HEUWELTJIES: A WINDOW INTO THE PALAEOCLIMATE AND PALAEOVEGETATION OF THE WESTERN CAPE?

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A *Heuweltjie* in cross section.

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Abstract

Late Pleistocene terrestrial climate information in the Western Cape, South Africa may be preserved in oxygen and carbon isotope ratios in pedogenic calcrete that has formed in *heuweltjies* (large circular earth mounds). *Heuweltjies* are common landscape features and their potential as palaeoclimatic archives is not known, simply because it has never been investigated. Samples were taken from three depth-profiles down a single *heuweltjie* near Worcester. Carbon and oxygen isotope ratios were determined. In total, fifty-four samples were analysed. The $\delta^{13}C$ values vary from -7.4‰ to -4.9‰ relative to PDB, whereas $\delta^{18}O$ vary from 28.05‰ to 30.91‰ relative to SMOW. Five radiocarbon dates were also obtained and range from 31,290±820 BP to 18,770±190 BP. The $\delta^{13}C$ values were found to have significant positive correlation with $\delta^{18}O$ ($r = 0.82$, $p < 0.01$), with values for both isotope ratios decreasing from 31,290±820 BP to 18,770±190 BP. This may represent a period of continuous drying and warming. No dating of calcrete layers produced ages earlier than 18,770±190 BP and no samples have outlying isotopic values suggesting that conditions have not been suitable for calcrete formation during the Holocene.

Introduction:

Heuweltjies

Heuweltjies are large circular mounds that are evenly distributed across the landscape (Lovegrove & Siegfried 1986; Picker *et al.* 2006) and form a noticeable part of the topography in the Western Cape. There have been a number of hypotheses regarding their origin (reviewed in Moore & Picker 1991), but the current hypothesis is that they have been formed by the harvester termite, *Microhodotermes viator* (Picker et al. 2006). Despite the current dispute regarding the age of the *heuweltjies* and the agents responsible for their formation (Midgley *et al.* 2002; Picker *et al.* 2006) it is generally accepted that they are of zoogenic origin. *Heuweltjies* have been found to alter the structuring of the landscape, increasing its heterogeneity. There are significant differences between on- and off-mound soil chemical compositions (Midgley & Musil 1990) with the *heuweltjies* forming localized areas of improved soil fertility with higher macro- and micro-nutrients. This localized enrichment pattern has also been observed in other species of termites (e.g. Okello-Oloya *et al.* 1985; Jones 1990; reviewed in Bruyn & Conacher 1990). Calcrete lenses have been observed to occur in termite mounds (refs) and within *heuweltjies* (Lovegrove & Siegfried 1986), and are possibly a by-product of the observed nutrient enrichment and increased soil porosity (Dean 1992). Calcretes are soils that form under specific climatic conditions, and which retain a signature of the conditions during development (Dubbin 2001). Palaeosols, such as calcrete, have been used to elucidate past climate and vegetation conditions (refs), such as temperature and precipitation regimes and type of vegetation (plants with C3 vs C4 photosynthetic pathways). The aim of this study is to investigate the potential use of calcrete found in a *heuweltjie* as a palaeoclimatic archive. Both carbon and oxygen isotopes will be analysed in a single *heuweltjie* in the Worcester area to see if there are systematic changes related to climate and vegetation.

The nature and significance of pedogenic carbonates

The precipitation and dissolution of calcite can be summarised by a single equation:

$CO_2 + H_2O + CaCO_3 \Leftrightarrow Ca_2^+ + 2HCO_3^-$ (Birkeland 1984),

However, the origin of pedogenic calcrete is not fully understood (Rowe and Maher 2000). Calcium can be supplied by either silicate weathering or from the atmosphere via dust fallout. Atmospheric contributions of calcium have been found to account for as much as 98% of soil carbonate calcium (Capo & Chadwick 1999). The CO_2 is generally from the atmosphere. Calcium carbonate is leached from the soil profile by dissolved CO_2 derived from the decay of plant material and root respiration. The calcium carbonate is then transported in solution down the soil profile and then reprecipitates at some depth, usually > 25cm (Cerling and Quade 1993). The calcium carbonate reprecipitates when the soil solution becomes supersaturated with respect to calcite (Rowe and Maher 2000). Supersaturation occurs when: i) evaporation or evapotranspiration causes an increase in the concentration of dissolved calcium or hydrogen carbonate, ii) microbial activity or iii) a decrease in $p(CO_2)$ leading to a degassing of dissolved CO_2 in the soil water (Cerling and Quade 1993). The amount of annual precipitation required for calcrete formation is generally in the region of 400-700mm (Cerling 1984).

The nature of carbon and oxygen isotopes

Carbon has three isotopes ^{12}C, ^{13}C and ^{14}C. The ^{12}C and ^{13}C isotopes are stable. The ^{14}C is unstable and decays radioactively over time, and so can be used to date material that contains sufficient quantities of carbon. All three carbon isotopes react chemically in the same way; however they do react at slightly different rates due to their different atomic weights and relative sizes. This discrimination between a light and heavy isotope is termed kinetic fractionation. The carbon isotopes are fractionated differently depending on the photosynthetic pathway used by plants. Plants using C3 photosynthesis will strongly fractionate CO_2 and have a mean $\delta^{13}C$ value of -26.5‰, whereas C4 plants display significantly less fractionation and so have a higher mean $\delta^{13}C$ value of -12.5‰. Plants using C3 or C4 will have significantly different $\delta^{13}C$ signatures. These signatures are stored in calcrete as most of the carbon is derived from decaying plant material. This means that calcretes can be used to infer palaeovegetation during the time of their formation. However, as calcretes may integrate signals over thousands of years they have low temporal resolution.

Similarly, oxygen has three stable isotopes (^{16}O, ^{17}O and ^{18}O). Of the heavier isotopes, ^{18}O is much more abundant that ^{17}O. Only $^{18}O/^{16}O$ ratios were determined in this study. The $\delta^{18}O$ of calcrete is controlled by the $\delta^{18}O$ of soil water and the temperature-dependent fractionation between calcite and water. The $\delta^{18}O$ of soil water is dependent on the $\delta^{18}O$ of rain water which itself depends on i) the altitude, ii) the temperature, iii) amount of rain, iv) continentality, an v) source of water. Of these, the first three can vary at any one place. Evaporation causes ^{18}O enrichment of the soil water. The $\delta^{18}O$ values of calcrete are unlikely to give accurate quantitative measurements of past environmental temperatures, but they can be used to determine the relative trend of temperatures through time (Koch 1998).

In this study, I have determined the C and O isotopic composition of calcrete from a single *heuweltjie* to use as palaeoclimate tracers. Carbon-14 ages were obtained to indicate the age range of the pedogenic carbonate found in the *heuweltjie*. The calcrete values obtained for carbon and oxygen will be compared to the results of previous studies.

