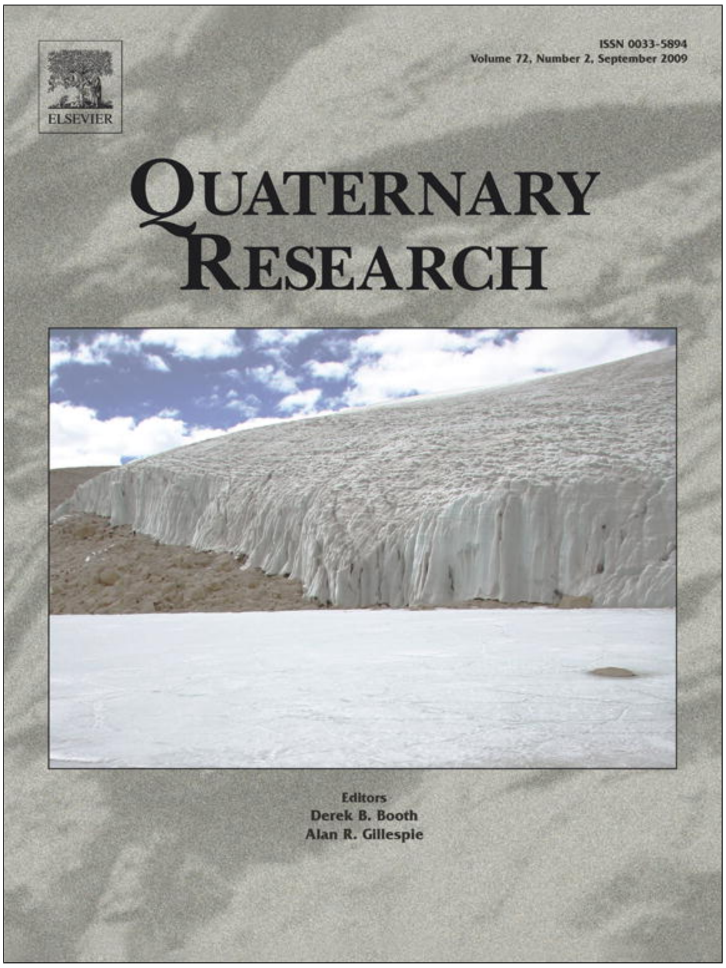

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Stable isotope and ^{14}C study of biogenic calcrete in a termite mound, Western Cape, South Africa, and its palaeoenvironmental significance

Alastair J. Potts [a], Jeremy J. Midgley [a,*], Chris Harris [b]

[a] Botany Department, University of Cape Town, South Africa
[b] Department of Geological Sciences, University of Cape Town, South Africa

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ABSTRACT

Late Quaternary terrestrial climate records from the semi-arid zone of the Western Cape of South Africa are rare. However, palaeoenvironmental information may be inferred from ancient termite mounds of the region. Calcrete lenses in these mounds have δ^{13}C and δ^{18}O values that show systematic changes with radiocarbon dates, which range from 33,629–36,709 to 21,676–23,256 cal yr BP. These dates confirm that these *heuweltjies* had been present in the landscape since the last glacial period. The decrease in δ^{13}C and δ^{18}O from 33,629–36,709 to 21,676–23,256 cal yr BP indicates that climate information is recorded by the calcretes. It is suggested that a progressive decline in air temperature and an increase in moisture availability, and a decline in abundance of C_4 or CAM plants, occurred in the region during the time *heuweltjie* calcite precipitated.

Introduction

Large termite mounds (up to 25 m in diameter and 3 m in height; Moore and Picker, 1991), locally termed *heuweltjies* (pronunciation: *hue-vil-key*; translation: 'small hills'), are found evenly distributed across large parts of the Western Cape Province and along the western region of the Northern Province in South Africa (Lovegrove and Siegfried, 1986; Picker et al., 2007). In some regions, *heuweltjies* cover as much as 14–25% of the landscape (Moore and Picker, 1991). There is uncertainty as to whether *heuweltjies* formed during the Holocene or the previous glacial period, or both. Mound density is reported to be in equilibrium with current climatic conditions, suggesting formation during the Holocene (Picker et al., 2007), which is supported by a number of ^{14}C ages of calcrete younger than 8000 ^{14}C yr BP (Moore and Picker, 1991). However, a number of calcrete ^{14}C ages from *heuweltjies* have been recorded ranging between 24 to 30 ^{14}C ka BP (Midgley et al., 2002). It is generally accepted that they are of biogenic origin and have been produced by the termite *Microhodotermes viator* (see Moore and Picker, 1991 for a review on the possible origins of *heuweltjies*; Picker et al., 2007).

