



## Three and half million year history of moisture availability of South West Africa: Evidence from ODP site 1085 biomarker records

Mark A. Maslin <sup>a,\*</sup>, Richard D. Pancost <sup>b</sup>, Katy E. Wilson <sup>a</sup>, Jonathan Lewis <sup>a</sup>, Martin H. Trauth <sup>c</sup>

<sup>a</sup> Department of Geography, University College London, Pearson Building, Gower Street, London, WC1H 0AP, UK

<sup>b</sup> Organic Geochemistry Unit, Bristol Biogeochemistry Research Centre and The Cabot Institute, School of Chemistry, University of Bristol, Cantock's Close, BS8 1TS, UK

<sup>c</sup> Institut für Geowissenschaften, Universität Potsdam, Karl-Liebknecht-Strasse 24, 14476 Potsdam, Germany

### ARTICLE INFO

#### Article history:

Received 27 April 2011

Received in revised form 29 November 2011

Accepted 12 December 2011

Available online 21 December 2011

#### Keywords:

Plio-Pleistocene

Aridity

SW Africa

Biomarkers

Palaeoclimate

Human evolution

### ABSTRACT

Ocean Drilling Program Site 1085 provides a continuous marine sediment record off southern South West Africa for at least the last three and half million years. The *n*-alkane  $\delta^{13}\text{C}$  record from this site records changes in past vegetation and provides an indication of the moisture availability of SW Africa during this time period. Very little variation, and no apparent trend, is observed in the *n*-alkane  $\delta^{13}\text{C}$  record, suggesting stable long-term conditions despite significant changes in East African tectonics and global climate. Slightly higher *n*-alkane  $\delta^{13}\text{C}$  values occur between 3.5 and 2.7 Ma suggesting slightly drier conditions than today. Between 2.5 and 2.7 Ma there is a shift to more negative *n*-alkane  $\delta^{13}\text{C}$  values suggesting slightly wetter conditions during a ~0.2 Ma episode that coincides with the intensification of Northern Hemisphere Glaciation (iNHG). From 2.5 to 0.4 Ma the *n*-alkane  $\delta^{13}\text{C}$  values are very consistent, varying by less than  $\pm 0.5\%$  and suggesting little or no long-term change in the moisture availability of South West Africa over the last 2.5 million years. This is in contrast to the long-term drying trend observed further north offshore from the Namib Desert and in East Africa. A comparison of the climate history of these regions suggests that Southern Africa may have been an area of long-term stability over the last 3.5 Myrs.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

While the late Cenozoic tectonic and moisture history of East Africa is well constrained (Levin et al., 2004; Wynn, 2004; Feakins et al., 2005; Trauth et al., 2005; 2007; Sepulchre et al., 2006), this is not the case for southern Africa (Dupont et al., 2005; Maslin and Christensen, 2007). Far from the major rifting centres, the region lacks the volcanic (basalt and ash) deposits that are characteristic of East Africa and permit the development of radiometric-based chronologies. Instead, most of the continental evidence for past climate change is derived either from estimations of denudation rate and landscape development using fission-track thermochronology and/or cosmogenic isotope analysis or by reconstructing regional geomorphological features associated with specific tectonic events. Estimations of denudation rate and landscape development for South West Africa (Brown et al., 1994; 2000; Cockburn et al., 1999; 2000; Gallagher and Brown, 1999; Raab et al., 2002; 2005) and South East Africa (Fleming et al., 1999; Brown et al., 2002; van der Beek et al., 2002) indicate denudation rates peaking at between 100–200 m/Myr during the late Cretaceous (80 to 60 Ma).

Subsequent denudation rates for Namibia are 15 m/Myrs or lower, and are typical for a passive margin setting (Raab et al., 2005); similar results have also been found for the Drakensberg Escarpment (Brown et al., 2002). This suggests that since 60 Ma there has been little or no uplift in South West Africa and that tectonic activity has been quiescent. Continental palaeoclimate records are also limited due to a lack of chronological control, e.g., Vaal River terraces, Florisbad Pan deposits, Tswaing Crater or lake deposits (Partridge et al., 1997; de Wit et al., 2000).

At present it is believed that a major change in southern African climate occurred during the late Cenozoic, resulting from the development of a strong cross-continental temperature gradient associated with the onset of the Benguela Current (BC) (Tyson and Partridge, 2000; Christensen et al., 2002). The upwelling associated with the BC initiated arid conditions in the western region, but there was substantial climate amelioration during the Pliocene when streams were rejuvenated and grasslands expanded (Tyson and Partridge, 2002). Uplift of the south-eastern and eastern hinterlands, including East Africa and Zimbabwe, created rain-shadow areas to the west of these regions (Tyson and Preston-White, 2000) and is thought to have further enhanced aridification. Tyson and Preston-White (2000) suggest the timing of this uplift was not well constrained and that it occurred at approximately the same time as the late Pliocene intensification of Northern Hemisphere Glaciation (iNHG; Li et al., 1998; Maslin et al., 1998). Subsequently Trauth et al. (2005) have shown East African uplift

\* Corresponding author at: UCL Department of Geography Environmental Change Research Centre University College London, Gower Street, WC1E 6BT. Tel.: +44 20 7679 0556; fax: +44 20 7679 7565.

E-mail address: [m.maslin@geog.ucl.ac.uk](mailto:m.maslin@geog.ucl.ac.uk) (M.A. Maslin).

URL: <http://www.ucl.ac.uk/ecrc> (M.A. Maslin).

started at about 12 Ma in northern Ethiopia and progressively shifted southward and occurred between ~4.5 Ma to 3.5 Ma in central Kenya and between 3.2 Ma to 2.3 Ma in southern Kenya and Tanzania. This coincides with a long-term drying trend in East Africa as well as that inferred from pollen records between 3.5 Ma and 1.7 Ma from ODP Site 1082 off the coast of the Namib Desert (Fig. 1). This record also suggests a possible rapid increase in local aridity at about 2.2 Ma (Dupont et al., 2005). Arguments to the contrary suggest that the late Miocene was more arid and that there is no indication of major change during the Pliocene (Diester-Haass et al., 2002; Giraudeau et al., 2002).

The most widely used method of reconstructing moisture availability is through the reconstruction of palaeovegetation using pollen analysis (e.g., Dowsett and Willard, 1996; Shi et al., 2000; Dupont et al., 2005). An alternative useful tool is carbon isotopic analysis (Hayes et al., 1990) of soil carbonates (Kingston et al., 1994; Morgan et al., 1994; Levin et al., 2004; Ségalen et al., 2007) or terrestrial higher plant biomarkers (e.g. Bird et al., 1995; Yamada and Ishiwatari, 1999; Huang et al., 2000). This allows the discrimination of inputs from isotopically distinct C<sub>3</sub> and C<sub>4</sub> plants. Average  $\delta^{13}\text{C}$  values of organic carbon in land plants (higher plants) vary according to the chemical pathway of photosynthesis (Ehleringer and Monson, 1993). Plants using the C<sub>3</sub> (Calvin-Benson or non-Kranz) photosynthesis pathway have a  $\delta^{13}\text{C}$  range between  $-22\text{‰}$  to  $-30\text{‰}$  (average  $-27\text{‰}$ ) (Ehleringer and Monson, 1993), compared with an average

atmospheric isotopic composition of  $-6\text{‰}$  to  $-7\text{‰}$ . Plants using the C<sub>4</sub> (Hatch-Slack or Kranz) pathway, including tropical and marsh grasses, have a  $\delta^{13}\text{C}$  range of between  $-9\text{‰}$  to  $-15\text{‰}$  (average  $-13\text{‰}$ ) (Ehleringer and Monson, 1993). C<sub>4</sub> plants re-evolved in the Miocene (Edwards et al., 2010; Brown et al., 2011) and the first proliferation of C<sub>4</sub> plants into Africa was between 12 and 15 Ma and then they became abundant between 7 and 8 Ma (Kingston et al., 1994; Morgan et al., 1994; Cerling et al., 1997; Ségalen et al., 2007). There is also a third type of plant, CAM (Crassulacean Acid Metabolism), which uses either C<sub>3</sub> or C<sub>4</sub> pathways depending on water availability. In terms of occurrence it is minor compared with the other two pathways, but is very important in the context of SW Africa due to their unusually high abundance (ca. 60% near the SW African coast; Werger and Ellis, 1981). In this study we use the distributions and  $\delta^{13}\text{C}$  values of *n*-alkanes from marine sediments recovered from Ocean Drilling Program (ODP) Leg 175 in the South East Atlantic Ocean to provide a long-term estimate of the vegetation water stress and thus moisture availability of the region over the last 3.5 million years.