Methods:

Study site

The *heuweltjie* selected for this study (33° 27′ 28.5″ E 19° 32′ 05.0″ S; Figure 1) is located near Worcester, which is 72 km north-east from Cape Town. It was selected because a two metre cross section has been exposed by a road cutting. The climate is semi-arid with winter rainfall. The mean annual precipitation is about 215 mm at the Worcester weather station at 221m elevation, 22 km from the study area. About 132 mm of precipitation occurs during the winter season, May-August, with the rest occurring during the summer months. Temperature is usually above 0° all year round, with a mean minimum and maximum air temperature of 16° and 32° in January, respectively, and 6° and 19° in July, respectively (SA Weather Service).

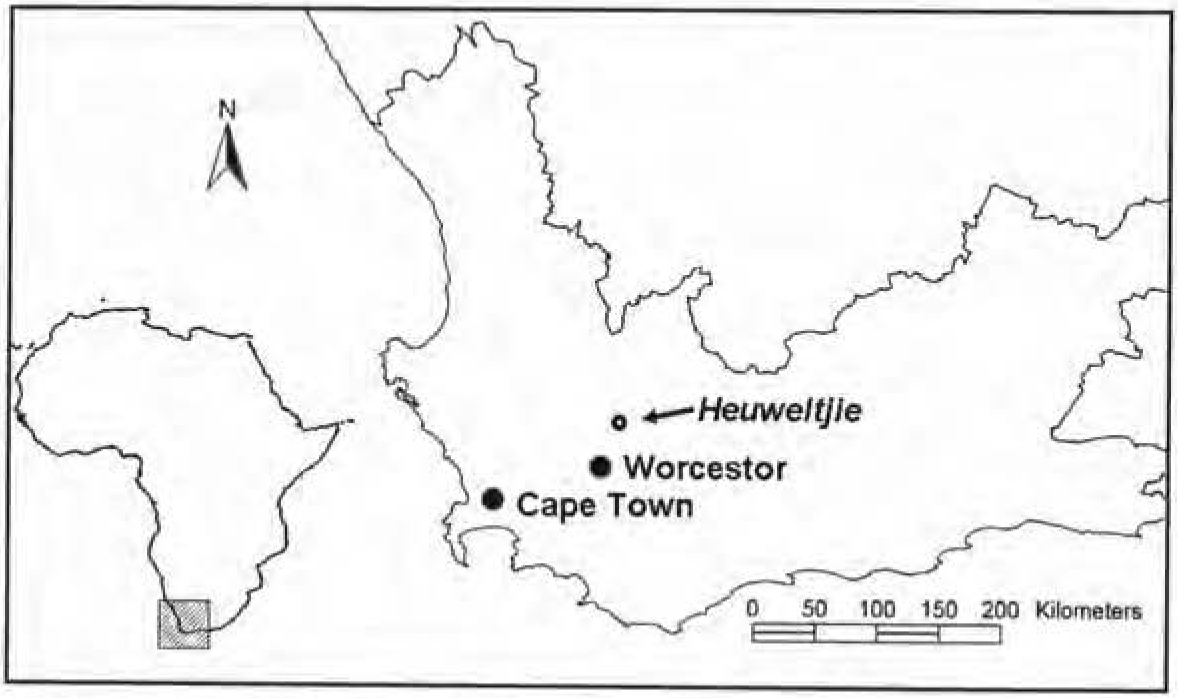

Figure 1: Location of the *heuweltjie* used in this study.

The *heuweltjie*'s current vegetation consists of *Drosanthenum montageuense*, a second unidentified *Drosanthenum* sp., *Pteronia incana, Pteronia pallens, Lycium cinereum, Leipoldtii schutzei, Phyllobolus splendens, Euphorbia burmannii,* and 2 *Ruschia* spp. Termite frass is evident on top of the *heuweltjie* indicating that at least part of it is still in use. Archaeological material in the form of Early Stone Age tools occurs below the *heuweltjie* and in the areas beyond the *heuweltjie*.

Calcrete

There is wide variation in calcrete morphology within the *heuweltjie* profile, i) loose and aggregated nodules that have homogeneous interiors, ii) powders, iii) large cemented nodules made up of heterogeneous material, and iv) nodules in matrices of softer calcrete. There appears to be a laminar layering of soft white calcrete through the profile. However this layering is interspersed with hard black-coated cemented calcrete nodules that range from 5 cm to 30 cm in diameter. Layers of calcrete extended to a depth of just under two meters from the surface of the *heuweltjie*. Many of the forms have complex internal structures, most likely due to the cyclical nature of carbonate deposition, dissolution, disruption and re-cementation. The percentage calcite was calculated for each sample in the profile as part of the stable isotope analysis, however three soil samples taken from 5, 10 and 15 meters away from the edge of the *heuweltjie* were analysed for their calcite content according to the "Karbonate-bombe" method (Mueller and Gastner, 1971). Approximately 100 mg of dried, crushed sample was reacted with ~3 mL of 10% HCl to produce CO_2 gas in a closed vessel. Carbonate content was determined by comparing the volume of CO_2 gas generated to that produced from known masses of laboratory-grade $CaCO_3$.

Calcrete Sampling

Three lateral profiles were sampled from the exposed *heuweltjie*. The profiles were selected so that three separate regions of the *heuweltjie* would be sampled, specifically the centre (profile I), the outskirts (profile III), and an intermediate (profile II) between these two. Each profile was 'cleaned' by removing approximately five centimetres of the exposed surface. This was done to prevent collecting samples that had been contaminated due to exposure. For each distinct layer encountered down a profile a sample was collected 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. Most of the samples were split into two subsamples and analysed separately.