Calcrete lenses have been observed within termite mounds generally (Wood and Sands, 1978) and in *heuweltjies* (Moore and Picker, 1991). Such biogenic calcrete may act as a proxy for the environmental conditions during calcrete formation (Dubbin, 2001). The carbon isotope composition of calcrete is dependent on the soil CO_2, which is in turn controlled by the photosynthetic pathways used by plants in the local ecosystem (Cerling and Quade, 1993). The oxygen isotope composition of calcrete depends on the isotope composition of soil water, which is related to local rain water (Cerling and Quade, 1993). The δ^{13}C and δ^{18}O values of calcrete have been used to elucidate past climate and vegetation conditions (e.g., Talma and Netterberg, 1983; Liu et al., 1996; Srivastava, 2001; Alonso-Zarza and Arenas, 2004; Schmid et al., 2006), such as temperature and precipitation regimes and vegetation types (plants with C_3 vs C_4/CAM photosynthetic pathways).

The purpose of this study is to investigate the potential use of *heuweltjie* calcrete as a palaeoenvironmental indicator. We have determined the carbon and oxygen isotope composition of calcrete from different horizons in a single termite mound. Radiocarbon dates were obtained to indicate the age range of the calcrete found in the termite mound. We also analysed the carbon isotope composition of the current vegetation and termite 'frass' (the debris or excrement produced by plant-eating insects) found on the termite mound, in order to determine whether the carbon isotope ratios of the calcrete are consistent with the current vegetation and termite feeding preferences.

Origins of calcrete in arid regions

Pedogenic calcretes are characteristic of arid regions where evaporation exceeds precipitation (Retallack, 1994), but the origins of pedogenic calcrete are still not fully understood (Rowe and Maher, 2000). Calcium can be supplied by either silicate weathering or from the atmosphere via dust fallout or marine aerosols. Atmospheric

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* Corresponding author. Postal Address: Department of Botany, University of Cape Town, University Private Bag, Rondebosch 7700, South Africa. Fax: +27 21 650 4041.
E-mail address: Jeremy.Midgley@uct.ac.za (J.J. Midgley).

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contributions of calcium can account for as much as 98% of soil carbonate calcium (Capo and Chadwick, 1999), although this is not the case in the Western Cape (Soderberg and Compton, 2007). Calcium carbonate is mobilised in the soil profile by dissolved CO_2, which is derived from the decay of plant material and root respiration. The calcium carbonate is then transported in solution through the soil profile and reprecipitates at some depth, usually >25 cm (Cerling and Quade, 1993). The calcium carbonate reprecipitates when the soil solution becomes supersaturated with respect to calcite. In terms of climate and vegetation reconstruction, reprecipitation preserves the carbon and oxygen composition of the soil water at the time of reprecipitation.

Calcrete formation within termite mounds is due either to “umbrella” or zoogenic processes. The former hypothesis (Lee and Wood, 1971, p. 161) states that calcrete forms near the surface from calcium-rich groundwater. Off-mound calcrete is leached away by precipitation, while the calcrete under the mound is protected by the termite-hardened surface layer, which decreases infiltration. The zoogenic origins hypothesis (Lee and Wood, 1971) states that foraging termites are responsible for concentrating calcium and carbon dioxide (from decaying organic matter) within the mound, which precipitates as calcrete. Calcrete precipitation would have occurred prior to mound formation under the “umbrella” hypothesis and after mound formation in the case of the zoogenic hypothesis. The “umbrella” hypothesis is very unlikely as *heuweltjies* form on slopes, and the SW Cape groundwaters are not $CaCO_3$-rich (van Wyk et al., 1992).

As it stands, the precise processes and organism that led to the formation of *heuweltjie* calcrete remain a matter for further study. However, the carbon isotope composition of the *heuweltjie* calcrete is likely to be a function of high CO_2 levels resulting from the plant material collected, stored and digested underground. The most likely termite species to have created the *heuweltjies* is *Microdotermes viator* (Moore and Picker, 1991). Coaton and Sheasby (1974) note that this harvester termite has a subterranean hive and galleries and that it seals off external tunnels after collecting plant material or ejecting waste material. In this paper we investigate the use of carbon and oxygen isotopes as indicators of vegetation and temperature change across the time period represented by the calcrete.

Study site

The study site consists of a single *heuweltjie* with an exposed cross-section of approximately 2 m in height that was fortuitously excavated by a road cutting (33°27.475' S, 19°32.083' E; Fig. 1). The site is located near Worcester, which is 72 km east-northeast from Cape Town.

The present-day climate is typically Mediterranean. The local mean annual precipitation at a weather station in Worcester (21 km from the *heuweljtie*) is about 215 mm (South African Weather Service unpublished data, 2006), with about 132 mm of precipitation occurring during the winter season (May to August). Temperature is usually above 0°C all year round, with a mean minimum and maximum air temperature of 16°C and 32°C in mid-summer (January), respectively, and 6°C and 19°C in mid-winter (July), respectively (South African Weather Service unpublished data, 2006).

