 in core GeoB1016-3 versus age using carbon isotopic fractionation of $C_{37:2}$ alkenone (triangles, from Andersen et al. 1999) and bulk organic matter (squares, from Müller et al. 1994). The line represents atmospheric CO_2 concentration recorded in Vostok ice core (Jouzel et al. 1993). The age model of the marine record is based on foraminiferal $\delta^{18}O$ that was tuned to the ice core chronology (for details see Müller et al. 1994).

lished empirical relationships between $\delta^{13}C_{org}$ and $[CO_2(aq)]$, and alkenone-derived (v_{37}^K) temperatures to estimate past PCO_2 levels (Müller et al. 1994). The results indicate that the Angola Current has generally acted as a source region for atmospheric CO_2 throughout the last two glacial-interglacial cycles, consistent with the modern situation. However, the difference between our surface-water estimate and atmospheric PCO_2 (Vostok ice core, e.g. Jouzel et al. 1993) appeared to be smaller in glacial periods suggesting a reduced CO_2 output into the atmosphere in periods of lowered sea-surface temperatures and enhanced biological productivity in this region (Schneider et al. 1996).

In a subsequent study, Andersen et al. (1999) used a different approach based on the isotopic composition of the $C_{37:2}$ alkenone in conjunction with that of bulk sedimentary nitrogen ($\delta^{15}N$). The latter was considered as indirect proxy for nutri-

ent-limited growth rates and used to calculate the growth-rate dependent parameter b in equation 1. This application was based on the observation that $\delta^{15}N$ in surface sediments from eutrophic regions is positively correlated with the phosphate concentration in overlying surface waters. For more details on the methods used in the above two studies the reader is referred to the original publications.

Figure 6 compares the paleo- PCO_2 records from the Angola Basin to the atmospheric record of the Vostok ice core. In general, the two oceanic reconstructions agree quite well and show generally higher PCO_2 values compared to the Vostok record supporting the initial contention of a permanent source for atmospheric CO_2 over the past 200,000 years. However, significantly different PCO_2 levels were obtained for the penultimate glacial, the marine isotope stage 6 (128-186 kyr in Fig. 6). While the PCO_2 record derived from bulk

$\delta^{13}\text{C}_{\text{org}}$ shows a glacial to interglacial pattern parallel to the atmospheric CO₂ variations indicated by the ice core, the biomarker approach yields high values for glacial stage 6 comparable to the level observed for interglacials. We have no definite explanation for this deviation and must consider several effects.

Reconstructions based on $\delta^{13}\text{C}$ of bulk organic matter may suffer from species-specific differences in isotope fractionation among marine photosynthetic organisms (e.g. Burkhardt et al. 1999), shifts in isotope composition of buried organic matter during degradation, and contamination by terrestrial organic matter (Jasper and Hayes 1990). Based on a strong positive relationship between C/N and $\delta^{13}\text{C}_{\text{org}}$ values in core GeoB1016-3, Müller et al. (1994) argued that differing proportions of marine and terrigenous organic matter can be ruled out as a cause for the $\delta^{13}\text{C}_{\text{org}}$ variability in this core. However, strictly speaking this is only valid for organic matter derived from C3 plants (e.g. Meyers 1997). A higher proportion of isotopically heavier C4 plant material in climatic periods with increased savannah vegetation (e.g. Partridge et al. 1999) could have led to generally higher bulk $\delta^{13}\text{C}_{\text{org}}$ values resulting in the lower PCO_2 estimates obtained for glacial stage 6. A critical review addressing problems and advantages associated with the use of bulk sedimentary $\delta^{13}\text{C}_{\text{org}}$ as tracer of dissolved carbon dioxide in the surface ocean was recently presented by Kienast et al. (2001).

The phytoplanktonic organic matter preserved in marine sediments represents a mixture derived from various groups, e.g. diatoms, dinoflagellates and coccolithophorids, which may grow at different rates and may show different isotopic signatures. It is well known that rapidly growing diatoms have ¹³C-rich isotopic compositions. Fry and Wainright (1991), for example, reported that diatoms in spring blooms were relatively rich in ¹³C, while other phytoplankton had ¹³C-depleted values. A significant contribution of diatoms or other rapidly growing phytoplankters to the bulk sedimentary organic matter deposited during glacial stage 6 could therefore also explain the different PCO_2 levels obtained by the bulk C_{org} and alkenone methods. Such an interpretation is also compatible with

recent sediment trap results from the Southern Ocean which show a coupling of $\delta^{13}\text{C}_{\text{org}}$ with the flux of opal and that of $\delta^{13}\text{C}_{\text{alkenones}}$ with the carbonate flux (S. Schulte, unpublished results).