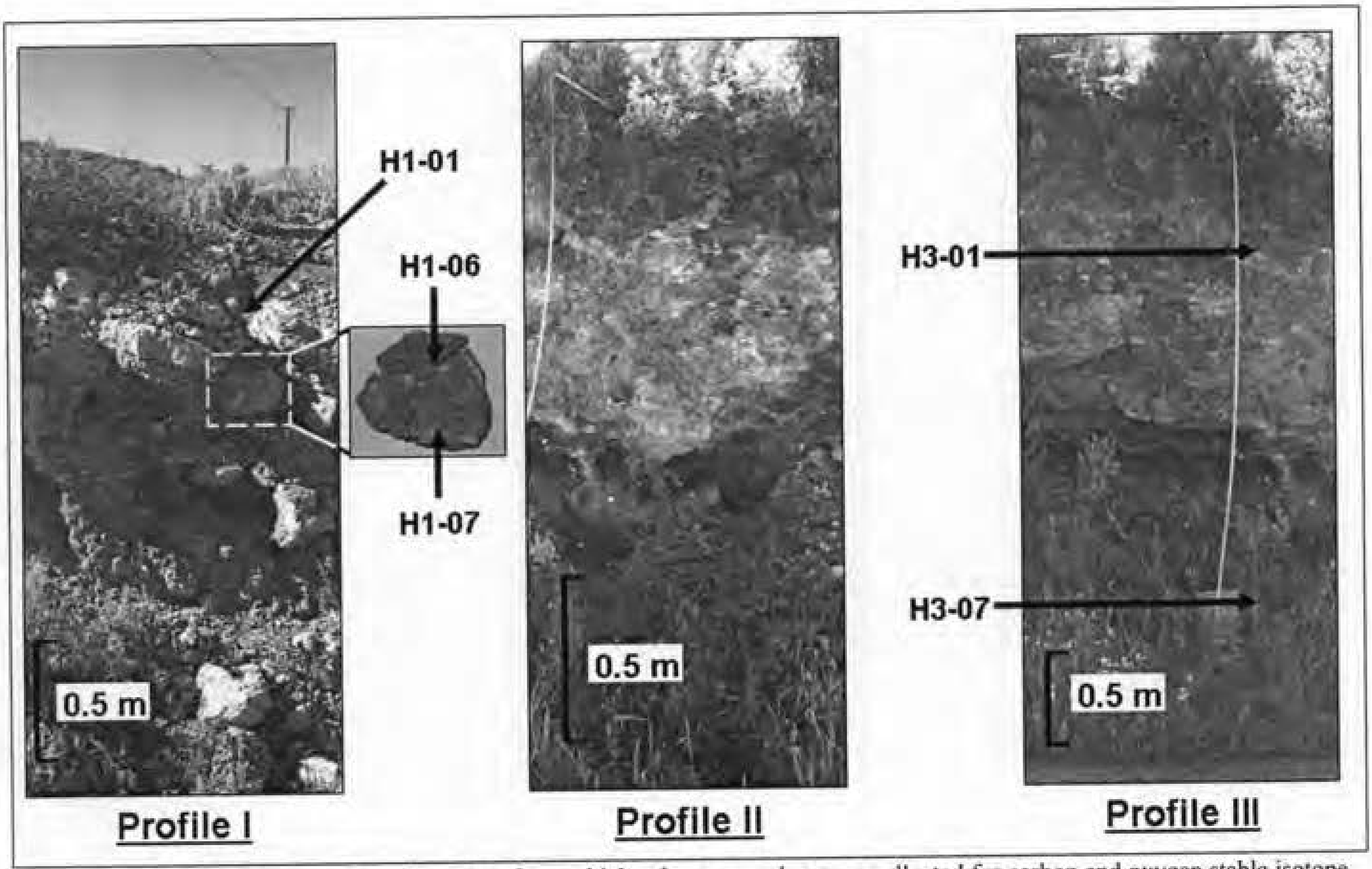

Figure 2: Three profiles through a *heuweltjie* from which calcrete samples were collected for carbon and oxygen stable isotope analysis and radiocarbon dating. The collection locations of the five samples that were aged using radiocarbon dating are shown.

Five samples across two cores were selected for Carbon-14 dating. 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 the surface fifteen centimetres above the boulder layer composed of powdery calcrete layer. Two samples were selected from the profile III at the outskirts of the *heuweltjie*, one from the topmost layer and one from the bottommost layer.

Stable isotopes

Samples from six termite frass heaps and ten plant species found on the *heuweltjie* were collected. The reduced carbon fraction from these samples was analysed by using continuous flow methods on a Finnegan MAT52 mass spectrometer in the Department of Archaeometry, University of Cape Town. These organic samples were freed of carbonates by dissolution in warm dilute HCl. Carbonates were freed of organics by being heated under vacuum at 400°C for 1 h. A value of -14.4‰ was used for the diagenic fractionation of organic to inorganic carbonate in calcretes as this value was observed in a *heuweltjie* in Clanwilliam (Midgley *et al.* 2002). Raw $\delta^{13}C$ values were corrected using NASTD and SUCROSE.

A total of 54 calcrete samples were analysed for both carbon and oxygen stable isotopes in the Department of Geological Sciences, University of Cape Town. Oxygen isotopes data are reported in δ notation where $\delta^{18}O = [(R_{sample}/R_{standard} - 1)*1000]$ with $R = {}^{18}O/{}^{16}O$. Carbon isotope results are also reported in δ notation where $\delta^{13}C = [(R_{sample}/R_{standard} - 1)*1000]$ and $R = {}^{13}C/{}^{12}C$. The calcite internal standard NM95 was analysed in duplicate along with nine samples in each run. The carbonate samples were oven-dried before loading into reaction vessels with 100% phosphoric acid, and then pumped in the vacuum system for at least two hours. The phosphoric acid was reacted with the carbonate to liberate CO_2 gas. The mass spectrometric analysis of the CO2 was undertaken using a MAT Delta XP Mass Spectrometer in dual-inlet mode. 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‰). All reactions took place overnight at 25.0°C. Repeated analyses of the internal standard suggest that $\delta^{18}O$ and $\delta^{13}C$ determinations are precise to better than 0.07‰ and 0.02‰, respectively. Resampling from original calcrete samples suggest that the $\delta^{18}O$ and $\delta^{13}C$ values are accurate to within 0.36‰ and 0.30‰ (n = 22). It is important to note that the data reduction procedure normalises the raw data to a fixed value of NM95. This eliminates any drift in reference gas isotope composition and any slight deviation of the water bath from 25° C.

All isotope data was tested for correlations (at a 5% level of significance) between $\delta^{13}C$, $\delta^{18}O$, sample depth, and percentage calcite 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 percentage calcite.

Results:

Present-day vegetation

The present-day vegetation growing on top of the *heuweltjie* consisted of only C3 and CAM plant species. The $\delta^{13}C$ values for the different plants species are shown in Table 1. The $\delta^{13}C$ values for the CAM plant species are similar to that of C3 species indicating that they are discriminating against the heavy ^{13}C isotope and are not under water-stress in the present-day climate. The photosynthetic pathways for the plant species were based on the value of the $\delta^{13}C$ value (Mooney *et al.* 1977), with facultative CAM species having higher $\delta^{13}C$ values.

Table 1: The $\delta^{13}C$ (PDB) values for ten plants species situated on top of the *heuweltjie*, as well as the mean [standard deviation] of five samples of termite frass.

Species	$\delta^{13}C$	Photosynthetic pathway
Euphorbia burmannii	-22.94	CAM / C3
Ruschia sp.	-22.45	CAM / C3
Phyllobolus splendens	-24.53	CAM / C3
Drosanthemum montaguense	-24.47	CAM / C3
Pteronia incana	-26.39	C3
Lycium cinereum	-26.04	C3
Ruschia sp.	-21.67	CAM / C3
Leipoldtii schutzei	-24.68	CAM / C3
Pteronia pallens	-27.09	C3
Drosanthemum sp.	-23.82	CAM / C3
Termite Frass	-24.76 [0.96]	

Calcrete samples

The samples taken from the three profiles have a high percentage of calcite. Percentage calcite values ranged from 10% to 77%, with a mean of 47% and a standard deviation of ±16%. Although there were many different forms of calcrete present, the different forms were not used as a grouping variable in any analyses as calcrete morphology is not believed to be a reliable indicator of age (Achyuthan 2003).