The site is located near the border of the Fynbos and Succulent Karoo biomes, and represents an outlying area of Succulent Karoo within the Robertson Karoo vegetation type (Fig. 1; Mucina and Rutherford, 2006). The Fynbos and Succulent Karoo are characterised by a lack or marginal component of C_4 grasses (Mucina and Rutherford, 2006). The Nama Karoo is the closest biome where C_4 grasses are a large component of the vegetation (Mucina and Rutherford, 2006) and this is at least 200 km from the *heuweltjie* site. The plant species currently growing on the *heuweltjie* are shown in Table 1. Termite frass is evident on top of the *heuweltjie* indicating that at least part of it is still in use, although no active tunnels were observed more than 30 cm below the surface.

Sample description

There is wide variation in calcrete morphology within the *heuweltjie* profile, ranging from i) large cemented nodules made up of heterogeneous material, ii) small nodules within matrices of softer calcrete, and iii) soft powdery calcrete. Samples from these different morphologies were labelled ‘nodule’, ‘matrix’, and ‘transitional’, respectively. There appears to be a horizontal laminar layering of soft white calcrete through the profile interspersed with hard black-coated cemented calcrete nodules that range from 5 to 30 cm in diameter. Layers of calcrete extended to a depth of just under 2 m from the surface of the *heuweltjie*.

Methods

Sampling

Three vertical sample profiles were selected so that separate regions of the *heuweltjie* would be sampled, specifically the center

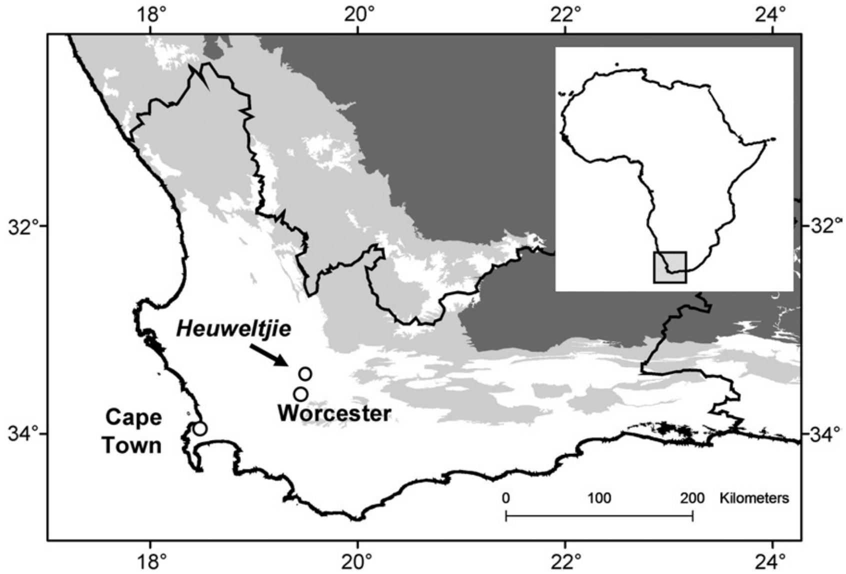

Figure 1. Map of Western Cape area showing the location of the *heuweltjie* used in this study (indicated by the arrow). The Fynbos (white), Succulent Karoo (light grey) and Nama-Karoo (dark grey) biomes are included (Mucina and Rutherford, 2006).

Table 1
The $\delta^{13}C$ (PDB) values for ten plants species situated on top of the *heuweltjie*.

Species	$\delta^{13}C$
Euphorbia burmannii	− 22.94 [−8.54]
Ruschia sp. 1	−22.45 [−8.05]
Phyllobolus splendens	−24.53 [−10.13]
Drosanthemum montaguense	−24.47 [−10.07]
Pteronia incana	−26.39 [−11.99]
Lycium cinereum	−26.04 [−11.64]
Ruschia sp. 2	−21.67 [−7.27]
Leipoldtii schutzei	−24.68 [−10.28]
Pteronia pallens	−27.09 [−12.69]
Drosanthemum sp.	−23.82 [−9.42]

Values in square brackets represent the $\delta^{13}C$ correcting for the fractionation from soil organic matter to carbonates using a value of 14.4‰ (Midgley et al., 2002).

(profile I) and intermediate (profile II) and distal (profile III) positions (Fig. 2). Profiles II and III were situated 2.4 m and 5.2 m from profile I, respectively. Each profile was 'cleaned' by removing approximately 5 cm of the exposed surface. This was to prevent collecting samples that had been contaminated due to recent exposure. A sample was collected for each distinct layer encountered down a profile and placed in a plastic bag. The depth of the sampled layer from the surface was measured. Seven samples were collected from profile I and profile III, and eleven samples from profile II. In addition, four samples were collected 50 cm away from profile III but following the contours of the layers of the first four samples. Two microsamples (8–10 mg) from twenty-two samples were collected, which were analysed separately to test the precision of the results. We also took samples from six termite frass heaps and of the ten most abundant plant species found growing on the *heuweltjie* for carbon isotope analysis. A single sample was also obtained from the nearest marble horizon within the Neo-Proterozoic Malmesbury Group on the farm Leipzig (33°37.858' S, 19°38.107' E).

