This is a postprint version of:


Published version: dx.doi.org/10.1016/j.orggeochem.2014.10.011

Link NIOZ Repository: www.vliz.be/nl/imis?module=ref&refid=243218

[Article begins on next page]
Testing the alkenone D/H ratio as a paleo indicator of sea surface salinity
in a coastal ocean margin (Mozambique Channel)

Sebastian Kasper* a, Marcel T.J. van der Meer a, Isla S. Castañeda a,b, Rik Tjallingii c,1, Geert-Jan A. Brummer c, Jaap S. Sinninghe Damsté a, Stefan Schouten a

a NIOZ Royal Netherlands Institute for Sea Research, Department of Marine Organic Biogeochemistry, P.O. Box 59, 1790 AB Den Burg (Texel), The Netherlands

b University of Massachusetts Amherst, Department of Geosciences, Amherst, MA 01003 USA

c NIOZ Royal Netherlands Institute for Sea Research, Department of Marine Geology and Chemical Oceanography, 1790 AB Den Burg (Texel), Netherlands

*Corresponding author. Tel.: +31 (0) 222 369 408; fax: +31 (0) 222 319 674.

E-mail address: sebastian.kasper@nioz.nl (S. Kasper).

1Present address: Geoforschungszentrum Potsdam, Telegrafenberg, C 327, Potsdam D-14473, Germany.
Reconstructing past ocean salinity is important for assessing paleoceanographic change and therefore past climatic dynamics. Commonly, sea water salinity reconstruction is based on planktonic foraminifera oxygen isotope values combined with sea surface temperature reconstruction. However, the approach relies on multiple proxies, resulting in rather large uncertainty and, consequently, relatively low accuracy of salinity estimates. An alternative tool for past ocean salinity reconstruction is the hydrogen isotope composition of long chain (C$_{37}$) alkenones ($\delta$D$_{\text{alkenone}}$). Here, we have applied $\delta$D$_{\text{alkenone}}$ to a 39 ka sedimentary record from the Eastern South African continental shelf in the Mozambique Channel, close to the Zambezi River mouth. Despite changes in global seawater $\delta$D related to glacial – interglacial ice volume effects, no clear changes were observed in the $\delta$D$_{\text{alkenone}}$ record throughout the entire 39 ka. The BIT index record from the same core, which provides information on relative contributions of soil organic matter (OM) vs. marine input, indicates high soil OM input during the glacial and low input during the Holocene. This suggests a more pronounced freshwater influence at the core location during the glacial, resulting in alkenones depleted in D during that time, thereby explaining the lack of a clear glacial-interglacial alkenone $\delta$D shift. The correlation between the BIT index and $\delta$D$_{\text{alkenone}}$ during the glacial period suggests that increased continental runoff potentially changed the growth conditions of the alkenone-producing haptophytes, promoting coastal haptophyte species with generally more enriched $\delta$D$_{\text{alkenone}}$ values. We therefore suggest that the application of $\delta$D$_{\text{alkenone}}$ for reconstructing past salinity in coastal settings may be complicated by changes in the alkenone-producing haptophyte community.

**Keywords:** stable hydrogen isotopes, alkenones, salinity, BIT index, coastal environment, Mozambique Channel, Zambezi River, glacial, interglacial.
1. Introduction

The interaction and feedback mechanisms at the interface between oceanic and atmospheric circulation on glacial – interglacial timescales are largely unknown, but are thought to play an important role in the global transmission of climate change (Manabe, 1969; Rahmstorf, 2002). Accurate reconstruction of past oceanic and atmospheric changes is crucial for a better understanding of these mechanisms and should eventually improve prediction of future climate development (Esper et al., 2005). Reconstruction of ocean circulation requires an estimate of seawater density, which is determined by salinity and temperature. Therefore, in order to understand past ocean circulation in relation to climate change it is essential to be able to reconstruct paleosalinity and temperature with reasonable accuracy.