Carbon and Oxygen isotopes

The $\delta^{13}C$ values of the calcrete range from -7.4‰ to -4.9‰ with a mean of -6.1‰ (standard deviation = ±0.6‰; Table 2). The $\delta^{18}O$ values for the calcrete samples range from 28.05‰ to 30.91‰ with an average of 29.66‰ (standard deviation = ±0.72‰; Table 2). The $\delta^{13}C$ and $\delta^{18}O$ values for each sample are plotted in Figure 4. There was a significant correlation between $\delta^{13}C$ and $\delta^{18}O$ ($r = 0.82$, $r^2 = 0.68$, $p < 0.01$). Significant negative correlations were found between the following log-transformed variables, however the very little of variation was explained by the correlations (i.e. r^2 value close to zero): $\delta^{13}C$ and depth of sample ($r = -0.39$, $r^2 = 0.15$, $p < 0.01$). $\delta^{18}O$ and depth of sample ($r = -0.33$, $r^2 = 0.11$, $p < 0.05$); percentage calcite and depth ($r = -0.31$, $r^2 = 0.10$, $p < 0.01$); percentage calcite and d13c ($r = -0.69$, $r^2 = 0.48$,$p < 0.01$); and percentage calcite $\delta^{18}O$ ($r = -0.49$, $r^2 = 0.24$,$p < 0.01$).

Both $\delta^{13}C$ and $\delta^{18}O$ values are compared to calcretes from other locations in Figure 6. The $\delta^{13}C$ values plot near the lower range of values observed for $\delta^{13}C$ from other calcrete studies (Figure 6). The $\delta^{18}O$ values are relatively high in compared to other localities, with similar values to those found in the Thar Desert, Broken Hill and Western Rajasthan, all of which are currently arid climates.

The radiocarbon dates for the five samples are reported in Table 3. Based on the current temperature range between summer and winter, the $\delta^{18}O_{calcrete}$ and the temperature-dependent fractionation between water and calcite, the isotopic composition of the soil water at calcite precipitation is constrained to between -2.0‰ and 3.5‰ SMOW (Shown in Figure 5 as C and G).

Table 2: Stable isotope composition of the Pleistocene calcretes of a *Heuweltjie* situated near Worcestor, Western Cape, South Africa

Heuweltjie Profile	Sample	Height (cm)	$\delta^{13}C$ PDB	$\delta^{18}O$ SMOW	% CC	Age (C14)
Profile I	H1-01	13	-6.1	29.6	66.0	26230±530
	H1-02	15	-5.9	29.6	48.8	
	H1-03	18	-5.9	30.0	50.8	
			-5.9	29.8	43.8	
	H1-04	18	-6.0	29.7	54.6	
			-6.1	29.5	48.6	
	H1-05	25	-6.5	29.1	57.8	
			-5.3	30.8	67.5	
	H1-06	30	-4.8	30.5	74.9	31290±820
			-4.9	30.5	77.0	
	H1-07	35	-5.1	30.5	68.4	30860±810
			-4.9	30.7	70.8	
	H1-08	40	-6.5	29.2	48.7	
	H1-09	62	-6.3	29.3	55.1	
			-6.3	29.3	51.6	
	H1-11	71	-5.2	30.9	61.1	
			-5.6	30.5	61.5	
	H1-12	84	-5.7	30.8	52.9	
			-5.7	30.6	55.7	
	H1-13	92	-5.8	30.3	58.1	
			-6.3	30.5	49.5	
Profile II	H2-01	65	-5.8	29.6	25.9	
	H2-02	76	-5.5	30.5	62.4	
	H2-03	79	-5.7	29.7	37.0	
	H2-04	81	-6.1	30.0	52.6	
	H2-05	103	-5.0	30.0	58.3	
	H2-06	105	-5.3	30.9	56.4	
			-6.0	30.7	28.6	
	H2-07	107	-5.8	29.7	54.7	
	H2-08	112	-6.1	30.2	44.6	
	H2-09	115	-5.4	29.6	72.4	
	H2-10	119	-6.2	30.2	46.0	
	H2-11	142	-5.8	29.2	69.7	
	H2-12	144	-6.7	29.0	40.5	
			-6.5	29.0	47.6	
	H2-13	171	-6.8	28.9	42.2	
Profile III-B	H4-01	83	-6.8	29.0	23.1	
	H4-02	120	-6.6	29.1	45.1	
			-6.4	29.3	32.7	
	H4-03	128	-6.5	29.6	38.6	
	H4-04	130	-6.9	28.9	23.2	
			-5.8	29.9	47.9	
Profile III-A	H3-01	84	-7.0	28.4	10.4	18770±190
			-7.4	28.0	11.4	
	H3-02	89	-6.4	29.9	16.9	
			-6.3	29.5	27.9	
	H3-03	112	-6.7	29.2	32.5	
	H3-04	117	-6.6	28.8	51.7	
	H3-05	130	-6.8	28.3	17.3	
			-6.1	29.1	44.1	
			-5.8	29.7	59.5	
	H3-06	155	-6.1	29.5	64.2	
			-6.4	28.7	46.3	
	H3-07	156	-6.3	29.5	46.8	25210±420

