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Stable carbon isotope ratios from archaeological charcoal as palaeoenvironmental indicators

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Abstract

The potential to provide environmental proxies using stable carbon isotopes from modern and archaeological charcoal is explored. Experiments on modern *Podocarpus* (Yellowwoods) show that $\delta^{13}C$ values of stems, branches and charcoal preserve proxy environmental conditions, including rainfall, humidity and temperature. An additional experiment showed that combustion temperature affects the carbon isotope signature of charcoal. Burning at 450 °C to 500 °C depletes $\delta^{13}C$ values with respect to the original wood, but the charcoal retains the seasonal and inter-annual isotopic trends recorded during the growth of the tree.

The $\delta^{13}C$ of *Podocarpus* charcoal from three levels from the Middle Stone Age site of Sibudu Cave, KwaZulu-Natal, South Africa, was compared with modern analogues from two different environments, Seaton Park (KwaZulu-Natal) and the Baviaans Kloof (Eastern Cape). Other environmental proxies from levels dated from >70 ka and ~48 ka, show that environmental conditions changed from warmer and wetter to colder and drier and finally becoming warmer and drier. The isotope data is consistent with this reconstruction. The results from this series of experiments indicate that it is possible to obtain meaningful palaeoenvironmental information from $\delta^{13}C$ values of archaeological charcoal.

Keywords: Stable carbon isotopes; Archaeological charcoal; Palaeoenvironmental signals; Middle Stone Age

1. Introduction

The carbon isotope composition of wood varies in response to environmental parameters such as temperature, humidity and precipitation (e.g. Edwards et al., 2000; Van Bergen and Poole, 2000; Leavitt, 2002; Briffa et al., 2004; McCarroll and Loader, 2004; Shu et al., 2005). Charcoal, char and ash are all forms of wood derived Black Carbon (BC) and it is possible that the isotopic environmental records will be preserved. Many climate and environmental studies have made use of stable isotope and other chemical data derived from burnt organic matter. These include examining changes in palaeovegetation (e.g. Behling and da Costa, 2001; Bendassoli et al., 2002; Biedenbender et al., 2004),

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carbon cycling and sequestration in ecosystems (e.g. Schmidt et al.; 1999, 2002a; Gleixner et al., 2001; Skjemstad et al., 1996) and changes in atmospheric carbon dioxide concentrations (e.g. Cope and Chaloner, 1980; Jones and Chaloner, 1991).

The processes by which charcoal is formed and preserved are well understood. Charcoal is defined as any blackened plant-derived material that has been significantly altered, chemically and structurally, through heating via fire (Forbes et al., 2006). It is considered to be biologically and chemically inert after formation and will undergo an extremely slow process of degradation (Cohen-Ofri et al., 2006; Forbes et al., 2006). Since charcoal has a high resistance to chemical oxidants (Skjemstad et al., 1996; Bird and Gröcke, 1997) it has a long residence time in deep soil profiles (Skjemstad et al., 2002) and geological records (Cope and Chaloner, 1980).

The goal of this paper is to demonstrate that it is possible to obtain meaningful palaeoenvironmental information from the carbon isotope ratios of archaeological charcoal. First we demonstrate that an environmental response to rainfall, temperature and humidity is recorded in modern samples of stems, branches and carbonised wood tissue of the selected genus, *Podocarpus*. We show that a degree of carbon isotope fractionation occurs during the conversion of wood to charcoal. We present a continuous record of carbon isotope values for a wood sample combusted at a range of temperatures under oxidizing and reducing conditions to demonstrate the range of isotopic variability in the products of wood tissue combustion. The carbon isotope ratios of archaeological *Podocarpus* charcoal (Allott, 2004, 2005, 2006) from selected layers representing three periods of the Middle Stone Age (MSA) sequence from the site of Sibudu Cave, KwaZulu-Natal, South Africa are then compared with the modern isotopic data. Additional archaeological isotopic data from *Celtis* charcoal are provided as further evidence that a palaeoenvironmental signal is preserved in archaeological charcoal.