Ocean salinity and the oxygen isotope composition of seawater are linearly correlated (Epstein and Mayeda, 1953) and this can be utilized for reconstruction of past seawater salinity using the $\delta^{18}O$ record of carbonate shells of foraminifera (Duplessy et al., 1991; Rostek et al., 1993) under the assumption of temporal consistency of the relationship between $\delta^{18}O$ and salinity (Rohling and Bigg, 1998; Rohling et al., 2000). However, salinity reconstruction based on $\delta^{18}O$ values of foraminiferal carbonate requires accurate correction for the global ice volume (Rostek et al., 1993) and knowledge of the temperature during calcification (Erez and Luz, 1983). The global ice volume can be estimated from the mean ocean $\delta^{18}O$ record (Waelbroeck et al., 2002), whereas the temperature is mostly obtained from Mg/Ca ratio values of foraminifera (Nürnberg et al., 1996; Lea et al., 1999; Mashiotta et al., 1999) or the alkenone-based $U_{K,37}^{\text{Index}}$ (Brassell et al., 1986; Rostek et al., 1993; Nürnberg et al., 1996). However, the correlation between $\delta^{18}O$ and salinity is affected by mixing and evaporation processes (Craig and Gordon, 1965), seasonality (Strain and Tan, 1993) and likely changes over glacial – interglacial periods (Rohling and Bigg,
Consequently, salinity reconstruction based on δ^{18}O values of foraminiferal carbonate is subject to uncertainty and is difficult to calibrate (Rohling and Bigg, 1998; Rohling, 2000).

In addition to the correlation between oxygen isotopes and salinity, there is also a strong correlation between the hydrogen isotope composition of seawater (δD_{sw}) and salinity (Craig, 1961; Friedman et al., 1964). δD_{sw} is recorded in the non-exchangeable hydrogen of organic matter (OM; Sessions et al., 1999; Sauer et al., 2001; Sachse et al., 2012) and can potentially be used for reconstructing past δD_{sw}. The hydrogen isotope composition of long chain alkenones, in particular C_{37} alkenones (δD_{alkenone}) appears well suited for reconstructing past δD values of seawater (Englebrecht and Sachs, 2005; Schouten et al., 2006). The isotopic composition of covalently bound hydrogen is thought to be preserved over long geological timescales (Sessions et al., 2004). Culture studies have shown that δD_{alkenone} of two common marine haptophytes, *Emiliania huxleyi* and *Gephyrocapsa oceanica*, depends mainly on salinity and the hydrogen isotope composition of the growth medium and, to a lesser extent, growth rate (Schouten et al., 2006). Attempts to reconstruct past salinity change based on δD_{alkenone} has led to reasonable results for the eastern Mediterranean Sea and Black Sea (van der Meer et al., 2007, 2008; Coolen et al., 2013) and the Panama Basin (Pahnke et al., 2007). Recently, the approach has also been applied to open marine sediments to evaluate relative salinity changes in the Agulhas Leakage area at the southern tip of the African continent over two glacial termination periods (Kasper et al., 2014). However, the lack of a clear correlation between δD_{alkenone} and seawater salinity in the Chesapeake Bay estuary suggests that the interpretation of this salinity proxy may become problematic for coastal environments (Schwab and Sachs, 2011). A possible explanation for the absence of a clear correlation relates to change in species composition since different haptophytes may have specific D/H fractionation characteristics. Comparison of the coastal haptophyte alga
Isochrysis galbana with the open ocean species *E. huxleyi* in a culture experiment (M’Boule et al., 2014) revealed a strong fractionation difference between the two species. *I. galbana* fractionated to an extent of ca. 90‰ less than *E. huxleyi*, although the rate of change in D/H fractionation per salinity unit remained similar for both species (M’Boule et al., 2014, Chivall et al., 2014). This raises the question as to which extent $\delta D_{\text{alkenone}}$ is applicable as a paleosalinity proxy in coastal settings, where differences in haptophyte communities are to be expected (Marlowe et al., 1990; Noble et al., 2003; Örnólfsdóttir et al., 2004; Schwab and Sachs, 2011).