In principle, the isotopic composition of alkenones is a less ambiguous proxy parameter for surface-water CO₂ than bulk $\delta^{13}\text{C}_{\text{org}}$ because alkenones are synthesized by a limited number of haptophytes only. However, their isotopic composition is also influenced by more than one factor as demonstrated above by the POM and core-top results. In the modern South Atlantic, the isotopic fractionation of the C_{37:2} alkenone appears to be mainly influenced by growth rate rather than CO₂. Variations in growth rate must therefore also be taken into account in paleoceanographic studies. There is indeed evidence for significant variations in paleoproductivity and, by inference, growth rate at site GeoB1016-3 (Schneider et al. 1996; Andersen et al. 1999). As described above, the influence of the growth rate on the isotopic fractionation of alkenones is included in the *b*-value (see equation 1) which may be derived from bulk sedimentary $\delta^{15}\text{N}$ values, at least in eutrophic regions (Andersen et al. 1999). However, $\delta^{15}\text{N}$ is also not unambiguous because a variety of environmental processes, independent from nutrient-growth rate relationships, can influence the nitrogen cycle and the isotopic signal in the sediments (e.g. mineralization, nitrification, denitrification, diagenesis; Altabet et al. 1999).

More reliable reconstructions of past dissolved CO₂ concentration and partial pressure in the surface ocean could be obtained if an independent proxy for variations in algal growth rate would be available. The Cd/Ca and $\delta^{13}\text{C}$ ratios of planktonic foraminifera have been suggested as nutrient proxies and useful indirect parameters to constrain the effects of growth rate on the isotopic composition of alkenones (e.g. Popp et al. 1999). However, the $\delta^{13}\text{C}$ of planktonic foraminiferal calcite is also controlled by a variety of other factors which complicates its interpretation as a proxy for dissolved phosphate (e.g. Spero et al. 1997; Bijma et al. 1999). Although benthic foraminiferal Cd/Ca ratios have proven useful as nutrient proxy in deep waters, the planktonic Cd/Ca ratio is no genuine al-

ternative for surface waters because the incorporation of Cd into foraminiferal calcite is temperature sensitive (Rickaby and Elderfield 1999).

Recently it has been suggested that the Sr/Ca ratio in coccoliths is mainly controlled by growth and calcification rates, although temperature also exerts some influence on this ratio (Stoll and Schrag 2000; Rickaby et al. 2002; Stoll et al. 2002). Sr/Ca measurements on coccoliths thus provide a promising alternative to constrain the effect of growth rate on the isotopic fractionation during photosynthesis. In combination with the $\delta^{13}\text{C}$ of alkenones, this would permit more reliable estimations of $[\text{CO}_2(\text{aq})]$ and PCO_2 in ancient oceanic surface waters.

Summary and Conclusions

The alkenone ϵ_p record in POM and surface sediments of the South Atlantic Ocean was compared with overlying surface-water concentrations of phosphate and dissolved carbon dioxide. The results demonstrate that regardless of the ϵ_p -controlling mechanism, the observed changes in the carbon isotopic composition of alkenones are linked to variations in phosphate concentrations rather than to $[\text{CO}_2(\text{aq})]$. Although an unambiguous evidence for a specific mechanism cannot be presented at the moment, the relationship between ϵ_p and $[\text{PO}_4^{3-}]$ found in our South Atlantic field studies suggest, in agreement with the theory of Bidigare et al. (1997), that a strong relationship exists between isotopic fractionation in haptophytes and nutrient-limited growth rate. Furthermore, the fact that the sediment data fit excellently with the water column data clearly indicates that the isotopic record of sedimentary alkenones reflects surface water conditions.

Estimates of ancient dissolved CO_2 concentrations based on compound specific $\delta^{13}\text{C}$ -values must consider the effect of changing growth rates of certain algae species which determine the CO_2 concentration gradient between ambient water and the phytoplanktonic cell. The bulk sediment $\delta^{15}\text{N}$ signal may be useful in some restricted areas of the ocean (e.g. the eastern Atlantic Ocean) as a paleo proxy for the b -value. The Sr/Ca-ratio in coccolithophorids might provide an independent record of past changes in coccolithophorid growth rates, which in combination with data on the carbon iso-

topic fractionation in coccolithophorid organic matter may permit more reliable calculations of past dissolved CO_2 in the surface ocean.

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