2. Recent stable carbon isotope research on charcoal

In many environmental studies it is assumed that carbon isotope ratios derived from naturally occurring and anthropogenic charcoal are a direct representation of the isotopic values of the wood tissues from which they were formed, and hence a record of environmental and climatic signals (e.g. Chaloner, 1980; Jones and Chaloner, 1991; Schmidt et al., 1999; Cope and Gleixner et al., 2001; Behling and da Costa, 2001; Bendassoli et al., 2002; Biedenbender et al., 2004; Skjemstad et al., 1996). This assumption implies that there is an insignificant or constant fractionation of carbon isotopes during the burning process (Turney et al., 2006), but the changes that take place in the stable carbon isotope composition of plant material during carbonisation are still not well understood. Wood is composed of a range of macromolecules such as cellulose, lignin and various polysaccharides. These all have a characteristic carbon isotope composition and their relative abundances contribute to the overall isotopic composition of wood (Poole et al., 2002). During combustion these macromolecules are broken down into various specific pyrolysis products, mostly furans and pyrans, and released (Steinbeiss et al., 2006). The removal of these compounds is driven by their relative chemical stability and strength of molecular cross bonds. Differences between how these macromolecules break down during combustion allow cross-reactions between their products and produce a number of additional compounds prior to release (Steinbeiss et al., 2006).

Studies carried out to determine the effects of combustion on the carbon isotope composition of plant tissues and their products of combustion have produced varied and often contradicting results. A study comparing C_3 and C_4 vegetation (Turekian et al., 1998) showed that under laboratory conditions the C_3 vegetation yielded small differences in $\delta^{13}C$ values between the source material and the products of combustion. For the C_4 material there was a substantial fractionation during combustion. The $\delta^{13}C$ values for the C_3 fatty acids from the burnt samples showed enrichment relative to the un-burnt material (Ballentine et al., 1998). This is in contrast to the $\delta^{13}C$ results for the ash and particles collected by Turekian et al. (1998), where there was little or no difference in the $\delta^{13}C$ values of the burnt and un-burnt material. The opposite was seen in data collected from sediment-derived charcoal samples where no significant changes in $\delta^{13}C$ values were observed between burnt and un-burnt C_4 samples (Cahier et al., 1985; Krull et al., 2003). Bird and Gröcke (1997) found that charring wood and leaf samples resulted in more negative $\delta^{13}C$ values when compared with the un-burnt source material. An isotopic analysis of the combustion products of cellulose and lignin (Steinbeiss et al., 2006) indicated that there were no significant differences between the $\delta^{13}C$ values of the bulk cellulose and lignin and the mean $\delta^{13}C$ values of the volatile compounds. These results are similar to those presented by Turekian et al. (1998). However, it should be noted that the $\delta^{13}C$ values of some of the individual compounds were substantially different from the $\delta^{13}C$ values of the bulk material (Steinbeiss et al., 2006).

Significant variations in the overall chemistry of wood tissues were observed at combustion temperatures higher than 200 °C (Baldock and Smernik, 2002), but despite the variability the overall chemical composition of the wood tissues was fixed within thirty minutes of combustion regardless of temperature (Turney et al., 2006). There are indications that the $\delta^{13}C$ values of the remaining source materials tend to be depleted, likely due to the selective removal of a ^{13}C enriched fraction and the degree of oxidation. The $\delta^{13}C$ depletion between the source material and the products of combustion in the various experiments ranges from as little as 0.1‰ to 0.4‰ (Turekian et al., 1998; Krull et al., 2003; Turney et al., 2006; Steinbeiss et al., 2006), whilst others show a more extensive change of between 1.0‰ to 7.0‰ (Leavitt et al., 1982; Turekian et al., 1998). There are however, exceptions to this. A set of propagules (peas) burnt at a range of temperatures showed enrichment in $\delta^{13}C$ values (Poole et al., 2002) and wood tissue subject to an artificial ageing treatment using heat and water (Schleser et al., 1999) produced enriched $\delta^{13}C$ values relative to the source material.

2.1. Charcoal stable carbon isotope research in southern Africa

In southern Africa research was carried out to determine the feasibility of obtaining climatic information from $\delta^{13}C$ analyses of archaeological charcoals by correlating modern data with rainfall records (February and van der Merwe, 1992; February, 1997, 2000). An initial study showed that $\delta^{13}C$ values of wood charcoal varied through time and that such change was climatically induced (February and van der Merwe, 1992; February, 1994). Archaeological charcoal from three sites in the Elands Bay area, Western Cape Province, identified from the family Ebenaceae (genus *Diospyros/ Euclea)* had significantly different $\delta^{13}C$ values from those of modern charcoal values from the same genera (February, 1992; February and van der Merwe, 1992). The archaeological $\delta^{13}C$ values also showed variability through time with the oldest charcoal (4200BP) having more negative values than the more recent material (460 BP). This result was attributed to a range of climate-influenced plant $\delta^{13}C$ values (February and van der Merwe, 1992).