To investigate the $\delta D_{\text{alkenone}}$-based sea surface salinity proxy in a freshwater runoff-influenced continental margin, we analyzed a 39,000 year (39 ka) long record of $\delta D_{\text{alkenone}}$ from a marine sediment core (64PE304-80) from the Mozambique Channel near the Zambezi River mouth inside the Zambezi River fan (Fig. 1; Beiersdorf et al., 1980). The core site is off the continental shelf in the channel, which is traversed by the Mozambique Current, a branch of the South Equatorial Current (SEC; Fig. 1). The Mozambique Current is dominated by large anti-cyclonic eddies passing through the Mozambique Channel, with an annual net flow rate of ca. 15 Sv (de Ruijter et al., 2002; Schouten et al., 2003; Ullgren et al., 2014). However, interannual net flow rate varies substantially by up to 9 Sv in volume transport (Ridderinkhof et al., 2010). Additionally, there is a substantial input of continental freshwater to the Mozambique Channel (Siddorn et al., 2001). A main contributor is the Zambezi River, with a runoff of ca. 224 km$^3$/yr (7.1 x 10$^3$Sv; Meybeck, 1982). Due to the location of the core site within the Zambezi River fan and independent reconstruction of high freshwater outflow by the BIT index, we would expect variation in freshwater runoff and therefore in salinity at the core site over time, suggesting it as a promising record for testing $\delta D_{\text{alkenone}}$ as a paleo sea surface salinity proxy at a river dominated ocean margin.
2. Material and methods

2.1. Core and chronology

Samples were taken from core 64PE304-80 (18° 14' 26.6274"S; 37° 52' 8.6874" E, 1329 m water depth), located north of the Zambezi River Delta at the Mozambique shelf (Fig. 1). The core was taken during the RV Pelagia cruise “64PE304, INATEX - GEO” (Brummer et al., 2009). The chronology was established from $^{14}$C dating of 20 samples consisting of ca.10 mg mixed surface-dwelling planktonic foraminifera (Globigerinoidess acculifer, G.trilobus and G. ruber). These samples were collected from the washed and sieved > 250 μm sediment fraction by selecting individual foraminifera specimens under a microscope (Fig. 2). The age model for the upper 6 m, spanning the last 20 ka, was constrained by 11 $^{14}$C dates and by stratigraphic correlation with a parallel core (GIK16160-3; Wang et al., 2013b; Van der Lubbe et al., 2014). The age model between 20 and 39.5 ka BP was constrained by 9 additional $^{14}$C dating points. The $^{14}$C age values were converted to calendar age using the MARINE09 calibration curve that applies a standard reservoir correction of ca. 400 yr (Reimer et al., 2011).

2.2. Extraction

Sediment samples were freeze dried and homogenized with a mortar and pestle. The homogenized material was extracted using accelerated solvent extraction (ASE) with dichloromethane (DCM):MeOH 9:1 (v/v) and a pressure of 6895 kPa in 3 extraction cycles. The
extract was separated over an Al₂O₃ column into apolar, ketone and polar fractions using hexane:DCM 9:1 (v/v), hexane:DCM 1:1 (v/v) and DCM:MeOH 1:1 (v/v), respectively. Column chromatography was carried out using about 4 cm activated Al₂O₃ (MPO Chemicals; technical quality, basic A) as stationary phase in a Pasteur pipette. Fractions were eluted with 3 column volumes of eluent.