## 2. Site location

The location of Ocean Drilling Program Site 1085 in the Benguela Current (BC) is shown in Fig. 1. The Site is located 260 km away

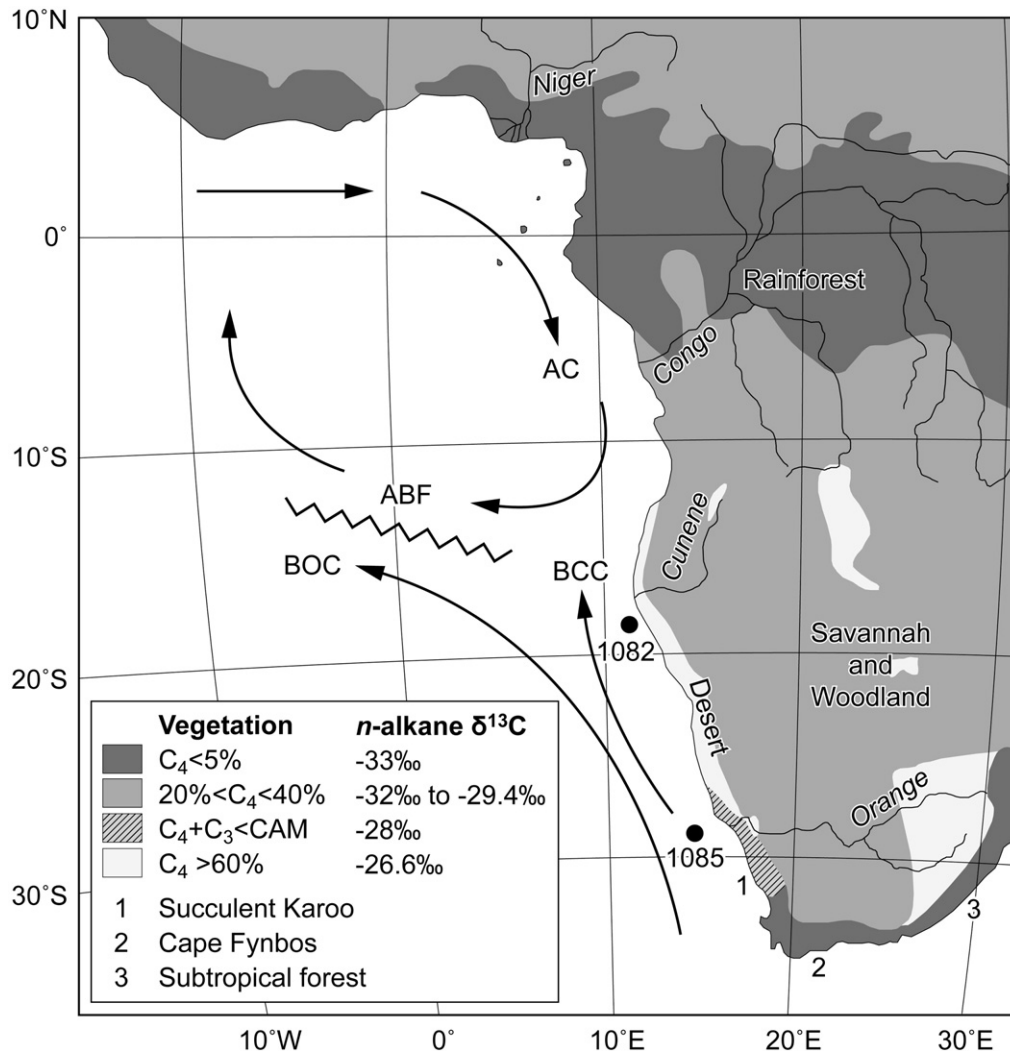


Fig. 1. Schematic representation of Southern African vegetation and rivers, including estimated average C<sub>31</sub> n-alkane  $\delta^{13}\text{C}$  values (adapted from Rommerskirchen et al., 2003), estimated surface ocean hydrography, and locations of ODP Sites 1082 and 1085 (adapted from Ettwein et al., 2001 and Christensen et al., 2002). BCC = Benguela coastal current, BOC = Benguela ocean current, ABF = Angola-Benguela Front, AC = Angola Current and SECC = South East Counter Current.

from the mouth of the Oranje River, 410 km away from the Olifant system and over a 1000 km from the Cunene River mouth. According to the review by Dupont (2011) if we were studying pollen ~300 km is the break between mixed river and aeolian input (<300 km) compared with just aeolian input (>300 km). Even if we assume fluvial transported biomarkers can travel further in the upper ocean, only input from the Oranje River need be considered. However the sediment from the Oranje River is deposited as a mud blanket along the continental shelf and very little of it moves off shore into the open Ocean (Meadows et al., 2002). Moreover, Site 1085 is directly opposite the mouth of the Oranje River and thus the predominate ocean currents will move sediment northward along the coast away from Site 1085. Hence we suggest that terrigenous material is delivered mainly to the Site via aeolian sources, which is supported by the detailed *n*-alkane distribution study of Rommerskirchen et al. (2003). Aeolian deposition is driven by the Southern Hemisphere trade wind system operating at the same latitude as the BC system. These predominantly south-westerly winds entrain terrestrial material from the adjacent continental areas of southern Africa and deposit them into the BC system (Shi and Dupont, 1997; Dupont and Wypytta, 2003).

The vegetation of Africa south of the equator is a complex mosaic of phytogeographies ranging from tropical rainforest to desert, with a high degree of diversity and endemism. Fig. 1 summarises the general vegetation types, the relative occurrence of C<sub>3</sub>, C<sub>4</sub> and CAM plants (Werger and Ellis, 1981; Rommerskirchen et al., 2003; Dension et al., 2005), and the average Holocene *n*-alkane δ<sup>13</sup>C values for each region (Rommerskirchen et al., 2003). The continental margin adjacent to ODP Site 1085 is dominated by desert and woody savannah. The Karoo-Namib Desert vegetation is dominated by C<sub>4</sub> plants, whereas the Zambezi and Kalahari-Highveld regions are mainly savannah and woodland and have a mixture of C<sub>3</sub> and C<sub>4</sub> plants with C<sub>3</sub> being more common (White, 1983). Large dust plumes occur during austral winter with winds blowing off the continent. There is also a small input of material from the Succulent Karoo during austral summer (Rommerskirchen et al., 2003). The Succulent Karoo is dominated by CAM plants, which can change their photosynthetic pathway between C<sub>3</sub> and C<sub>4</sub> depending on water availability, which potentially provides a wider range of *n*-alkane δ<sup>13</sup>C values.

### 3. Methodology

Based on the age model of Christensen et al. (2002), material from ODP Site 1085 was sampled every ~100 ka, generating 35 samples for *n*-alkane δ<sup>13</sup>C analysis representing the last 3.5 Ma and 55 samples for biomarker characterisation representing the last 5.5 Ma.