Calcrete samples: sample preparation and oxygen and carbon stable isotopes

A total of 53 calcrete samples and 1 marble sample were processed for both carbon and oxygen isotope analyses in the Department of Geological Sciences, University of Cape Town following the method of McCrea (1950). The carbonate samples were dried overnight at a temperature of 50°C before loading 8–10 mg of material into reaction vessels with 100% phosphoric acid, and then pumped in the vacuum system for at least 2 h. The phosphoric acid was reacted with the carbonate to liberate CO_2 gas at 25°C. The mass spectrometric analysis of the CO_2 gas was undertaken using a MAT Delta XP Mass Spectrometer in dual-inlet mode. Carbon and oxygen isotope data are reported in standard δ notation where $\delta^{18}O = [(R_{\text{sample}} / R_{\text{standard}} - 1) * 1000]$ with $R = {}^{13}C / {}^{12}C$ and ${}^{18}O/{}^{16}O$, respectively. A fractionation factor of 1.01025 was used to correct the $\delta^{18}O$ value of the acid liberated CO_2 to that of the calcite. The oxygen and carbon isotope δ values are reported with respect to SMOW and PDB, respectively. Raw delta values were calibrated to the SMOW and PDB scales using the values obtained for the internal carbonate standard NM95 analysed at the same time as each batch of samples. NM95 has been calibrated to the SMOW and PDB scales using the NBS19 carbonate standard ($\delta^{18}O = 28.64$‰; $\delta^{13}C = 1.95$‰). Repeated analyses of the internal standard suggest that $\delta^{18}O$ and $\delta^{13}C$ determinations are accurate to within 0.07‰ and 0.02‰, respectively (std. dev. of duplicates, $n = 9$). Duplicate analysis of calcrete samples suggests that the $\delta^{18}O$ and $\delta^{13}C$ values of the sample material are accurate to within 0.34‰ and 0.31‰, respectively (std. dev. of difference between duplicates, $n = 22$).

Calcrete samples: calcite content

The calcite content was calculated for each sample from the volume of gas produced during the reaction. In addition, the calcite content of six soil samples taken from 5 to 15 m away from the edge of the termite mound as well as three samples from within the *heuweltjie* was determined using the "Karbonate-bombe" method (Mueller and Gastner, 1971).

Calcrete age determination

Five samples along two depth transects were selected for radiocarbon dating (Fig. 2). Three of the samples were selected from profile I, two of which came from a large cemented nodule approximately 25 cm in diameter and the other coming from a powdery calcrete layer near the surface, about 15 cm above the cemented nodule. Two samples were selected from the profile III at the outskirts of the termite mound, one from the topmost layer and one from the bottommost layer. All ages have been calibrated using CalPal$^{\text{online}}$ Software (Danzeglocke et al., 2008) with the Hulu 2007 calibration curve (Weninger and Jöris, 2008).

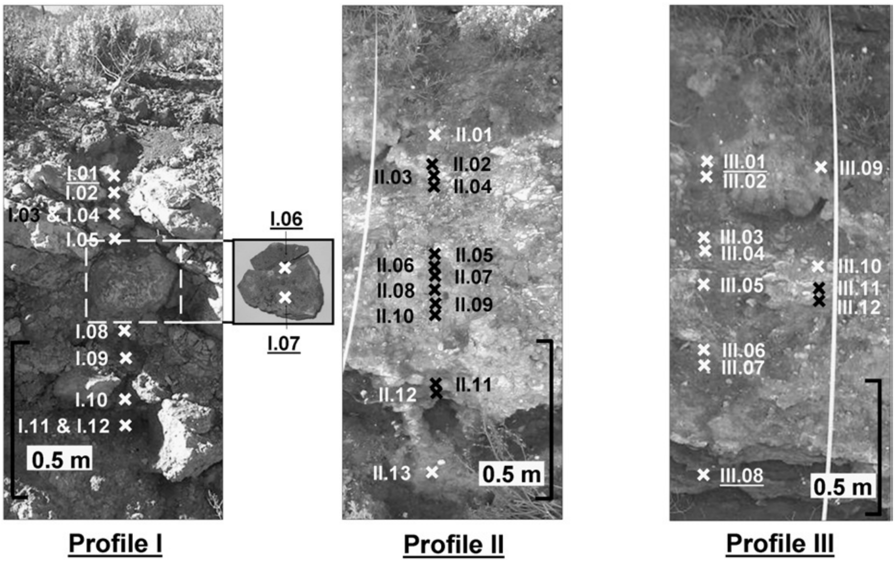

Figure 2. Profiles (I, II, III) through the *heuweltjie* from which calcrete samples were collected for carbon and oxygen isotope analysis and radiocarbon dating. The collection locations of the five samples that were dated using radiocarbon dating are shown (underlined samples).