2.3. Branched isoprenoid tetraether (BIT) index

The polar fraction was analyzed for the BIT index, a proxy originally thought to reflect the input of soil OM (Hopmans et al., 2004) but which has recently been shown to be affected by in situ production of branched glycerol dibiphytanyl glycerol tetraethers (br GDGTs) in rivers (Zell et al., 2013; De Jonge et al., 2014). Analysis was performed using high performance liquid chromatography-mass spectrometry (HPLC-MS) with an Agilent 1100 series instrument equipped with an auto-injector. Separation was achieved with an Alltech Prevail Cyano column (2.1 x 150 mm, 3μm), maintained at 30 °C. GDGTs were eluted with 99% hexane and 1% propanol for 5 min, followed by a linear gradient to 1.8% propanol in 45 min, followed by back-flushing with hexane/propanol (9:1, v/v) at 0.2ml/min for 10 min. Detection was achieved using atmospheric pressure positive ion chemical ionization MS (APCI-MS). APCI-MS settings were: nebulizer 414 kPa, vaporizer 400 °C, drying gas (N₂) at 6 l/min and 200 °C, capillary voltage -3 kV and a corona 5 μA (ca. 3.2 kV). GDGTs were detected using selected ion monitoring (SIM) of the [M+H]⁺ ions (m/z 1292 for crenarchaeol and m/z 1050, 1036 and 1022 for br GDGTs, respectively, dwell time 234 ms; Schouten et al., 2007) and integrated peak areas were used for quantification. BIT values were calculated according to the formula of Hopmans et al. (2004).
2.4. $C_{37}/C_{38}$ alkenone ratio

The ketone fraction, containing long chain alkenones, was analyzed using an Agilent 6890 gas chromatography (GC) instrument with a flame ionization detection (FID) and an Agilent CP Sil-5 fused silica column (50 m x 0.32 mm, film thickness 0.12 μm) with He as carrier gas. The GC oven was programmed from 70 to 200 °C at 20 °C/min and then at 3 °C/min to 320 °C (held 25 min). Peak integration for the calculation of ratio values for the total abundance of the $C_{37}/C_{38}$ alkenones was performed using the Atlas 8.2 Chromatography Data System software from Thermo Electron Cooperation.

2.5. Alkenone $\delta D$ analysis

The ketone fraction was analyzed using GC-high temperature conversion-isotope ratio MS (GC-TC-irMS) to determine the combined hydrogen isotope composition of the di- and triunsaturated $C_{37}$ alkenones (van der Meer et al., 2013). Isotope analyses were carried out with a Thermo – Scientific DELTA V GC-TC-irMS instrument. The GC temperature conditions were: 70 to 145 °C at 20 °C/min, then heated at 8 °C/min to 200 °C and to 320 °C (held 20 min) at 4 °C/min. An Agilent CP Sil-5 column (25 m x 0.32 mm) with a film thickness of 0.4 μm was used with He as carrier gas at 1 ml/min (constant flow). The high temperature conversion reactor was at 1420 °C. The $H_3^+$ correction factor was determined daily and was constant at 5.6 ± 0.5. The $\delta D_{\text{alkene}}$ values were calculated with the Isodat software relative to pulses of $H_2$ reference gas. A set of standard $n$-alkanes with known isotopic composition (Mix B prepared by A. Schimmelmann, University of Indiana) was analyzed daily prior to analyzing samples in order to monitor system
performance. Samples were only analyzed when the alkanes in Mix B had an average deviation from their off-line determined value of < 5‰. Squalane was co-injected as internal standard with each sample to monitor the accuracy and precision of alkenone isotope values. The standard had an average δD value of -165 ± 3.6‰, which compared favorably with that of -170‰ determined offline. The alkenone fraction was analyzed in duplicate if sufficient amount of material was available. Standard deviation of replicate analyses varied from ± 0.1‰ to ± 5.9‰.

3. Results

3.1. BIT index

To trace the relative importance of the river outflow at the core location we determined the BIT index, indicating riverine transported soil OM (Hopmans et al., 2004; Kim et al., 2007; Walsh et al., 2008; Schouten et al., 2013) as well as in situ produced crenarcheol from the river system (Zell et al., 2013; De Jonge et al., 2014). Values ranged between 0 and 1- a value near 0 indicates marine dominated OM and values near 1 a dominance of soil/river OM. Values were relatively high at ca. 0.50 between 39 and 38 ka and decreased to ca. 0.3 at 37 ka (Fig. 2). Between 37 and 16 ka they increased continuously to a maximum of ca. 0.7 during Heinrich Event 1 (HE1). Subsequently, they decreased to a plateau of ca. 0.25 between 15 and 12 ka in the Younger Dryas (YD). At ca. 12 ka they decreased to the Holocene level of ca. 0.1.