Further work was carried out to compare stable carbon isotopes in charcoal, whole wood and cellulose and to examine their isotopic relationship to rainfall (February, 1997). The $\delta^{13}C$ values from two woody species, *Combretum apiculatum* and *Protea roupelliae* were differently affected by rainfall. *C. apiculatum* $\delta^{13}C$ values for the whole wood and cellulose correlated significantly with rainfall values across a rainfall gradient. The $\delta^{13}C$ values from the *P. roupelliae* samples did not show any significant correlation with the same rainfall data. February (1997) attributed this difference to plant habits: *C. apiculatum* is drought deciduous with specific habitat requirements, whereas *P. roupelliae* is evergreen and grows in a wide range of habitats. None of the charcoal $\delta^{13}C$ values of either species showed a significant correlation to rainfall. This was thought to be a result of the loss of hemicelluloses, cellulose and lignin during various stages of pyrolysis. The loss of tissue during combustion resulted in $\delta^{13}C$ values becoming depleted on average by 0.5‰ at 400 °C and 1.0‰ at 500 °C. This fractionation is not constant, with different pieces of wood reacting differently during pyrolysis.

It is obvious, based on the examples, that there is no clear explanation for the changes seen in carbon isotope ratios from burnt and un-burnt plant material. Whether products of combustion are depleted or enriched in their respective $\delta^{13}C$ values is dependent on a number of factors. These include the type of plant material burnt (e.g. leaves, wood, seeds), size and surface area, available oxygen, photosynthetic pathway, cellulose/ lignin ratio and amount and concentration of volatile compounds as well as the temperature at which the material is combusted (Leavitt et al., 1982; Cahier et al., 1985; Bird and Gröcke, 1997; Ballentine et al., 1998; Turekian et al., 1998; Schleser et al., 1999; Baldock and Smernik, 2002; Poole et al., 2002; Krull et al., 2003; Steinbeiss et al., 2006; Turney et al., 2006). In addition the heating temperature and length of burn will also influence $\delta^{13}C$ ratios. A further consideration is the various sample pre-preparation methods employed prior to combustion and the methods of combustion used before carbon isotope ratios are measured (Krull et al., 2003). Laboratory experiments may not produce results completely comparable to results derived from material produced in natural fires. Carbon isotope values of compounds released from flash pyrolysis experiments will differ from those produced under slow combustion conditions, such as natural burns or anthropogenic fires. This will be due to the production of secondary reaction compounds during a longer period of combustion. In this study we present $\delta^{13}C$ values from compounds and source material produced under combustion where the overall temperature increase is slow and the length of burn is considerably longer than flash pyrolysis.

Notwithstanding the complexity, there have been a number of studies that have shown that it is possible to obtain significant palaeoenvironmental information

from $\delta^{13}C$ values from charcoal (e.g. February and van der Merwe, 1992; Bird and Gröcke, 1997; Bendassoli et al., 2002). It may be some time before an all-encompassing theoretical framework will predict the $\delta^{13}C$ of all trees from environmental conditions therefore we restrict ourselves to an empirical approach. We focus specifically on *Podocarpus*. The data presented in this paper show that it is possible to obtain meaningful environmental information from archaeological charcoal of this species since environmental causality is demonstrated in modern specimens.

3. Study area, material and methods

3.1. Background to Sibudu Cave

Sibudu Cave is located approximately 40 km north of Durban, about 15 km inland of the Indian Ocean, on a forested cliff overlooking the Tongati River (Fig. 1). The site has a deep, well-preserved and well-dated MSA sequence that has been subject to archaeological excavation since 1998 (Wadley and Jacobs, 2004, 2006). Preservation of organic material, such as bone, charred