Total Organic Matter (TOC), was determined by weighing and drying sediments overnight in an oven at 110 °C, then placing them in a furnace at 550 °C for 3 h; the loss-on-ignition is taken as the amount of organic material present in the sample. Samples to be analysed for biomarker distributions were freeze-dried, ground and extracted via ultra-sonication in a sequence of solvents with increasing polarity: hexane (x2); a 1:1 (v/v) azeotrope of dichloromethane (DCM): methanol (MeOH) (x2); MeOH (x2). After extraction, the samples were evaporated and a standard mixture containing androstane and hexadecyldecanoate was added. In order to achieve GC-resolved peaks for isotopic analysis, each total lipid extract was further separated into five fractions using silica gel chromatography, eluting with: 3 ml of hexane for saturated hydrocarbons; 1.5 ml of 9:1 (v/v) hexane:DCM for aromatic hydrocarbons; 5.5 ml of DCM for ketones and wax esters; 3 ml of 1:1 (v/v) DCM:MeOH for alcohols and sterols; 3 ml of MeOH for more polar compounds. The samples were evaporated to dryness under a N<sub>2</sub> stream and were re-dissolved in a standard quantity of solvent. Only the saturated hydrocarbon and ketone/wax ester fractions were analysed further.

Individual compounds in each of the fractions were quantified using gas chromatography. After being dissolved in 100 μl ethyl

acetate, each sample was injected into a Carlo Erba 5300 series High Resolution Gas Chromatograph fitted with a CP-Cil 5CB silica column (internal diameter 0.32 mm, length 50 m, df 0.11 μm), which was heated from 40 °C to 140 °C at 20 °C/min, then at 4 °C/min to 300 °C at which temperature it was held for 20 min. Compounds were quantified against the known concentrations of internal standards described above. All fractions were subsequently analysed using gas chromatography/mass spectrometry (GC/MS) with a Thermoquest Finnigan Trace chromatograph interfaced to a Thermoquest Finnigan Trace mass spectrometer operating with electron ionization at 70 eV and scanning an *m/z* range of 50 to 850. GC conditions for GC/MS were identical to those used for GC analysis.

Compounds were assigned by comparing mass spectra and relative retention times with those in the literature. Sedimentation rates derived from the AMS age model described above were used along with the dry bulk density to calculate MARs for the various molecular components along with the average chain length (ALC) for the *n*-alkanes (Boot et al., 2006):

$$\text{MAR}_{\text{component}} = \left( \text{Conc}_{\text{component}} \cdot \text{SR} \cdot \text{DBD} \right),$$

where MAR<sub>component</sub> is the MAR in ng cm<sup>-2</sup> kyr<sup>-1</sup>, Conc<sub>component</sub> is the mass of component in ng g<sup>-1</sup> dry sediment, SR the sedimentation rate in cm kyr<sup>-1</sup> and DBD is the dry bulk density in g cm<sup>-3</sup>.

Average chain lengths (ACLs) for the *n*-alkanes were calculated as:

$$\text{ACL}_{27-33} = \frac{27[C_{27}] + 29[C_{29}] + 31[C_{31}] + 33[C_{33}]}{([C_{27}] + [C_{29}] + [C_{31}] + [C_{33}])}$$

with [C<sub>*x*</sub>] signifying the concentration of the *n*-alkane with *x* carbon atoms. Carbon preference indices (CPIs) were calculated for *n*-alkanes and *n*-alkanols as:

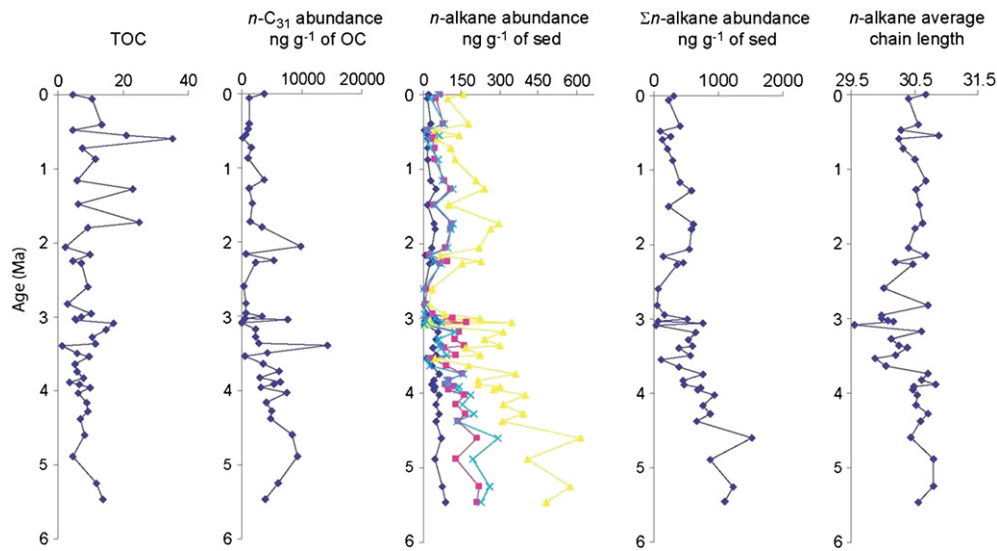
$$\text{CPI} = \left[ 0.5 \sum (X_j + X_{j+2} + \dots + X_n) / \sum (X_{j-1} + X_{j+1} + \dots + X_{n-1}) + 0.5 \sum (X_j + X_{j+2} + \dots + X_n) / \sum (X_{j+1} + X_{j+3} + \dots + X_{n+1}) \right],$$

where *i* = 25 and *n* = 33 in the case of *n*-alkanes and *i* = 21 and *n* = 31 in the case of *n*-alkanols.

Gas Chromatography-Isotope Ratio Monitoring Mass Spectrometry (GC-IRMS) was used to measure the carbon isotopic composition of compounds in the *n*-alkane fraction. Each sample was dissolved in 100 μl ethyl acetate and placed in 1 ml auto-sample vials before being analysed on a Varian GC fitted with a ZB-1 column linked to a ThermoFinnigan Mat DeltaS mass spectrometer via a combustion interface; the GC temperature program was the same as that used for standard GC analysis. Each sample was analysed twice and values are expressed in standard δ<sup>13</sup>C notation as parts per mil (‰) deviations from the Vienna Pee Dee Belemnite (VPDB) standard, measured during analyses against a pulsed reference gas input whose isotopic composition relative to VPDB had been determined by an external facility. Fatty acid and *n*-alkane mixtures, for which the individual compounds δ<sup>13</sup>C values had been determined offline by external facilities, were analysed every day, revealing instrumental precision better than 0.3‰ (see error bars on Figs. 2 and 3). This is consistent with the error recorded by duplicate measurement of the samples. Only 25 out of the 35 samples taken from Site 1085 yielded sufficient quantities of *n*-alkanes for isotope analysis.