3.2. δDalkenone

The δDalkenone values were measured as the combined signal from C_{37:2} and C_{37:3}, as this has been suggested to yield a more robust water δD and salinity signal and to reduce additional biosynthetic effects related to the synthesis of C_{37:3} alkenone from the C_{37:2} alkenone (van der
Meer et al., 2013). The total variability in the δD_{alkenone} record was ca. 23‰, with absolute values ranging between -181 and -204‰. They varied around a mean of \(-191‰ \pm 5‰\) (1σ standard deviation) over the entire record (Fig. 2). No trend from glacial Marine Isotope Stage (MIS) 3, through the Last Glacial Maximum (LGM) to the Holocene, was observed. Instead, the record was highly variable, showing a minor tendency of ca. 5‰ to increasingly D-depleted values with decreasing age during the Holocene. The record showed several periods of relatively D-enriched values of ca. -185‰ to -180‰ at 31 ka, 23 ka and during HE1, and more D-depleted values of ca. -200‰ at 37 ka, 27 ka and the LGM.

3.3. \(C_{37}/C_{38}\) alkenone ratio

The ratio ranged between 0.8 and 1.7, with an average of 1.3 ± 0.2 over the entire record (Fig. 2). During the period between 39–21 ka, it was 1.3 ± 0.1, and after 21 ka it increased to a maximum of 1.7 at 19 ka, followed by a decrease to 1.3 at 10 ka. After this, it increased slightly to 1.4 at 9 ka and then rapidly decreased to the minimum value of ca. 0.8 at 8 ka. It was generally lower at 1.1 ± 0.1 during the Holocene compared with the glacial period.

4. Discussion

The transition from glacial to interglacial periods is marked by a significant decrease in the stable oxygen isotope ratio (\(\delta^{18}O_{sw}\)) and the stable hydrogen isotope ratio (\(\delta D_{sw}\)) of seawater as a consequence of melting of a large ice volume accumulated during the glacial (Shackelton, 1987). Global change in \(\delta^{18}O_{sw}\) was obtained from a mean global benthic isotope record (Waelbroeck et al., 2002) and indicates a gradual increase in \(\delta^{18}O_{sw}\) values from 0.53 to 1.02‰ between 39 and
20 ka BP (Fig. 2e). The values decrease linearly between 18 and 8 ka by almost 1‰. Based on a meteoric water line for the Indian Ocean (Srivastava et al., 2010), this record suggests an increase in the mean global $\delta D_{sw}$ of ca. 4‰ during the last glacial and a decrease of nearly 8‰ during the deglaciation. In contrast, the $\delta D_{alkenone}$ record from the upstream Mozambique slope showed fairly constant average values of $-191 \pm 5 \%$, with no trend that could be attributed to the inferred change related to the glacial – interglacial transition (Fig. 2b). The absence of a clear glacial-interglacial change related to the changing global ice volume is unlike that for a $\delta D_{alkenone}$ record obtained for open ocean sediments in the Agulhas Leakage area (Kasper et al., 2014). This suggests that additional environmental factors affect the $\delta D$ values of alkenones in the Mozambique Channel. This could be related to the change in salinity, in combination with the input of relatively D-depleted freshwater via the Zambezi River outflow (Schefuß et al., 2011).

An impact of temperature induced change in the $^{13}C_{37}$ ratio on the fractionation of hydrogen isotopes seems unlikely as this effect has not been observed in marine haptophyte algae (Schouten et al., 2006; van der Meer et al., 2013). Furthermore, the temperature change in this region has found to be relatively small (3.5 °C; Wang et al., 2013b) and we did not find any correlation between $\delta D_{alkenone}$ and local $^{13}C_{37}$ sea surface temperature (SST; data not shown).