Modern vegetation: sample preparation and carbon stable isotopes

A total of 10 vegetation samples and 5 termite frass samples were processed for carbon isotope analysis in the Department of Archaeology, University of Cape Town. The oven-dried plant material was milled in a Wiley mill using a 0.5-mm mesh and 2.1–2.2 mg of leaf or frass material weighed into a tin capsule (Elemental Microanalysis Ltd., Okehampton, UK). The samples were combusted in a Thermo Flash EA 1112 series elemental analyser and the gasses fed into a Delta Plus XP isotope ration mass spectrometer (Thermo Electron Corporation, Milan, Italy). The results were calibrated using NASTD ($\delta^{13}C = -28.68‰$) and ANU SUCROSE ($\delta^{13}C = -10.6‰$), both of which are in-house standards calibrated against IAEA standards.

All isotope data was tested for correlations (at a 5% level of significance) between $\delta^{13}C$, $\delta^{18}O$, sample depth, and calcite content using the STATISTICA 7.0 computer package (STATISTICA for Windows, StatSoft Inc.). All values were log-transformed for the correlations between isotope ratios and either sample depth or calcite content.

Results

Modern vegetation

The modern average $\delta^{13}C$ of the termite frass was $-24.76‰$ ($n = 6$, $\sigma = 0.96‰$), suggesting vegetation consisting mainly of C_3 plants and very little C_4 or CAM (Table 1). The modern average $\delta^{13}C$ of the plant species growing on the *heuweltjie* was $-24.41‰$ ($n = 10$, $\sigma = 1.74‰$). Midgley et al. (2002) recognised a difference of 14.4‰ in organic and inorganic $\delta^{13}C$ from the same soil sample taken from a *heuweltjie* in Clanwilliam. This value falls within the demonstrated range of enrichment of 14–16‰ that takes place in calcite relative to the isotopic composition of the soil organic matter (Cerling, 1984). Hence it was used to correct for the diagenetic shift of organic to inorganic carbonate in calcretes to make the δ values comparable with the calcrete (Fig. 3). The $\delta^{13}C$ values for the termite frass and plant species translate into carbonate $\delta^{13}C$ values of $-9.66‰$ (min $= -7.58‰$, max $= -11.77‰$) and $-10.00‰$ (min $= -12.69‰$, max $= -7.27‰$), respectively (Fig. 3).

Stable isotope composition of calcrete and marble samples

The $\delta^{13}C$ values of the calcrete range from $-7.38‰$ to $-4.85‰$ with a mean of $-6.16‰$ (Fig. 4). The $\delta^{18}O$ values ranged from 28.1‰ to 30.9‰ with an average of 29.7‰ (Fig. 4). The $\delta^{13}C$, $\delta^{18}O$ and calcite content can be found in the supplementary online information. There was a significant correlation between $\delta^{13}C$ and $\delta^{18}O$ ($r = 0.82$, $r^2 = 0.68$, $p < 0.01$; Fig. 4). No other correlations were found that were both significant and with an r^2 value greater than 0.5. The $\delta^{13}C$ and $\delta^{18}O$ values of the marble sample from the Neo-Proterozoic Malmesbury Group were 3.38‰ and $\delta^{18}O = 12.7‰$, respectively.

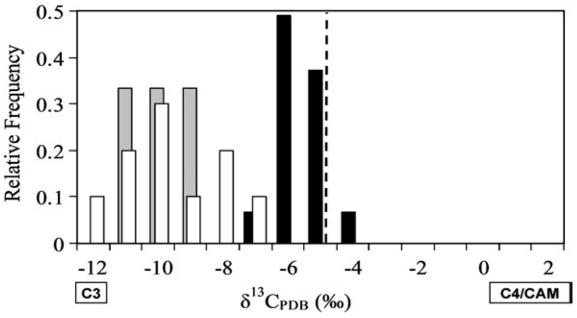

Figure 3. Histogram showing the relative frequency of C isotope data collected from calcrete samples ($n = 54$; black), and the expected present-day $\delta^{13}C$ of carbonate that would form from current plant species ($n = 10$; white) and termite frass ($n = 6$; grey) associated with the *heuweltjie* studied. The bin range is 1‰ with the lowest range value shown on the x-axis. The $\delta^{13}C$ values for plant material and termite frass have been corrected for the shift between organic carbon and carbonate (+14.4‰, Midgley et al., 2002). Pure C3 and C4/CAM source plants produce carbonate $\delta^{13}C$ values of $-12‰$ and $+2‰$, respectively. $-5‰$ corresponds to a 1:1 ratio of C3 and C4 plants (dotted line).