### 4. Concentrations and distributions of *n*-Alkanes

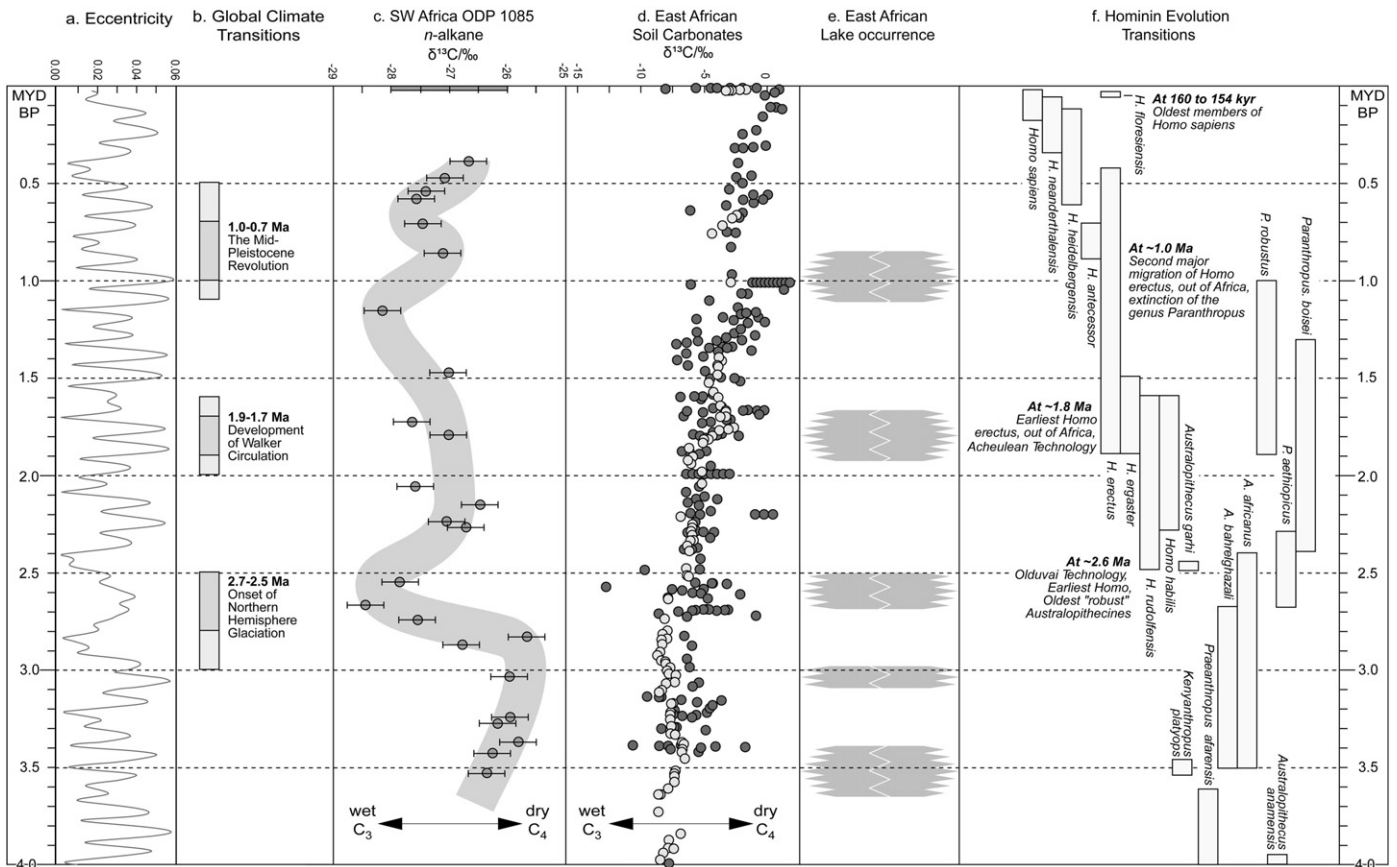
*N*-alkanes, along with long-chain acids and alcohols, occur in vascular plant leaf extracts with an odd-over-even predominance (OEP) and carbon chain-lengths ranging from C<sub>25</sub> to C<sub>35</sub> (Eglinton et al., 1962; Eglinton and Hamilton, 1967). In Site 1085 sediments, the high-molecular-weight (HMW) *n*-alkanes are characterised by a



**Fig. 2.** Total organic carbon contents (A) and n-alkane concentration (B–D) and distribution (E) parameters in OPD Site 1085 over the past 5.5 million years. Specifically, (B) shows the C<sub>31</sub> n-alkane concentrations normalised to TOC (ng/g<sup>-1</sup> of OC), (C) shows concentrations of the C<sub>27</sub>, C<sub>29</sub>, C<sub>31</sub> & C<sub>33</sub> n-alkane homologues as ng/g<sup>-1</sup> of dry sediment and (D) shows summed n-alkane concentrations (C<sub>27–33</sub>) in ng/g<sup>-1</sup> of dry sediment. Average Chain Lengths (ACLs) of the HMW n-alkanes are shown in (E).

predominance of the C<sub>27</sub>, C<sub>29</sub>, C<sub>31</sub> and C<sub>33</sub> homologues, exhibiting a strong OEP (CPI values range from 4 to 10, with no systematic variation through the section) and consistent with a leaf wax origin. Total HMW n-alkane concentrations vary by about two orders of magnitude, from ca 10 to 1000 ng g<sup>-1</sup> sediment (Fig. 2). In general, a decrease in total and individual HMW n-alkane concentrations occurs over the 5.5 Ma study interval despite an increase in TOC contents. In detail, this occurs

as a gradual decline from the base of the study interval at 5.5 Ma to 3.5 Ma; concentrations then decrease dramatically at ca 3 Ma and remain low (<100 ng g<sup>-1</sup> sediment) until ca 2.5 Ma when they increase to intermediate values (100 to 500 ng g<sup>-1</sup> sediment). These trends are still apparent or even enhanced if n-alkane concentrations are normalized to TOC contents or converted to mass accumulation rates (Fig. 2). N-alkanes are resistant to degradation and relatively easily



**Fig. 3.** Comparison of eccentricity variations (Berger and Loutre, 1991) with ODP Site 1085 n-alkane δ<sup>13</sup>C values (this study), East African soil carbonate δ<sup>13</sup>C values (light dots = Levin et al., 2004; dark dots = Wynn, 2004), East African lake occurrence (Trauth et al., 2005, 2007) and Hominin Evolution Transitions (see full references in Trauth et al., 2007).



transported from continental to marine (or lacustrine) settings via either aeolian or fluvial mechanisms (see [Pancost and Boot, 2004](#) review and references therein). As described above, *n*-alkanes at Site 1085 almost certainly derive from aeolian processes. Thus, the changes in concentration could reflect changes in wind strength. However, such an interpretation should be done cautiously as the controls on leaf wax concentrations or the distribution of *n*-alkanes relative to functionalised leaf waxes (*n*-alkanols and *n*-alkanoic acids) remain poorly understood and do vary amongst plant types. Biomarker concentration changes can also reflect OM degradation, although we consider that less likely due to the lack of similar changes in TOC contents. Changes in the distribution of *n*-alkanes can be evaluated by the average chain length (ACL). ACLs are generally stable, ranging from 29.9 to 30.7 (except for a single sample with an ACL of 29.5). However, average ACLs are generally lower from ca. 3.6 to 2.5 Ma, having an average value of 30.0 compared to an average of 30.5 over the rest of the record. Interpretation of *n*-alkane ACLs is unclear, with suggestions that higher values are associated with hotter or more arid conditions ([Hinrichs and Rullkötter, 1997](#); [Hinrichs et al., 1998](#)). However, *n*-alkane ACLs in plant extracts are rather variable and interpretation remains unclear.