In order to assess changes in freshwater input, we examined the BIT index for the same core (64PE304-80). The values indicate a relative increase in continental OM input during MIS2/3, with a relative maximum at ca. 17 ka during HE1 and at ca. 12 ka during the Younger Dryas, suggesting an increased influence of river outflow (Fig. 2; Van der Lubbe et al., 2014). These events were followed by a rapid decrease in the index during the deglaciation phase between 15-12 ka and the period between 11-8ka, showing reduced input of continent-derived OM. This could indicate a strongly reduced river outflow, consistent with the rising sea level at the time and the
subsequent transgression of the shelf (Walford et al., 2005; März et al., 2008), moving the Zambezi River mouth further away from the core site. Based on δD values of leaf wax alkanes, Schefuß et al. (2011) demonstrated that, during northern hemisphere cold events, such as the Younger Dryas and HE1, rainfall was enhanced in the Zambezi catchment area in response to a southwards forcing of the intertropical convergence zone (ITCZ). In contrast, a northward shift of the ITCZ in the Holocene would have resulted in reduced rainfall and decreasing river discharge as compared with glacial conditions (Schefuß et al., 2011; Wang et al., 2013a). The BIT record covering the last 17 ka from the Zambezi River mouth presented by Schefuß et al. (2011) is in good agreement with the BIT record here. The constant high BIT values during the glacial indicate an increased impact of freshwater input at the study site compared with the Holocene when BIT values were low. Increased freshwater input, either via closer proximity to the coast or increased precipitation or a combination of both, would lead to a relative depletion in δDsw at the core site and subsequently to a decrease in δDalkene during the glacial. The combination of lower salinity, resulting in increased biosynthetic hydrogen isotope fractionation (Schouten et al., 2006) and the more negative δDsw values from the freshwater runoff may have resulted in production of relatively D-depleted alkenones during the glacial; this may have counteracted the global ice volume-induced increase in δDsw, potentially leading to relatively constant values of alkenone δD during the glacial-interglacial transition.

During MIS 2/3, positive excursions in δDalkene of up to 10‰ correspond with elevated BIT values (Fig. 2), such as between 34 and 31 ka, between 26 and 24 ka, and during HE1 (19-16 ka) (Fig. 2). In fact, a crossplot of BIT values vs. δDalkene showed (Fig. 3) that, during the glacial period (39.4 to 16.2 ka), BIT index and δDalkene correlated significantly ($R^2$ 0.209, p value 0.0001), whilst during the Holocene no statistically significant relationship was observed ($R^2$...
This suggests that variation in freshwater input had a significant impact on the variability in $\delta D_{\text{alkenone}}$ during the glacial. However, a negative correlation between BIT and $\delta D_{\text{alkenone}}$ would be expected, as an increasing freshwater input would lead to an input of D-depleted water, as well as increasing fractionation due to a decrease in salinity. Thus, the trend cannot be explained by a salinity effect or by an increasing influx of D-depleted water.

Alternative factors, which could lead to the apparent positive correlation between BIT values and $\delta D$ of alkenones during the glacial period, are changes in growth rate or in haptophyte species composition (Schouten et al., 2006; Wolhowe et al., 2009; M’Boule et al., 2014). The reason why this effect is apparent in the glacial and not in the interglacial, may be because the core site was in much closer proximity to the coast during glacial sea level low stands (Walford et al., 2005; März et al., 2008; van der Lubbe et al., 2014), thereby allowing a potential proliferation of coastal haptophyte species as well as an increased impact of river-transported nutrients on growth rate. Regarding the latter hypothesis, although high freshwater input might have provided nutrients to the core site, thereby promoting algal growth (Verity et al., 1993; Pedersen and Borum, 1996; Gillanders and Kingsford, 2002), increased growth rate would be expected to lead to a depletion in $\delta D_{\text{alkenone}}$ (Schouten et al., 2006) and so cannot explain the positive excursions in $\delta D_{\text{alkenone}}$.