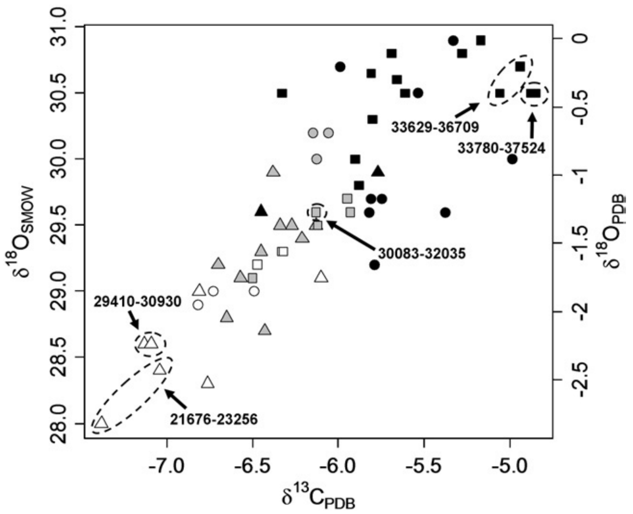

Figure 4. Plot of $\delta^{13}C$ vs. $\delta^{18}O$ for calcite from calcrete samples taken from three profiles (profile I – squares; profile II – circles; profile III – triangles) with the type of calcrete (nodule – black; matrix – grey; transition – white). The ages of samples sent for radiocarbon dating are shown.

Radiocarbon ages of calcrete samples

Previous studies have shown the potential of radiocarbon dating calcretes that have formed in the Quaternary (Amundson et al., 1994; Geyh and Eitel, 1998; Deutz et al., 2001); however, many limitations have been identified. A number of possible factors can influence radiocarbon ages but can be dismissed in this case. Firstly, radiocarbon ages can be affected by changes in the ^{14}C levels in atmospheric CO_2. This argument can be rejected because the contribution of atmospheric CO_2, and hence atmospheric ^{14}C, is minimal in arid region soils below a depth of 20–40 cm (Quade et al., 1989; Cerling and Quade, 1993). Secondly, erroneous ages may arise due to the incorporation of ^{14}C-depleted detrital or aeolian carbonate. This is unlikely because there is no carbonate present in the rocks underlying the termite mound, which is based on alluvial fan deposits. The nearby marbles of the Neo-Proterozoic Malmesbury Group have very different $\delta^{13}C$ and $\delta^{18}O$ isotopic values ($\delta^{13}C = 3.38‰$ PDB and $\delta^{18}O = 12.7‰$ SMOW). Addition of calcrete from this source ought to produce negative correlations between $\delta^{18}O$ or $\delta^{13}C$ and age, rather than the observed positive correlations. Thirdly, incorporation of ^{14}C-depleted CO_2 from decaying organic matter may result in older ages. Any overestimation caused by the last mechanism is likely to only be in the order of 10^1–10^2 yr in arid regions (Parker et al., 1983), as this is the estimated mean residency time of organic matter in arid regions. Lastly, ^{14}C averaging may arise due to repetitive stages of dissolution and reprecipitation (Geyh and Eitel, 1998). Yet, even if the calcrete has undergone reprecipitation the dominant isotope signal should be a function of the $\delta^{18}O$ values of ambient water and $\delta^{13}C$ and ^{14}C values of the local atmosphere of the soil at the time of reprecipitation. However, to avoid any possible homogenising effects in this study, all stable isotope analyses were carried out on the smallest obtainable samples (8–10 mg).

The radiocarbon dates for the five samples range from 31,290 ± 820 BP to 18,770 ± 190 ^{14}C yr BP (33,780–37,524 to 21,676–23,256 cal yr BP) and are reported in Table 2. Two field observations support the long-term persistence of this *heuweltjie* in the landscape as suggested by the radiocarbon ages. Firstly, the intermound soils comprise of rock debris due to a mudflow event. No rocks or stones

Table 2
Radiocarbon ages (± 1 standard deviation) and calibrated ages with carbon (PDB) and oxygen (SMOW) isotope data for five calcrete samples from a *heuweltjie* near Worcester.

Sample[a]	Profile	Depth (cm)[b]	Lab. sample #	^{14}C yr BP[c]	Cal yr BP[c]	δ^{13}C	δ^{18}O	Description
I-01	I	13	GX-32681	26,230 ± 530	30,083–32,035	−6.13	29.6	Surrounding matrix
I-06	I	30	GX-32679	31,290 ± 820	33,780–37,524	−4.86	30.5	Upper nodule
I-07	I	35	GX-32680	30,860 ± 810	33,629–36,709	−5.00	30.6	Lower nodule
III-01	III	84	GX-32682	18,770 ± 190	21,676–23,256	−7.21	28.2	Topmost layer
III-07	III	200	GX-32683	25,210 ± 420	29,174–31,066	−7.11	28.7	Bottommost layer

[a] See Figure 2 for stratigraphic relations.

[b] The sampling depth is the vertical distance from the surface of the termite mound to the sample.