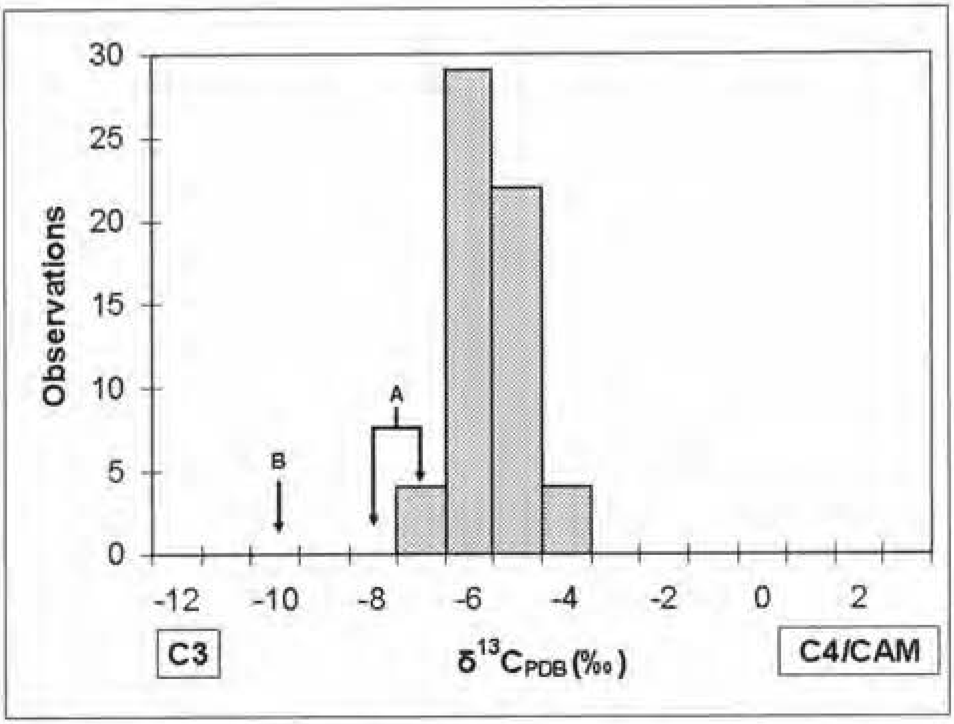

Figure 3: Histogram of C isotope data collected from calcrete samples from a *heuweltjie*. C3 and C4/CAM source plants produce carbonate $\delta^{13}C$ values of -12‰ and +2‰, respectively. -5‰ corresponds to a 1:1 ratio of C3 and C4 plants. (A) represents the range of $\delta^{13}C$ calcrete values of a *heuweltjie* in the Clanwilliam District (Midgley *et al.* 2002). (B) represents the $\delta^{13}C$ value for the present-day plants and termite frass found on the Worcester *heuweltjie*, corrected for the fractionation between organic carbon and carbonate.

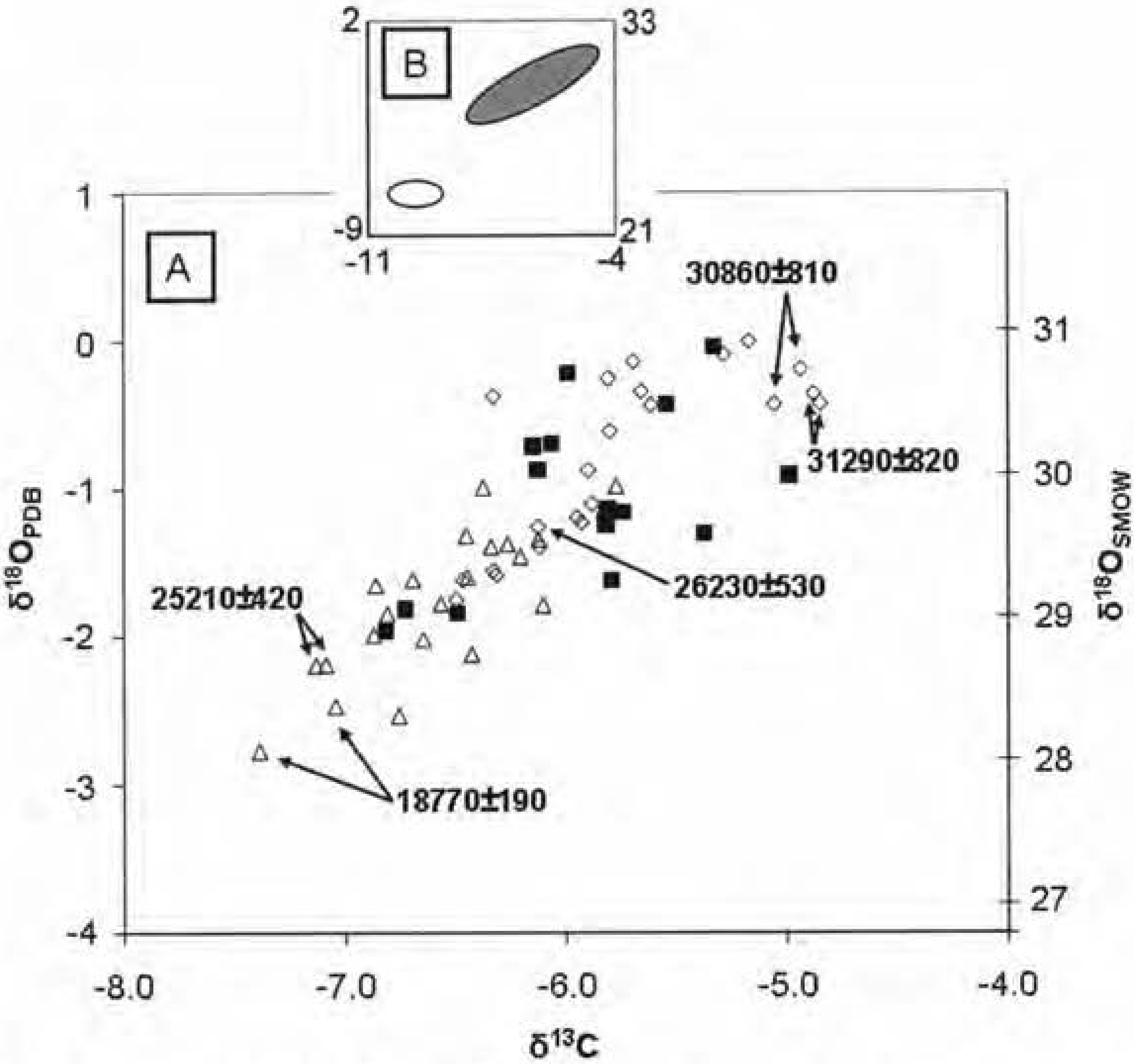

Figure 4: (A) - The $\delta^{13}C$ and $\delta^{18}O$ values for calcrete samples taken from three profiles (Profile I - ◇ ; Profile II - ■; profile III - Δ) in a *heuweltjie* situated near Worcester. $\delta^{13}C$ and $\delta^{18}O$ values for sub-samples of material sent for radiocarbon dating are shown with dates obtained. The inset (B) represents the calculated range of $\delta^{13}C$ and $\delta^{18}O$ values for the present-day formation of calcrete is shown as the open circle and the calcrete values from (A) are shown as the shaded circle.

Table 3: Radiocarbon dates (± 1 standard deviation) and carbon and oxygen isotope data for five calcrete samples from a *heuweltjie* near Worcester.

Sample	**^{14}C date**	**$\delta^{13}C_{carbonate}$**	**$\delta^{18}O_{carbonate}$**
Profile I: H1-06 (upper nodule)	31,290±820	-4.86	30.5
Profile I:H1-07 (lower nodule)	30,860±810	-5.00	30.6
Profile I: H1-01 (surrounding matrix)	26,230±530	-6.13	29.6
profile III: H3-07 (bottommost layer)	25,210±420	-7.11	28.7
Profile III: H3-01 (topmost layer)	18,770±190	-7.21	28.2