Since coastal haptophytes produce alkenones 90‰ enriched in D compared with open ocean haptophytes (M’Boule et al., 2014; Chivall et al., 2014), changes in marine vs. coastal haptophytes could explain the positive excursions of ca. 10‰ in hydrogen isotopic composition during the glacial period. The relative amount of the C$_{37:4}$ alkenone has been suggested as a marker for low salinity haptophyte algae (Schulz et al., 2000; Liu et al., 2008; 2011), but its abundance was very low in the sediment record (data not shown). However, the hypothesis of a changing contribution to the alkenone pool is supported by the observed change in the ratio between C$_{37}$ and C$_{38}$ alkenones (Fig. 2). This ratio has been reported
to be more elevated for coastal haptophytes than for open ocean species (Marlowe et al., 1984; Prahl et al., 1988; Schulz et al., 2000; Liu et al., 2011). No significant positive anomalies in the $C_{37}/C_{38}$ ratio were apparent between 39 and 22 ka. Nevertheless, $C_{37}/C_{38}$ ratio indicated elevated values during the glacial, with the highest at ca. 18.5 ka (Fig. 2), which coincides with relatively more enriched $\delta D_{\text{alkenone}}$ values and elevated BIT values (Fig. 2). After 18.5 ka the ratio generally decrease to values of ca. 1.1 throughout the Holocene. This suggests that, during these periods of elevated $C_{37}/C_{38}$ alkenone ratio, coastal haptophyte species may have contributed more to the alkenone pool and consequently shifted $\delta D_{\text{alkenone}}$ towards more positive values at times of increased freshwater input. Changing haptophyte assemblages in coastal settings in response to changing environmental conditions appear, therefore, to have a strong effect on $\delta D_{\text{alkenone}}$. This highlights the care that has to be taken when using the $\delta D_{\text{alkenone}}$ as a proxy for freshwater input in coastal settings or other environments where changes in the dominant alkenone producer(s) are likely to have occurred.

5. Conclusion

Despite changes in global seawater $\delta D$ related to glacial – interglacial ice volume effects, no long term change in the 39 ka record of $\delta D_{\text{alkenone}}$ off the Mozambique shelf was observed. We suggest that glacial – interglacial changes in the $\delta D_{\text{alkenone}}$ were masked by changing freshwater input to the core site, as evidenced by the BIT index. During the glacial, the site was in closer proximity to the coast, when there was likely also larger river outflow. These conditions probably led to locally more D-depleted water and increased fractionation of hydrogen isotopes during alkenone biosynthesis due to decreased salinity. The correlation between periods of enriched $\delta D_{\text{alkenone}}$ and elevated BIT values during the glacial is possibly related to an increased contribution from coastal alkenone-producing haptophyte species coinciding with elevated river outflow. This
complicates the application of $\delta D_{\text{alkenone}}$ as a proxy for freshwater input in coastal settings. However, the technique appears promising in more open ocean settings.

Acknowledgments

We thank the two anonymous reviewers for their comments, which improved the manuscript. D. Chivall (Royal NIOZ) is thanked for input to the manuscript. We acknowledge financial support from The Seventh Framework Programme PEOPLE Work Programme, Grant 238512 (Marie Curie Initial Training Network 'GATEWAYS'). The Netherlands Organization for Scientific Research (NWO) is acknowledged for funding M.v.d.M (VIDI), S.S. (VICI), I.S.C. (NEBROC II) and R.T. (INATEX program, G.-J. B.; project number 839.08.434). R.T. acknowledges the SCAN2 program on advanced instrumentation. A. Mets is thanked for laboratory assistance. We thank the Captain and crew of the R/V Pelagia and participants of the INATEX cruise for collecting core 64PE304-80. Y. Wang at Kiel University is acknowledged for extracting some of the 64PE304-80. Data presented here can be found at Pangaea.de; doi:10.1594/PANGAEA.836271.

Associate Editor – S. Wakeham

References


Friedman, I., Redfield, A.C., Schoen, B., Harris, J., 1964. The variation of the deuterium content of natural waters in the hydrologic cycle. Reviews of Geophysics 2, 177-224.


Buck, C.E., Burr, G.S., Edwards, R.L., Friedrich, M., Grootes, P.M., Guilderson, T.P., 
F.G., Manning, S.W., Reimer, R.W., Richards, D.A., Southon, J.R., Talamo, S., Turney, 
Age Calibration Curves, 0-50,000 Years cal BP. Radiocarbon 51, 111-115.