[c] Both radiocarbon ages (^{14}C yr BP) and calibrated ages (cal yr BP) are expressed in years before AD 1950. ^{14}C ages were converted to calibrated years using CalPal-2007$^{\text{online}}$ (Danzeglocke et al., 2008) using the Hulu 2007 calibration curve (Weninger and Jöris, 2008). The age range represents the 95% confidence interval based on the 1-σ error limits of the ^{14}C age.

larger than 3 cm are observed within the *heuweltjie* but are found as a condensed layer of rocks and stones below the *heuweljtie*. This suggests that long-term biopedturbation by termites has had a particle-sorting effect within the *heuweltjie*. Secondly, fossilised or partially fossilised termite tunnels were observed in the lower reaches of the *heuweltjie*. This has been observed in other *heuweljties* (Moore and Picker, 1991).

Calcrete samples: calcite content

The calcite content observed varied from 10.4% to 77.0% with a mean of 47.8% ($n = 47$; see Supplementary data). Results from the "Karbonate-bombe" method gave values of 23.2%, 35.5% and 65.2% for the on-mound samples and no calcite was detected for all six off-mound samples.

Discussion

Reconstructing Quaternary palaeoenvironmental conditions within the Western Cape, South Africa, has been hampered by a lack of possible sources for such data (Chase and Meadows, 2007). The stable isotope records contained in *heuweltjies* may therefore provide a novel record of environmental change for the region. The calcite content for on-mound and off-mound samples show that, in this case, the calcrete is a *heuweltjie*-associated phenomenon, as off-mound samples contained no traces of calcite.

The following discussion of the stable isotope of the calcrete assumes that the δ^{18}O and δ^{13}C of calcite precipitated in isotope and chemical equilibrium with the ambient water and soil CO_2, respectively (Cerling and Quade, 1993). This assumption has been widely employed in studies of pedogenic carbonates without testing, although there is some evidence that it may be invalid in some cases (e.g., Budd et al., 2002).

Heuweltjie calcrete formation

Pedogenic calcrete can form in discrete temporal layers due to a succession of rapidly buried soils. Alternatively, pedogenic calcrete formation can take place in the form of 'overprinting' (Deutz et al., 2001), where carbonate accumulation occurs slowly (10^3–10^6 yr) in unburied soils and earlier generations of calcrete are overgrown with later generations with minimal recrystallisation of pre-existing calcrete (Cerling, 1984; Deutz et al., 2001). The lack of correlation of the δ^{13}C, δ^{18}O values or the ^{14}C ages with depth suggest that the calcrete in the studied *heuweltjie* formed through overprinting. Deutz et al. (2001) have demonstrated that overprinted carbonates are still reliable palaeoenvironmental archives if interpreted in a chronological framework. We believe the chronological trend shown in Figure 4 is reliable because the different observed calcrete types fall within different ranges of δ^{13}C and δ^{18}O values and the ^{14}C ages display the expected shift from older to younger with a shift from more cemented to less cemented calcrete (Fig. 4).

Significance of carbon isotopes

Our results suggest that formation of the calcrete occurred in the late Pleistocene, from 33,780–37,524 to 21,676–23,256 cal yr BP. Similar radiocarbon ages have been recorded in calcrete from six other *heuweltjies* (Midgley et al., 2002), suggesting that they have been present in the landscape for at least the last 36,000 yr.

The δ^{13}C values of calcrete are a function of the δ^{13}C values of the soil CO_2 at the time of precipitation. In general, the δ^{13}C values of the soil CO_2 are influenced by the δ^{13}C values of atmospheric CO_2, the relative proportion of C_3 or C_4-like photosynthesising plants, and the soil respiration rate. The contribution of atmospheric CO_2 is unlikely to be a compounding factor as previous studies have shown that it has minimal contribution below 20–40 cm in arid regions (Quade et al., 1989; Cerling and Quade, 1993; Latorre et al., 1997). In the case of *heuweltjies*, the δ^{13}C values of the soil CO_2 are likely to be greatly influenced by the plant material that was harvested, stored and digested underground by the termites. This introduces a potential caveat in interpreting the δ^{13}C values from *heuweltjie* calcrete because termites may bias their harvesting to a subset of the available plant species. However, our results indicate that this is not the case in the present-day situation as the δ^{13}C values of the frass and available plant material are analogous (Fig. 3), and this may well be the case in the past.

A shift to a more negative soil carbonate δ^{13}C values from 36.7 to 21.7 cal yr BP can be interpreted as either a decreased proportion of plants utilising the C_4 or CAM photosynthetic pathways, or an increasing of soil respiration rate in the *heuweltjie* due to increased plant cover or an increased termite population. An increase in soil respiration rate seems unlikely when the δ^{13}C values are considered in conjunction with the δ^{18}O calcrete values (discussed in the next section).