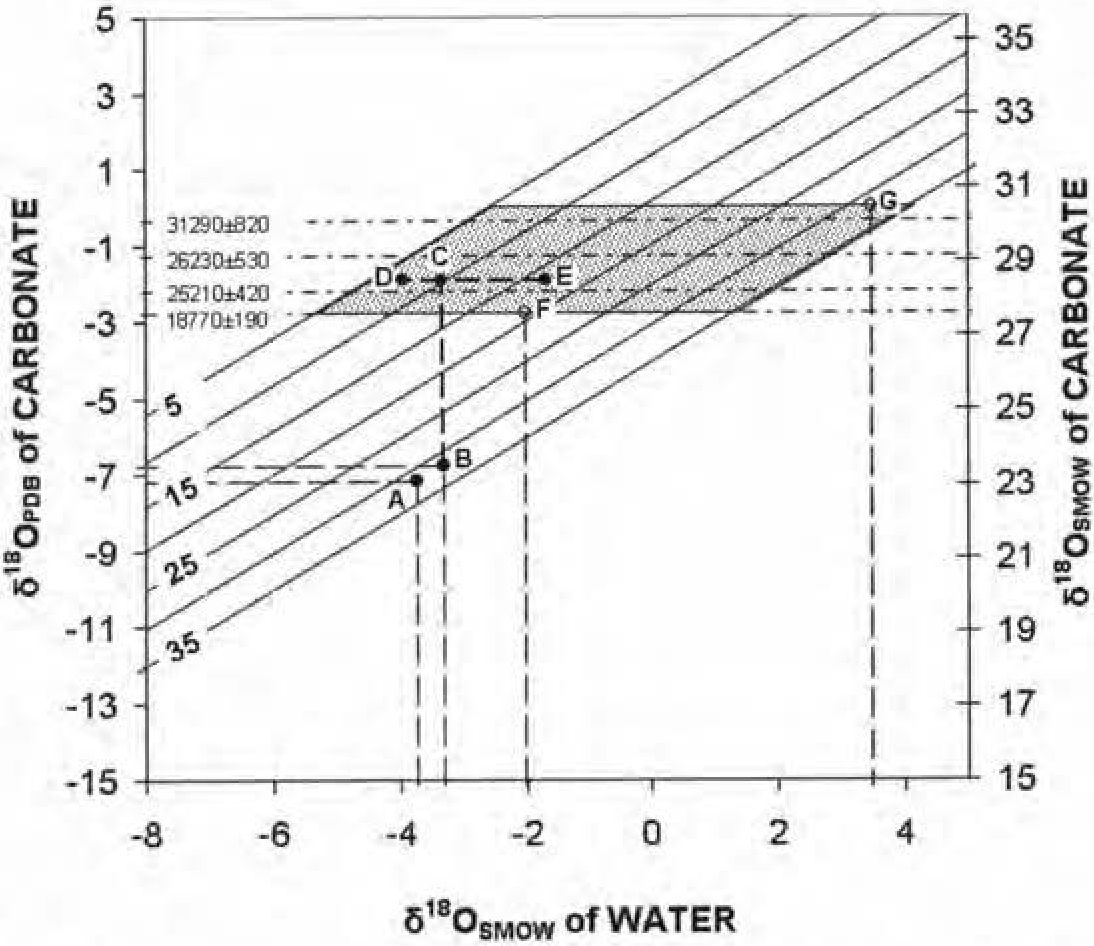

Figure 5: The relationship between temperature, $\delta^{18}O$ of water and $\delta^{18}O$ of calcrete for calcium carbonate precipitation in isotopic equilibrium using equation: $1000\ln\alpha_{calcite-water} = (2.78 \times 10^6\ T^{-2}) - 2.89$. The stippled area represents the range of $\delta^{18}O$ calcrete values recorded for samples from a single *heuweltjie* near Worcester. Labelled horizontal lines (dot and dash) refer to $\delta^{18}O$ calcrete values of the nodules dated here (Table 3). See text for explanation of A-F.

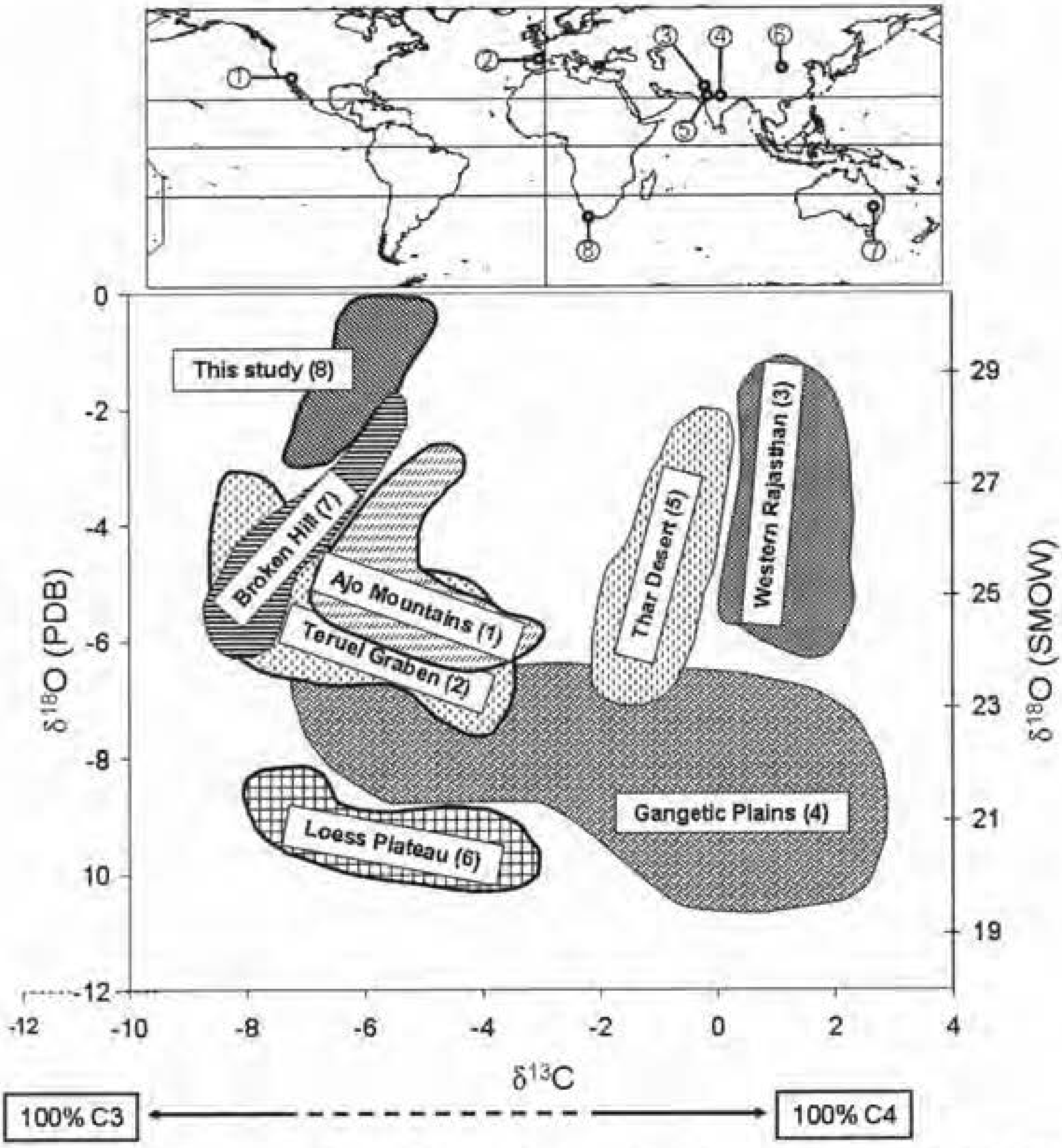

Figure 6: Literature summary of $\delta^{13}C$ and $\delta^{18}O$ values for calcrete from seven studies with distribution displaying each locality. The data were obtained from: Liu *et al.* 1996 (Ajo Mountains), Alonso-Zarza & Arenas 2004 (Teruel Graben), Achyuthan 2003 (Western Rajasthan), Srivastava 2001 (Gangetic Plains), Andrews *et al.* 1998 (Thar Desert), Rowe & Maher 2000 (Loess Plateau), and Schmid *et al.* 2006 (Broken Hill)