### 5. Long-term Plio-Pleistocene trends in SW African moisture availability

Palaeovegetation and relative moisture availability can be reconstructed using *n*-alkane  $\delta^{13}\text{C}$  values.  $\text{C}_3$  and  $\text{C}_4$  plant species, as discussed above, each have distinct isotopic signatures ([Pancost and Pagani, 2006](#)). The species balance can be recorded by bulk sedimentary organic matter (e.g. [Kastner and Goñi, 2003](#)), but bulk OM  $\delta^{13}\text{C}$  values can be skewed by contributions from marine inputs. Compound-specific  $\delta^{13}\text{C}$  analyses of refractory *n*-alkanes of exclusively higher plant origin avoids this problem (e.g. [Eglinton et al., 1962](#); [Eglinton and Hamilton, 1967](#)), and they have been shown to record  $\text{C}_3$  and  $\text{C}_4$  species differences with fidelity (e.g. [Collister et al., 1994](#); [Schefuß et al., 2003](#); [Pancost and Boot, 2004](#)). [Collister et al. \(1994\)](#) observed that in  $\text{C}_3$  and  $\text{C}_4$  species, the *n*-alkanes  $\delta^{13}\text{C}$  values were depleted relative to biomass by  $\sim 5.9\%$  and  $\sim 9.9\%$  making the observed  $\text{C}_3$  range  $-28$  to  $-36\%$  (average  $-33\%$ ) and  $\text{C}_4$  range  $-19$  to  $-26\%$  (average  $-13\%$ ) in *n*-alkanes. Consequently, they have been used widely to determine the relative contribution of  $\text{C}_3$  and  $\text{C}_4$  plants to lacustrine and marine sediments (e.g. [Schefuß et al., 2003](#); [Street-Perrott et al., 2004](#); [Feakins et al., 2007](#)). The late Holocene range of *n*-alkane  $\delta^{13}\text{C}$  values from South Africa, from  $-26\%$  to  $-28\%$  ([Rommerskirchen et al., 2003](#)), reflects the mixed vegetation of South Africa and provides a baseline for comparison to the long-term record from Site 1085.

The ODP Site 1085 *n*-alkane  $\delta^{13}\text{C}$  values are presented in [Fig. 3](#) and exhibit no long-term trend over the last 3.5 Ma. In fact, the total range over the last 3.5 Ma years is between  $-25.5\%$  and  $-28.5\%$ , with similar values and only a slightly greater range than that observed for the Holocene. Interpretation of *n*-alkane  $\delta^{13}\text{C}$  values (as with those of bulk organic or paleosol carbon) as indicators of  $\text{C}_3$ – $\text{C}_4$ –CAM vegetation shifts needs to be done cautiously because water-stress of  $\text{C}_3$  and CAM plants can also produce heavier carbon isotope values ([Diefendorfa et al., 2010](#)). The Site 1085 *n*-alkane  $\delta^{13}\text{C}$  record, therefore, implies that the vegetation in southern South West Africa under went very little or no change in the water stress. This may reflect very little change in the proportion of  $\text{C}_3$  to  $\text{C}_4$  to CAM plants in SW Africa over the past 3.5 Ma. We note, however, that our record could be consistent with shifts in the proportion of  $\text{C}_3$  to  $\text{C}_4$  to CAM, which result in the same average *n*-alkane  $\delta^{13}\text{C}$  values.

Recently, [Tippie et al. \(2010\)](#) suggested that the  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  could have become up to  $1\%$  more negative over the last 4 million years. If so then this should be reflected in our long-term *n*-alkane  $\delta^{13}\text{C}$  records. In fact this is exactly what is observed, with slightly higher  $\delta^{13}\text{C}$  values between 3.5 Ma and 3 Ma ( $-26\%$ ) and slightly lower values between 0.9 Ma to 0.4 Ma ( $-27\%$ ). We suggest that further work is

required to validate the proposed decrease in atmospheric  $\delta^{13}\text{C}$  values but if confirmed it would indicate that there was even less variation in the *n*-alkane  $\delta^{13}\text{C}$  record of southern SW Africa, implying that very stable conditions persisted throughout the last 3.5 million years.

Although interpretation of *n*-alkane  $\delta^{13}\text{C}$  values should be done cautiously, it is clear that the 1085 record provides no evidence for a long-term decrease or increase in SW Africa moisture availability over the last 3.5 Ma. In fact, moisture availability appears to have been incredibly stable, despite large-scale tectonic activity in East Africa and major shifts in global climate. This is in contrast with the pollen record of ODP Site 1082 (see [Fig. 1](#)), about  $10^\circ\text{N}$  further north, which suggests a long-term trend towards drier conditions between 3.5 Ma and 1.7 Ma ([Dupont et al., 2005](#)). [Dupont et al. \(2005\)](#) suggest this aridification of the Namib Desert is due to the suppression of local sea surface temperatures caused by increased upwelling of cold water and less convective atmospheric moisture transport towards land.

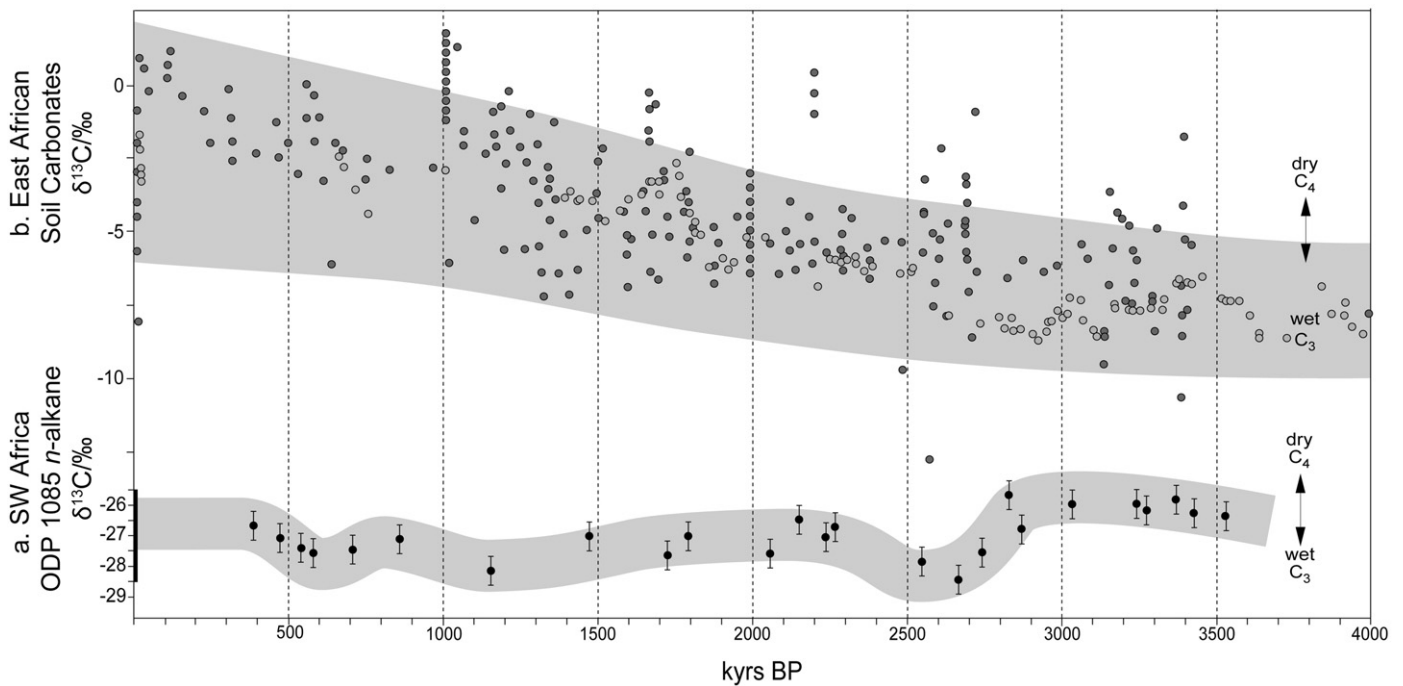
Despite its overall stability, the Site 1085 *n*-alkane  $\delta^{13}\text{C}$  record does exhibit some variations. Between 3.5 Ma and 2.7 Ma, *n*-alkane  $\delta^{13}\text{C}$  values are less negative than average suggesting slightly drier conditions. Intriguingly, this interval also corresponds to the interval characterised by the lowest *n*-alkane ACLs. Although low ACLs have been interpreted as reflecting wetter conditions, we caution that interpretation of such signatures remains unclear. Instead, both the high  $\delta^{13}\text{C}$  values and low ACLs might reflect a different vegetation regime ([Boot et al., 2006](#)).