Significance of oxygen isotopes

The δ^{18}O of calcrete is controlled by the δ^{18}O of soil water and the temperature-dependent fractionation between calcite and water. The δ^{18}O of soil water is dependent on the δ^{18}O of rain water which itself depends on i) source of water, ii) temperature, iii) amount of rain, iv) degree of continentality, and v) altitude (Dansgaard, 1964). Of these, the first three can vary at any one place. Also, evaporation causes ^{18}O enrichment of the soil water. However, previous studies of Quaternary soils in arid regions indicate the degree of evaporative enrichment at depths below 50 cm is relatively minor (Quade et al., 1989; Amundson et al., 1996). Due to these many factors, Koch (1998) warned that palaeosol carbonates do not yield accurate quantitative estimates of temperature or δ^{18}O value of meteoric water, but may be used to determine the relative trend of temperatures or moisture availability through time.

The pedogenic carbonate δ^{18}O values in this study display three trends: (1) decreasing δ^{18}O values correlated with declining δ^{13}C values, (2) a decline in δ^{18}O from 36.7 to 21.7 cal yr BP, and (3) a degree of homogeneity within calcrete of different morphologies and heterogeneity between different morphologies (Fig. 4). We interpret these trends as either a general decrease in temperature or an increase in moisture availability from 36.7 to 21.7 ka. The decrease in calcrete $\delta^{18}O$ values and possible decrease in temperature from 36.7 to 21.7 ka corresponds to the decrease observed in the EDML Antarctic ice core over the same period (EPICA, 2006). The possibility that changes in $\delta^{13}C$ values of the calcrete are the result of changes in the rate of soil respiration seems unlikely because soil respiration ought not to affect the $\delta^{18}O$ values. Hence, the significant positive correlation between $\delta^{13}C$ and $\delta^{18}O$ values would not be expected. Also, a colder or wetter climate would be expected to result in lower $\delta^{18}O$ and more C_3 plants, hence lower $\delta^{13}C$ values.

Palaeoenvironmental implications

The maximum difference in $\delta^{13}C$ values of calcrete observed in this study is about 2.5‰, which suggests that the proportion of plants using the C_4 or CAM photosynthetic pathways declined from 35% to 15% during the period of calcrete formation between 36.7 to 21.7 ka (Cerling, 1984; Cerling and Quade, 1993). After correcting for diagenic shift between soil organic matter and calcrete, the $\delta^{13}C$ values of the current vegetation and termite frass are much more depleted than that of the calcrete (Fig. 3). If the diagenic shift found by Midgley et al. (2002) is applicable in the present situation, calcrete formed from present-day organic matter would have $\delta^{13}C$ values about 4‰ lower than those observed in the calcrete. This suggests that a greater proportion of plants were using C_4/CAM photosynthesis during the period of calcrete formation compared to the present day. The trend of decreasing calcrete $\delta^{13}C$ values of calcrete from 36.7 to 21.7 ka also indicates a relative increase of plants using the C_3 pathway (Fig. 4). This suggests that as conditions became cooler and/or wetter it reduced the impact of low glacial-age CO_2 levels on C_4/CAM plants, given the advantages of the C_4/CAM photosynthetic pathway at high temperatures, low moisture availability and low CO_2 (Tieszen et al., 1979; Ward et al., 1999; Veste et al., 2001). The decrease observed in the $\delta^{13}C$ values of calcrete with decreasing age is, therefore, consistent with the decrease in $\delta^{18}O$ values of the calcrete with decreasing age.

The absence of calcrete formation observed in this *heuweltjie* for the past 22,000 yr is most likely due to a combination of decreasing rainfall and increasing temperatures in the local environment, which causes evaporation to exceed precipitation. Calcrete formation generally occurs where there is in the region of 250–1000 mm annual precipitation, and the present-day annual precipitation of about 215 mm (South African Weather Service unpublished data, 2006) is probably too low to facilitate such formation. This may also be the case in other *heuweltjies* where similar radiocarbon dates have been obtained (e.g., Midgley et al., 2002), but not for *heuweltjies* where considerably younger ages have been recorded (e.g., Moore and Picker, 1991). Such a change in local climate suggested by the lack of calcrete formation from 22,000 yr is supported by the interpolations made by Chase and Meadows (2007), which show that this region would have been much wetter from 36.7 to 21.7 ka compared to the present day.

Conclusions

Heuweltjies (this study; Midgley et al., 2002) have not only formed during the Holocene, as some have been present in the landscape for at least the last 36,000 yr. This is significantly older than suggested by Moore and Picker (1991) and Picker et al. (2007). Based on the stable and ^{14}C isotope data presented in this study, we conclude that the local climate underwent a period of cooling from 36.7 to 21.6 cal yr BP, during which calcrete formation occurred. Since then the local climatic conditions surrounding the *heuweltjie* have not been suitable for calcrete formation. A significant finding of this work is that C_4 or CAM plants were probably more abundant in the landscape up until the last glacial maximum (24–18 cal yr BP). This may have been due to progressive declines in CO_2, and its aridifying effect on plants, during the late Quaternary. Finally, this study shows that calcrete associated with termite mounds is a useful potential source for reconstructing past climate and vegetation type.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.yqres.2009.04.008.

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