Discussion:

The aim of this study was to use calcrete that has formed within a single *heuweltjie* to infer systematic changes in palaeoclimatic and palaeovegetation conditions. The Carbon-14 dates place the formation of the calcrete in the Late Pleistocene, during a glacial maximum. The $\delta^{13}C$ values suggest that the palaeovegetation was C3/CAM dominated, and that C3 dominance increased from 31 thousand years ago (ka) until 18 ka. The $\delta^{18}O$ values suggest this same time period experienced some degree of warming.

Carbon isotopes

Three factors affect the C3 and C4 plant distribution, specifically temperature, moisture and atmospheric CO_2. The C4 pathway is favoured when there are increases in temperature, decreases in moisture or atmospheric CO_2, because C4/CAM plants can maintain optimum photosynthetic levels with little stomatal conductance which limits water loss. The current vegetation growing on top of the *heuweltjie* consisted of only C3 and CAM plant species. The $\delta^{13}C$ of the termite frass is consistent with the vegetation growing on the *heuweltjie*. The $\delta^{13}C$ values for the CAM plant species are similar to that of C3 species indicating that they are discriminating against the heavy ^{13}C isotope and are not under water-stress in the present-day climate which means that they are in a period of CAM idling (Veste *et al.* 2001). The spread of data shown in Figure 3 suggests a mixture of isotopic contributions from C3 and C4/CAM palaeovegetation. Pure C3 and C4/CAM plants would generate isotope values of -12‰ and +2‰, respectively (Quade *et al*, 1995). A 1:1 ratio of C3:C4/CAM plant contributions to the calcrete should produce a $\delta^{13}C$ value of -5‰. The $\delta^{13}C_{plant}$ values (corrected to calcite values) indicate that $\delta^{13}C_{calcrete}$ values are not in equilibrium with present day vegetation (Figure 3). The higher $\delta^{13}C_{calcrete}$ values may be due to a greater proportion of C4 plants or CAM plants experiencing water stress. However, the $\delta^{13}C$ value of calcrete may also have become ^{13}C enriched by either: a) isotopic mixing with atmosphere CO_2, or b) degassing of ^{12}C-enriched CO_2 closer to the ground surfaces (Achyuthan 2003). The $\delta^{13}C$ values of this *heuweltjie* are higher than values found for a *heuweltjie* in the Clanwilliam District (Midgley *et al.* 2002), which ranged from -7.03‰ to -8.53‰. However, this may be a simple reflection of vegetation composition differences between the two sites. The Carbon-14 dates for the calcrete are consistent with the ages from a *heuweltjie* dated in the Clanwilliam District (Midgley *et al.* 2002) and with a small fossilized termite nest from also from Clanwilliam (Coaton 1981).

Oxygen isotopes

The $\delta^{18}O$ values of pedogenic carbonates are thought to be controlled by two variables, specifically the $\delta^{18}O$ value of soil water and temperature (Cerling 1984, Liu *et al.* 1996). The $\delta^{18}O$ of calcrete forms in equilibrium with the local soil water, and the $\delta^{18}O$ of soil water is in turn related to the oxygen isotopic composition of meteoric water (Khadkikar *et al.* 2000). Interpreting trends in soil carbonates tend to be complicated by the fractionation between water and calcite as it is temperature-dependent. Given the strong observed correlation between temperature and the isotopic composition of precipitation (Dansgaard 1964), a significant decrease in the $\delta^{18}O$ of meteoric water would be expected if there is regional cooling. The $\delta^{18}O$ values of the calcrete were used to estimate the both the average annual temperature and $\delta^{18}O$ of the meteoric water at the time of calcrete formation using the following equation:

$1000\ln\alpha_{\text{calcite-water}} = (2.78 \times 10^{6}\,T^{-2}) - 2.89$ (Friedman & O'Neil 1977),

where T is temperature in Kelvin and $\alpha_{\text{calcite-water}}$ is the fractionation between water and calcite (Figure 5). The calculated value of $\delta^{18}O$ if it were to form under present-day conditions using the average $\delta^{18}O$ of meteoric water at UCT and Cape Town International Airport (Harris *et al.* 1999) is indicated by points A and B (Figure 5). It is possible to identify the formation conditions of the calcrete by examining the relationship of the modern temperature and meteoric water $\delta^{18}O$ data (B) and the isotopic datum for a single calcrete sample. For example, calcrete forming under present day conditions would have a $\delta^{18}O$ value of approximately -7‰. Calcrete $\delta^{18}O$ values observed in the *heuweltjie* could be produced by a number of scenarios: i) the calcrete formation temperature being ~22° C cooler (B-C in Figure 5), with the isotopic composition of soil water being similar to the modern value; or ii) the formation temperature being < 22° C colder and soil water ^{18}O-enriched relative to the present day (B-C-E); or iii) formation temperatures being cooler than present and precipitation being isotopically more depleted by > 0.5‰ (B-C-D). However, Koch (1998) warns that palaeosol carbonates do not yield accurate quantitative estimates of or temperature or $\delta^{18}O$ of meteoric water, but rather serve as general indicators or environmental differences through time and so can be used to track systematic changes. A temperature of 10° C for the period of calcrete formation seems unlikely. The temperature was probably much higher than the value estimate. This would mean that the $\delta^{18}O$ of the soil water, and hence the $\delta^{18}O$ of precipitation, must have been much higher than current conditions. The palaeo-$\delta^{18}O$ of meteoric water is estimated to be between -2‰ and +3.6‰, based on the present-day range of temperature and the highest and lowest observed value of $\delta^{18}O_{calcrete}$ (represented by F and G, respectively). This relative $\delta^{18}O$ decrease of meteoric water from 32 ka (E & F in Figure 5) to 18 ka (C & D in Figure 5) suggests that the cooling occurred between these two periods. However, shifts in temperature would also have affected the fractionation factor between water and calcite. The increase in the carbonate-water fractionation factor associated with decreasing temperature likely offset the decrease in the $\delta^{18}O$ of precipitation, producing little net change in the $\delta^{18}O$ of the soil carbonate. So the relatively small decrease in $\delta^{18}O$ of meteoric water observed in Figure 5 may be greater than the values actually measured.