Ridderinkhof, H., van der Werf, P.M., Ullgren, J.E., van Aken, H.M., van Leeuwen, P.J., de 
Ruijter, W.P.M., 2010. Seasonal and interannual variability in the Mozambique Channel 
from moored current observations. Journal of Geophysical Research: Oceans 115, 
C06010.

163, 1-11.

Geophysical Research-Oceans 103, 1307-1318.

Reconstructing sea surface temperature and salinity using δ¹⁸O and alkenone records. 

Sachse, D., Billault, I., Bowen, G.J., Chikaraishi, Y., Dawson, T.E., Feakins, S.J., Freeman, K.H., 
Magill, C.R., McInerney, F.A., van der Meer, M.T.J., Polissar, P., Robins, R.J., Sachs, J.P., 
Paleohydrology: Interpreting the hydrogen-isotopic composition of lipid biomarkers from 


specific D/H ratios of lipid biomarkers from sediments as a proxy for environmental 
and climatic conditions. Geochimica et Cosmochimica Acta 65, 213-222.

phases in southeast Africa over the past 17,000 years. Nature 480, 509-512.

variability in the Mozambique Channel. Deep Sea Research Part II: Topical Studies in 

Schouten, S., Hopmans, E.C., Sinninghe Damsté, J.S., 2013. The organic geochemistry of 

Analytical methodology for TEX₈₆paleothermometry by high-performance liquid 
chromatography/atmospheric pressure chemical ionization-mass spectrometry. Analytical 
Chemistry 79, 2940-2944.

Schouten, S., Ossebaar, J., Schreiber, K., Kienhuis, M.V.M., Langer, G., Benthen, A., Bijma, J., 
2006. The effect of temperature, salinity and growth rate on the stable hydrogen isotopic 
composition of long chain alkenones produced by Emiliania huxleyi and Gephyrocapsa 

Schulz, H.-M., Schönér, A., Emeis, K.-C., 2000. Long-chain alkenone patterns in the Baltic sea-
an ocean-freshwater transition. Geochimica et Cosmochimica Acta 64, 469-477.


Fig. 1. Map of oceanic currents in the study region and core location. (a) Main ocean current systems in the Western Indian Ocean (white arrows), showing the South Equatorial Current (SEC), the Eastern Madagascar Current (EMC), the Mozambique Current (MC) and the greater Agulhas Current (Beal et al., 2011). The location of core 64PE304-80 is given by the red circle in the Mozambique Channel. Fig. (b) Shows an enlargement of the Mozambique Channel and the location of the Zambezi River mouth; the large gray arrow indicates the general current direction of the Mozambique Current, small gray arrows coastal circulation cells, and white shaded area represents the sediment distribution of Zambezi River fan (Sætre and Da Silva, 1984).
Fig. 2. (a) Temperature variation over Greenland indicated by the $\delta^{18}$O record of GRIP ice core (blue; Greenland Ice-core Project, 1993); (b) $\delta$D₃₇/₃₈ alkenone record (red line) with analytical error ($1\sigma$), (c) C₃₇/C₃₈ alkenone ratio (black line) and (d) BIT index (green) for core 64PE304-80; (e) mean global benthic $\delta^{18}$Oₚsw curve (Waelbroeck et al., 2002). Gray shaded bars indicate Younger Dryas (YD) (ca. 12.5-11 ka), Heinrich Event 1 (HE1) (ca. 19-14.6 ka), Last Glacial Maximum (LGM; ca. 23-19 ka) and Heinrich Event 2 (HE2; ca. 24 ka). Radiocarbon samples are indicated as black triangles.

Fig. 3. Cross plot of $\delta$D₃₇/₃₈ vs. BIT index. Values for Holocene (ca.12.7 – 0.5 ka) are indicated by closed gray circles, regression II (dashed line). Values for pre-LGM (ca. 39.4 – 16.1 ka) are indicated by open squares, regression I (solid line).