Between 2.5 and 2.7 Ma *n*-alkane  $\delta^{13}\text{C}$  values become more negative, and this interval contains the most negative values of the whole record. The same interval is also characterised by the lowest *n*-alkane concentrations ([Fig. 2](#)), suggesting decreased aeolian transport of *n*-alkanes (e.g. [Pancost and Boot, 2004](#); [Schefuß et al., 2005](#)). Although both signatures could have multiple interpretations, both suggest that slightly wetter conditions in SW Africa coincided with the intensification of Northern Hemisphere Glaciation (iNHG). This is in agreement with the Site 1082 pollen record further north which shows an increase in *Stoebe*-type pollen between 3 Ma and 2.3 Ma. This pollen is indicative of the fynbos biome in southwest Africa, and [Dupont et al. \(2005\)](#) suggest this indicates a northward extension of the winter rainfall area.

From 2.4 Ma until 0.4 Ma (the end of the record) the *n*-alkane  $\delta^{13}\text{C}$  values are relatively consistent, varying by less than  $\pm 0.5\%$  suggesting that there has been little or no change in SW African moisture availability over the last 2.4 million years. This stability of SW African climate suggests that changes in the ocean currents both in the South East Atlantic and Indian Oceans had little or no effect on continental climate, contrary to the suggestions of [Tyson and Partridge \(2002\)](#) and [Tyson and Preston-White \(2000\)](#).

### 6. Comparison between SW and E African moisture availability

The long-term moisture history of SW Africa is radically different from that of East Africa. Our *n*-alkane  $\delta^{13}\text{C}$  record suggests that moisture availability in SW Africa was characterised by long-term stability, with no discernable trend. This suggests that the stable, if not quiescent, tectonic activity in SW Africa ([Raab et al., 2005](#)) provided a stable geography leading to a stable climate over the last 3.5 million years. In contrast, soil carbonate and *n*-alkane  $\delta^{13}\text{C}$  records ([Levin et al., 2004](#); [Feakins et al., 2005](#); [2007](#); [Ségalen et al., 2007](#)) from East Africa and the adjacent Indian Ocean show a significant  $10\%$  increase over the last 2 million years indicating a strong increase in the aridity of extreme periods due to the continued development of the East African Rift system ([Trauth et al., 2005](#); [2007](#)), see [Fig. 4](#). Using Plio-Pleistocene terrestrial dust flux records to the Indian and Atlantic Oceans and the Mediterranean Sea, [Trauth et al. \(2009\)](#) have shown that the aridity trend ([deMenocal, 2004](#)) may in fact be a trend towards increasing environmental variability through time. They postulate that after approximately 2 Ma, dry periods became drier whilst wet periods may have remained similar in character. There is strong evidence that this aridity



**Fig. 4.** Comparison of SW African ODP Site 1085  $n$ -alkane  $\delta^{13}\text{C}$  values (this study) and East African soil carbonate  $\delta^{13}\text{C}$  values (light dots = Levin et al., 2004; dark dots = Wynn, 2004) on the same scale. Note that the moisture availability reconstructed for South West Africa is essentially flat, while in East Africa the range of variability increases from approximately 2 millions years BP.

trend in East Africa was punctuated by episodes of precessionally-forced extreme wet and dry periods lasting a few hundred thousand years (see Fig. 2). These periods are characterised by the appearance and disappearance of large deep lakes within the East African Rift Valley (Kingston et al., 2007; Trauth et al., 2007) in conjunction with corresponding changes in the flux of terrigenous material reaching the oceans (deMenocal, 2004; Trauth et al., 2009). In contrast to these marked extremes in climatic variability observed in East Africa over the last 3 million years ago, the results from ODP Site 1085 suggest that SW African climate was relatively stable during this time. Our data suggest that SW Africa, like East Africa, seems to be wetter during the iNHG but currently there is no evidence that this region responded to either the onset of Walker Circulation at ca. 1.9–1.8 Ma (Ravelo et al., 2004) or the Mid-Pleistocene Revolution at ca. 1.0–0.8 Ma. However, in order to further evaluate past climate variability in SW Africa, it is necessary to improve the quantity and resolution of available palaeoclimate records.

## 7. Conclusions

The long-term moisture history of SW Africa over the last 3.5 million years is one of stability with no discernable trend. This suggests that previously inferred late Pliocene tectonic changes must have occurred much earlier and that large global climate shifts and local oceanic changes had little or no effect on the region. These results have interesting implications for the study of early hominin evolution and migration. The climatic stability of the region, even on short precessional time scales (Densson et al., 2005), contrasts sharply with East Africa which experienced not only a long-term increase in aridity, but alternating periods of extreme wet and dry climatic conditions (Maslin and Trauth, 2009). This implies that Southern Africa could have been a safe refuge for hominins and other animals during periods of extremely climate variability in East Africa.

## Acknowledgements

Many thanks to Ian Bull and Rob Berstan (Bristol Node of the NERC Life Sciences Mass Spectrometry Facility, School of Chemistry,

University of Bristol) for analytical support, and Janet Hope for assistance in London. We would like to thank Lydie Dupont for comments on earlier versions of this manuscript. The compiling of figures by the UCL Drawing Office (Department of Geography) was much appreciated. This research was supported by NERC grant GST/02/2690 and the NERC Life Sciences Mass Spectrometry Facility at Bristol.

## References

- Berger, A., Loutre, M.F., 1991. Insolation values for climate of the last 10 million years. *Quaternary Science Reviews* 10, 297–317.
- Bird, M.I., Summons, R.E., Gagan, M.K., Roksandic, Z., Dowling, L., Head, J., Fifield, L.K., Cresswell, R.G., Johnson, D.P., 1995. Terrestrial vegetation change as inferred from  $n$ -alkane  $\delta^{13}\text{C}$  analysis in the marine environment. *Geochimica et Cosmochimica Acta* 59, 2853–2857.
- Boot, C.S., Ettwein, V.J., Maslin, M.A., Weyhenmeyer, C.E., Pancost, P.D., 2006. A 35,000 years record of terrigenous and marine lipids in Amazon Fan sediments. *Organic Geochemistry* 37, 208–219.
- Brown, R.W., Gallagher, K., Duane, M.J., 1994. A quantitative assessment of the effects of magmatism on the thermal history of the Karoo sedimentary sequence. *African Journal of Earth Science* 18, 227–243.
- Brown, R.W., Gallagher, K., Gleadow, A.J.W., Summerfield, M.A., 2000. Morphotectonic evolution of the South Atlantic margins of Africa and South America. In: Summerfield, M.A. (Ed.), *Geomorphology and Global Tectonics*. John Wiley and Sons Ltd., Chichester, pp. 257–283.
- Brown, R.W., Summerfield, M.A., Gleadow, A.J.W., 2002. Denudational history along a transect across the Drakensberg Escarpment of southern Africa derived from apatite fission-track thermochronology. *Journal of Geophysical Research* 107. doi:10.1029/2001JB000745.
- Brown, N.J., Newell, C.A., Stanley, S., Chen, J.E., Perrin, A.J., Kajala, K., Hibberd, J.M., 2011. Independent and parallel recruitment of pre-existing mechanisms underlying  $\text{C}_4$  photosynthesis. *Science* 332, 1436–1439.
- Cerling, T.E., Harris, J.M., MacFadden, B.J., Leakey, M.G., Quade, J., Eisenmann, V., Ehleringer, J.R., 1997. Global vegetation change through the Miocene/Pliocene boundary. *Nature* 389, 153–158.
- Christensen, B.A., Kalbas, J.L., Maslin, M.A., Murray, R.W., 2002. Paleoclimatic changes in southern Africa during the intensification of Northern Hemisphere glaciation: evidence from ODP Leg 175 Site 1085. *Marine Geology* 180, 117–131.
- Cockburn, H.A.P., Seidl, M.A., Summerfield, M.A., 1999. Quantifying denudation rates on inselbergs in the central Namib Desert using in situ-produced cosmogenic  $^{10}\text{Be}$  and  $^{26}\text{Al}$ . *Geology* 27, 399–402.
- Cockburn, H.A.P., Brown, R.W., Summerfield, M.A., Seidl, M.A., 2000. Quantifying passive margin denudation and landscape development using a combined fission-track thermochronology and cosmogenic isotope approach. *Earth and Planetary Sciences Letters* 179, 429–435. doi:10.1016/S0012-821X(00)00144-8.