Comparisons of calcrete isotopic data with published data

The $\delta^{13}C$ values fall within the low range of $\delta^{13}C$ values compared with the seven other studies (Figure 6). There appears to be cut-off of $\delta^{13}C$ values at about -8‰. The predicted $\delta^{13}C$ value for soil carbonate which formed in a totally C3-dominated vegetation is about -12‰ (ref). The fact that none of the studies have values near -12‰ suggests that i) C3 plants have never been completely dominant at the respective localities during the time of calcrete formation, or ii) there is a relative enrichment of the carbon isotopes during calcrete formation or over time, possibly due to atmospheric carbon.

The $\delta^{18}O$ values are relatively high compared to the other localities and compare well with the values obtained from localities in Broken Hill, the Thar Desert and Western Rajasthan, which are arid areas. The calcrete nodules from the Loess Plateau are believed to have formed during climatic conditions that were cooler than the present semi-arid conditions (Rowe & Maher 2000). The calcrete in the Gangetic Plains (Srivastava 2001) has been found to track a climate change from cool arid/semi-arid conditions to a warm humid phase that was correlated with a change in vegetation, as the vegetation pattern changed from a C4 grassland to a woodland, and this would explain the wide range of

$\delta^{13}C$ values. Unfortunately, there are not many supporting climate proxies to allow us to make categorical claims regarding the climatic conditions during the calcrete formation.

Paleoenvironment implications

The maximum difference in $\delta^{13}C$ observed in this study is about 2.5‰. The magnitude of this difference suggests that the proportion of C4 (or CAM) plants ranges from 35% to 15% during the period of calcrete formation. This shift may be attributed to a change in climate because there is a corresponding shift in $\delta^{18}O_{calcrete}$.

A number of samples dated using Carbon-14 provides a trend of isotopic compositions with time. The dates for the five samples range from 32-18 ka. These samples were selected to represent the diversity of morphological calcrete types present at different positions in the *heuweltjie*. These ages suggest a number of possibilities: i) climate for the past 18,000 years has not been suitable for calcrete formation in the Worcester area, or ii) the calcrete samples have been contaminated by an ancient ^{14}C-depleted source, which would cause sample dates to estimated to be older than they really are, and iii) younger calcrete samples were somehow missed during sampling.

The formation of calcrete is dependent on a specific suite of environmental conditions; it requires sufficient rain to mobilise calcium carbonate in the upper layers, but insufficient rain to leach it out of the system, as well as high enough temperatures to cause enough evaporation reconstitute the calcrete at depth. Current climatic conditions that may be preventing calcrete formation is lower annual rainfall or lower annual temperatures. The current mean annual rainfall is insufficient for calcrete formation (Cerling 1984). The significant correlation between $\delta^{13}C$ and $\delta^{18}O$ of calcrete appears to be a function of time, as the decrease in both $\delta^{18}O$ and $\delta^{13}C$ is associated with younger and younger ^{14}C ages (Figure 4). There may be some similarities between the pattern of climatic changes in the *heuweltjie* and that inferred by Talma and Vogel (1992) in the Western Cape Province, as well as Holmgren *et al.* (2003) in the Limpopo Province. Both spelotherm studies show a decreasing trend in $\delta^{18}O$ during this period, although the Makanspansgat speleotherm (Holmgren *et al.* 2003) only extends to 28 ka. The decrease in $\delta^{13}C$ values suggests a *relative* increase of C3 plants or CAM plants using the C3 pathway. This would mean that conditions may have become cooler between 32,000 ya and 18,000 ya, given the preference of C4 species for high temperatures during the summer months (Edwards & Walker 1983) or CAM plants switching to the C3 pathway during cooler periods. This is consistent with the findings of the $\delta^{18}O_{calcrete}$ and the calculated $\delta^{18}O_{water}$ values. Parkington *et al.* (2000) suggest that evidence based on wood charcoal and pollen deposits situated in the Elands Bay Cave, indicates that the climate was much wetter at the last glacial maximum (20 ka). However, their findings also suggest that the climate was much cooler than present-day, and this is opposite to the findings of this study.

It is possible that the calcrete samples in the *heuweltjie* have been contaminated by an ancient ^{14}C-depleted source, for example by an underlying layer of limestone below the *heuweltjie*. If this were the case, the pollutant must be affecting the entire profile (>1m) and one would expect to find calcrete from the ^{14}C-depleted source in the soil next to the *heuweltjie*. Three soil samples, taken from profiles off the mound at similar depths as the *heuweltjie* calcrete layers, contained no calcite. Therefore, the Carbon-14 values likely represent true ages.

It is unlikely that younger calcrete is present in the *heuweltjie*. Younger samples would have significantly different $\delta^{13}C$ and $\delta^{18}O$ isotopic values from those of the dated samples. However, all of the samples, which were taken from many depths through the three profiles, all lie within the isotopic ranges of the Carbon-14 samples.

Potential problems with inferring palaeoclimate conditions from stable isotopes in calcrete (Rowe & Maher 2000) are that i) detrital carbonate that is isotopically enriched may be contaminating the calcrete, which is difficult to accurately predict or correct, and ii) the chronological relationship of secondary remobilised calcrete in the profile is unknown.

An interesting side note is that *heuweltjies* are acknowledged to increase the heterogeneity of the landscape by creating nutrient hotspots. However, how much of the nutrients are locked up in *heuweltjies* in the form of inorganic carbonate and unavailable to the system? The agents responsible for creating the *heuweltjies* may have caused an overall decline in nutrient availability to the system as a whole. Calcium is a micronutrient that is an essential part of plant cell wall structure, and provides for normal transport and retention of other elements. Based on the mean *heuweltjie* diameter of 17m (Moore & Picker 1991), a mean density of 297 *heuweltjies* per square kilometre (Picker *et al.* 2006), a depth of 1 m and a mean percentage calcite of 47% (this study), I estimate that *heuweltjies* may have removed over 30 tons of calcium from the system per square kilometre in the past 30,000 years, at a rate of just over 1 kg per square kilometre per annum.

Conclusions

Based on Carbon-14 ages of the calcrete found in *heuweltjies* (this study; Midgley *et al.* 2002), it would appear that they have been present in the landscape for at least the last 32,000 years. This is significantly older than suggested by Picker *et al.* (2006). The results of this study show that the climate underwent a period of cooling and drying from 32 ka to 18 ka, and that climatic conditions have not been suitable for calcrete formation since 18 ka. This suggests that the climate of the Western Cape was wetter and warmer than present-day prior to the end of the last glacial period. This study shows that the calcrete associated with *heuweltjies* may be used to infer relative systematic changes in palaeoclimate and palaeovegetation conditions during the last glacial period.

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