- Collister, J.W., Rieley, G., Stern, B., Eglinton, G., Fry, B., 1994. Compound-specific  $\delta^{13}\text{C}$  analyses of leaf lipids from plants with differing carbon dioxide metabolisms. *Organic Geochemistry* 2, 619–627.
- Diefendorf, A.F., Mueller, K.E., Wing, S.L., Koch, P.L., Freeman, K.H., 2010. Global patterns in leaf  $^{13}\text{C}$  discrimination and implications for studies of past and future climate. *PNAS* 5738–5743. [www.pnas.org/cgi/doi/10.1073/pnas.0910513107](http://www.pnas.org/cgi/doi/10.1073/pnas.0910513107).
- de Wit, M.C.J., Marshal, T.R., Partridge, T.C., 2000. Fluvial Deposits and Drainage Evolution. In: Partridge, T.C., Maud, R.R. (Eds.), *The Cenozoic of Southern Africa*. Oxford University Press, Inc., New York, pp. 55–72.
- deMenocal, P., 2004. African climate change and faunal evolution during the Pliocene–Pleistocene. *Earth and Planetary Science Letters* 220, 3–24.
- Densson, S., Maslin, M.A., Boot, C., Pancost, R., Ettwein, V., 2005. Precession-forced changes in South West African vegetation during marine oxygen isotope stages 100 and 101. *Palaeogeography, Palaeoclimatology, Palaeoecology* 220, 375–386.
- Diestler-Haass, L., Meyers, P.A., Vidal, L., 2002. The late Miocene onset of high productivity in the Benguela Current upwelling system as part of a global pattern. *Marine Geology* 180, 87–103.
- Dowsett, H., Willard, D., 1996. Southeast Atlantic marine and terrestrial response to middle Pliocene climate change. *Marine Micropaleontology* 27, 181–193.
- Dupont, L.M., 2011. Orbital scale vegetation change in Africa. *Quaternary Science Reviews* 30, 3589–3602.
- Dupont, L.M., Wyputta, U., 2003. Reconstructing pathways of aeolian pollen transport to the marine sediments along the coastline of SW Africa. *Quaternary Science Reviews* 22, 157–174.
- Dupont, L.M., Donner, B., Vidal, L., Pérez, E.M., Wefer, G., 2005. Linking desert evolution and coastal upwelling: Pliocene climate change in Namibia. *Geology* 33, 461–464. doi:10.1130/G21401.1.
- Edwards, E.J., Osborne, C.P., Strömberg, C.A.E., Smith, S.A., C 4 Grasses Consortium, 2010. The origins of  $\text{C}_4$  grasslands: integrating evolutionary and ecosystem science. *Science* 331, 587–591. doi:10.1126/science.1177216.
- Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. *Science* 156, 1322–1335.
- Eglinton, G., Gonzalez, A.G., Hamilton, R.J., Raphael, R.A., 1962. Hydrocarbon constituents of the wax coatings of plant leaves – a taxonomic survey. *Phytochemistry* 1, 89–102.
- Ehleringer, J.R., Monson, R.K., 1993. Evolutionary and ecological aspects of photosynthetic pathway variation. *Annual Review of Ecology and Systematics* 24, 411–439.
- Ettwein, V.J., Stickley, C.E., Maslin, M.A., Laurie, E.R., Rosell-Melé, A., Vidal, L., Brownless, M., 2001. Fluctuations in Productivity and Upwelling Intensity at Site 1083 during the Intensification of Northern Hemisphere Glaciation (2.40–2.65 Ma). *Proceedings of the Ocean Drilling Program: Scientific Results*, 175, pp. 1–24 (online).
- Feakins, S.J., deMenocal, P.B., Eglinton, T.I., 2005. Biomarker records of late Neogene changes in northeast African vegetation. *Geology* 33, 977–980.
- Feakins, S.J., Eglinton, T.I., deMenocal, P.B., 2007. A comparison of biomarker records of northeast African vegetation from lacustrine and marine sediments ca. 3.40 Ma. *Organic Geochemistry* 38, 160–1624.
- Fleming, A., Summerfield, M.A., Stone, J.O., Fifield, L.K., Cresswell, R.G., 1999. Denudation rates for the Southern Drakensberg Escarpment, SE Africa, derived from in-situ-produced cosmogenic  $\text{Cl-36}$ : initial results. *Journal of the Geological Society of London* 156, 209–212.
- Gallagher, K., Brown, R.W., 1999. Denudation and uplift at passive margins: the record on the Atlantic Margin of southern Africa. *Philosophical Transactions of the Royal Society* 357, 835–859.
- Giraudeau, J., Meyers, P.A., Christensen, B.A., 2002. Accumulation of organic and inorganic carbon in Pliocene–Pleistocene sediments along the SW African margin. *Marine Geology* 180, 49–69.
- Hayes, J.M., Freeman, K.H., Popp, B.N., Hoham, C.H., 1990. Compound-specific isotopic analyses: a novel tool for reconstruction of ancient biogeochemical processes. *Advances in Organic Geochemistry* 16, 1115–1128.
- Hinrichs, K.-U., Rullkötter, J., 1997. Terrigenous and marine lipids in Amazon Fan sediments: implications for sedimentological reconstructions. In: Flood, R.D., Piper, D.J.W., Klaus, A., Peterson, L.C. (Eds.), *Proceedings of the Ocean Drilling Program: Scientific Results*, 155, pp. 539–553.
- Hinrichs, K.-U., Rinna, J., Rullkötter, J., 1998. Late Quaternary palaeoenvironmental conditions indicated by marine and terrestrial molecular biomarkers in sediments from the Santa Barbara basin. In: Wilson, R.C., Tharp, V.L. (Eds.), *Proceedings of the Fourteenth Annual Pacific Climate (PACLIM) Workshop*, pp. 125–133.
- Huang, Y., Dupont, L., Sarnthein, M., Hayes, J.M., Eglinton, G., 2000. Mapping of  $\text{C}_4$  plant input from North West Africa into North East Atlantic sediments. *Geochimica et Cosmochimica Acta* 64, 3505–3513.
- Kastner, T.P., Goni, M.A., 2003. Constancy in the vegetation of the Amazon basin during the late Pleistocene: evidence from the organic matter composition of Amazon deep sea fan sediments. *Geology* 31, 291–294.
- Kingston, J., Hill, A., Marino, B.D., 1994. Isotopic evidence for Neogene hominid Palaeoenvironments in the Kenya Rift Valley. *Science* 264, 955–959. doi:10.1126/science.264.5161.955.
- Kingston, J., Deino, A., Hill, A., 2007. Astronomically forced climate change in the Kenyan Rift Valley 2.7–2.55 Ma: implications for the evolution of early hominin ecosystems. *Journal of Human Evolution* 53, 487–503.
- Levin, N.E., Quade, J., Simpson, S.W., Semaw, S., Rogers, M., 2004. Isotopic evidence for Pliocene–Pleistocene environmental change at Gona, Ethiopia. *Earth and Planetary Science Letters* 219, 93–110.
- Li, X.S., Berger, A., Loutre, M.-F., Maslin, M.A., Haug, G.H., Tiedemann, R., 1998. Simulating late Pliocene Northern Hemisphere climate with the LLN 2-D model. *Geophysical Research Letters* 25, 915–918.
- Maslin, M.A., Christensen, B., 2007. Tectonics, orbital forcing, global climate change, and human evolution in Africa. *Journal of Human Evolution* 53, 443–464.
- Maslin, M.A., Trauth, M.H., 2009. Chapter 13: Plio-Pleistocene East African Pulsed Climate Variability and its influence on early human evolution. In: Grine, F.E., Leakey, R.E., Fleagle, J.G. (Eds.), *The First Humans – Origins of the Genus Homo*, pp. 151–158.
- Maslin, M.A., Li, X.S., Loutre, M.-F., Berger, A., 1998. The contribution of orbital forcing to the progressive intensification of Northern Hemisphere glaciation. *Quaternary Science Reviews* 17, 411–426.
- Meadows, M.E., Rogers, J., Lee-Thorp, J.A., Bateman, M.D., Dingle, R.V., 2002. Holocene geochronology of a continental-shelf mudbelt off southwestern Africa. *The Holocene* 12, 59–67.
- Morgan, M.E., Kingston, J., Marino, B.D., 1994. Carbon isotope evidence for the emergence of  $\text{C}_4$  plants in the Neogene from Pakistan and Kenya. *Nature* 367, 162–165.
- Pancost, R.D., Boot, C.S., 2004. The palaeoclimatic utility of terrestrial biomarkers in marine sediments. *Marine Chemistry* 92, 239–261.
- Pancost, R.D., Pagani, M., 2006. Controls on the carbon isotopic compositions of lipids in marine environments. *The Handbook of Environmental Chemistry* 2N, 209–249. doi:10.1007/698\_2\_007.
- Partridge, T.C., deMenocal, P.B., Lorentz, S.A., Paiker, M.J., Vogel, J.C., 1997. Orbital forcing of climate over South Africa: a 200,000 year rainfall record from the Pretoria Saltpan. *Quaternary Science Reviews* 16, 1125–1133.
- Raab, M.J., Brown, R.W., Gallagher, K., Carter, A., Weber, K., 2002. Late Cretaceous reactivation of major crustal shear zones in northern Namibia: constraints from apatite fission track analysis. *Tectonophysics* 349, 75–92.
- Raab, M.J., Brown, R.W., Gallagher, K., Weber, K., Gleadow, A.J.W., 2005. Denudational and thermal history of the Early Cretaceous Brandberg and Okenyenia Igneous Complexes on Namibia's Atlantic passive margin. *Tectonics* 24. doi:10.1029/2004TC001688.
- Ravelo, C., Andreasen, D., Olivarez, A., Lyle, M., Wara, M., 2004. The role of torpid and extratropical processes on Northern Hemisphere Glaciation. *Nature* 429, 263–267.
- Rommerskirchen, F., Eglinton, G., Dupont, L., Gunter, U., Wenzel, C., Rullkötter, J., 2003. A north to south transect of Holocene southeast Atlantic margin sediments: relationship between aerosol transport and compound-specific  $\text{d}^{13}\text{C}$  land plant biomarker and pollen records. *Geochemistry, Geophysics, Geosystems* 4, 12. doi:10.1029/2003GC000541.
- Scheffuß, E., Schouten, S., Jansen, J.H.F., Sinnighe Damsté, J.S., 2003. African vegetation controlled by tropical sea surface temperatures in the mid-Pleistocene period. *Nature* 422, 418–422.
- Scheffuß, E., Schouten, S., Schneider, R.R., 2005. Central African hydrologic changes during the past 20,000 years. *Nature* 437, 1003–1006.
- Ségalen, L., et al., 2007. Timing of  $\text{C}_4$  grass expansion across sub-Saharan Africa. *Journal of Human Evolution* 53, 549–559.
- Sepulchre, P., Ramstein, G., Fluteau, F., Schuster, M., Tiercelin, J.J., Brunet, M., 2006. Tectonic uplift and Eastern Africa Aridification. *Science* 313, 1419–1423.
- Shi, N., Dupont, L.M., 1997. Vegetation and climatic history of south-west Africa: a marine palynological record of the last 300,000 years. *Vegetation History and Archaeobotany* 6, 117–131.
- Shi, N., Dupont, L.M., Beug, H.-J., Schneider, R., 2000. Correlation between vegetation in Southwestern Africa and oceanic upwelling in the past 21,000 years. *Quaternary Research* 54, 72–80.
- Street-Perrott, F.A., Ficken, K.J., Huang, Y., Eglinton, G., 2004. Late Quaternary changes in carbon cycling on Mt. Kenya, East Africa: an overview of the  $\delta^{13}\text{C}$  record in lacustrine organic matter. *Quaternary Science Reviews* 23, 861–879.
- Tipple, B.J., Meyers, S.R., Pagani, M., 2010. Carbon isotope ratio of Cenozoic  $\text{CO}_2$ : a comparative evaluation of available geochemical proxies. *Paleoceanography* 25, PA3202. doi:10.1029/2009PA001851.
- Trauth, M.H., Maslin, M.A., Deino, A., Strecker, M.R., 2005. Late Cenozoic moisture history of East Africa. *Science* 309, 2051–2053.
- Trauth, M.H., Maslin, M.A., Deino, A., Strecker, M.R., Bergner, A.G.N., Dühnforth, M., 2007. High- and low-latitude forcing of Plio-Pleistocene African climate and human evolution. *Journal of Human Evolution* 53, 475–486.
- Trauth, M.H., Larrasoana, J.C., Mudelsee, M., 2009. Trends, rhythms and events in Plio-Pleistocene African climate. *Quaternary Science Reviews* 28, 399–411.
- Tyson, P.D., Partridge, T.C., 2000. Evolution of Cenozoic Climates. In: Partridge, T.C., Maud, R.R. (Eds.), *The Cenozoic of Southern Africa*. Oxford University Press, New York, pp. 371–387.
- Tyson, P.D., Preston-White, R.A., 2000. *The Weather and Climate of Southern Africa*. Oxford University Press Southern Africa, Cape Town, South Africa, p. 396.
- Tyson, P.D., Partridge, T.C., 2002. Evolution of Cenozoic climates. In: Partridge, T.C., Maud, R.R., Oxford Monographs on Geology and Geophysics No. 40: *The Cenozoic of Southern Africa*. Oxford University Press, New York, pp. 371–387.
- van der Beek, P., Summerfield, M.A., Braun, J., Brown, R.W., Flemming, A., 2002. Modelling post-break-up landscape development and denudation history across the eastern margin (Drakensberg Escarpment) of southern Africa. *Journal of Geophysical Research* 107 (B12). doi:10.1029/2001JB000744.
- Werger, M.J.A., Ellis, R.P., 1981. Photosynthetic pathways in the arid region of South Africa. *Flora* 171, 64–75.
- White, F., 1983. The vegetation of Africa. *Unesco. Natural Resources Research* 20, 356.
- Wynn, J.G., 2004. Influence of Plio-Pleistocene aridification on human evolution: evidence from paleosols of the Turkana Basin, Kenya. *American Journal of Physical Anthropology* 123, 106–118.
- Yamada, K., Ishiwatari, R., 1999. Carbon isotopic compositions of long-chain n-alkanes in the Japan Sea sediments: implications for paleoenvironmental changes over the past 85 kyr. *Organic Geochemistry* 30, 367–377.