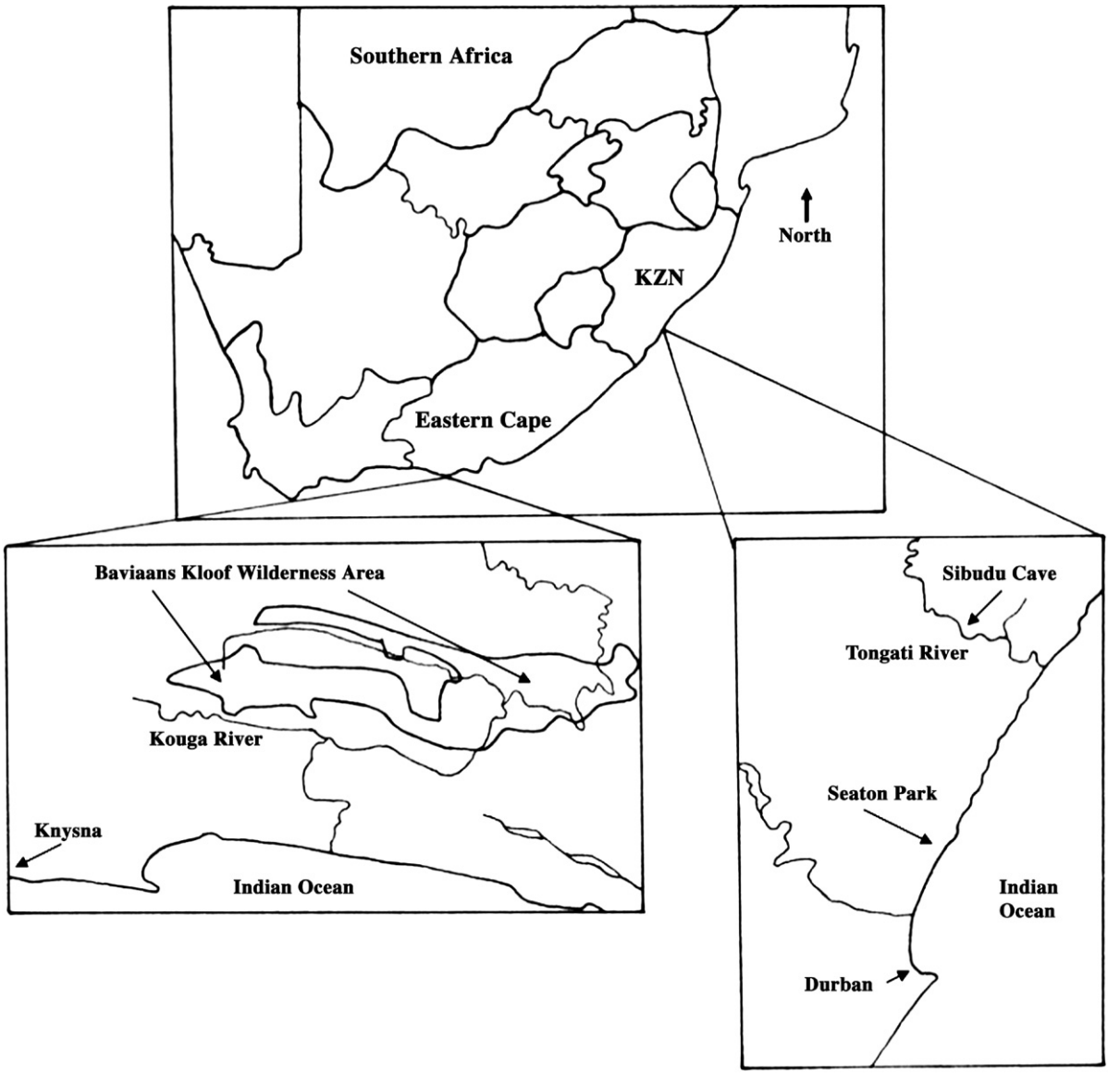

Fig. 1. Map of southern Africa indicating the locations of Seaton Park and the Middle Stone Age site of Sibudu Cave, KwaZulu-Natal and the Baviaans Kloof Wilderness Area, Eastern Cape. Archaeological material used in this study originates from Sibudu Cave. The modern *Podocarpus* samples were collected from Seaton Park and the Baviaans Kloof.

botanical remains and charcoal from fireplaces is extremely good. The range of additional published environmental evidence currently available from the site includes charcoal and seed analyses (Wadley, 2004; Allott, 2004, 2005, 2006; Sievers, 2006), micro and macrofaunal analyses (Plug, 2004, 2006; Cain, 2006; Glenny, 2006; Wells 2006), sedimentological studies including magnetic susceptibility, palynological and phytolith analyses (Schiegl et al., 2004; Herries, 2006; Pickering, 2006; Renaut and Bamford, 2006; Schiegl and Conard, 2006) and tracking of temporal changes in communities through correspondence analysis (Reynolds, 2006).

The site was excavated by natural stratigraphy and layers are individually named using a nomenclature that refers to the colour of the predominant matrix (Wadley and Jacobs, 2006). The MSA stratigraphy is complex, but is generally clear with numerous thin, coloured interfingered layers and distinct well-preserved hearth structures (Fig. 2). Sedimentological analyses of the deposit (Pickering, 2002, 2006) indicate that sediments mainly comprise anthropogenically derived material with very little evidence of water-borne transportation. These layers have been given abbreviated letter designations.

Fourteen optically stimulated luminescence (OSL) dates have been obtained and they suggest that the currently excavated MSA layers range in age from >70 ka to ~35 ka years ago (Jacobs et al., in press). The cultural sequence is broadly divided into undated layers older than 60 ka and three younger age clusters (Jacobs et al in press). The undated period includes the Howiesons Poort (HP) lithic assemblage, the Still Bay and several informal lithic industries. The three age clusters have been informally named on the basis of the lithic assemblages within them. The ~58 ka assemblages

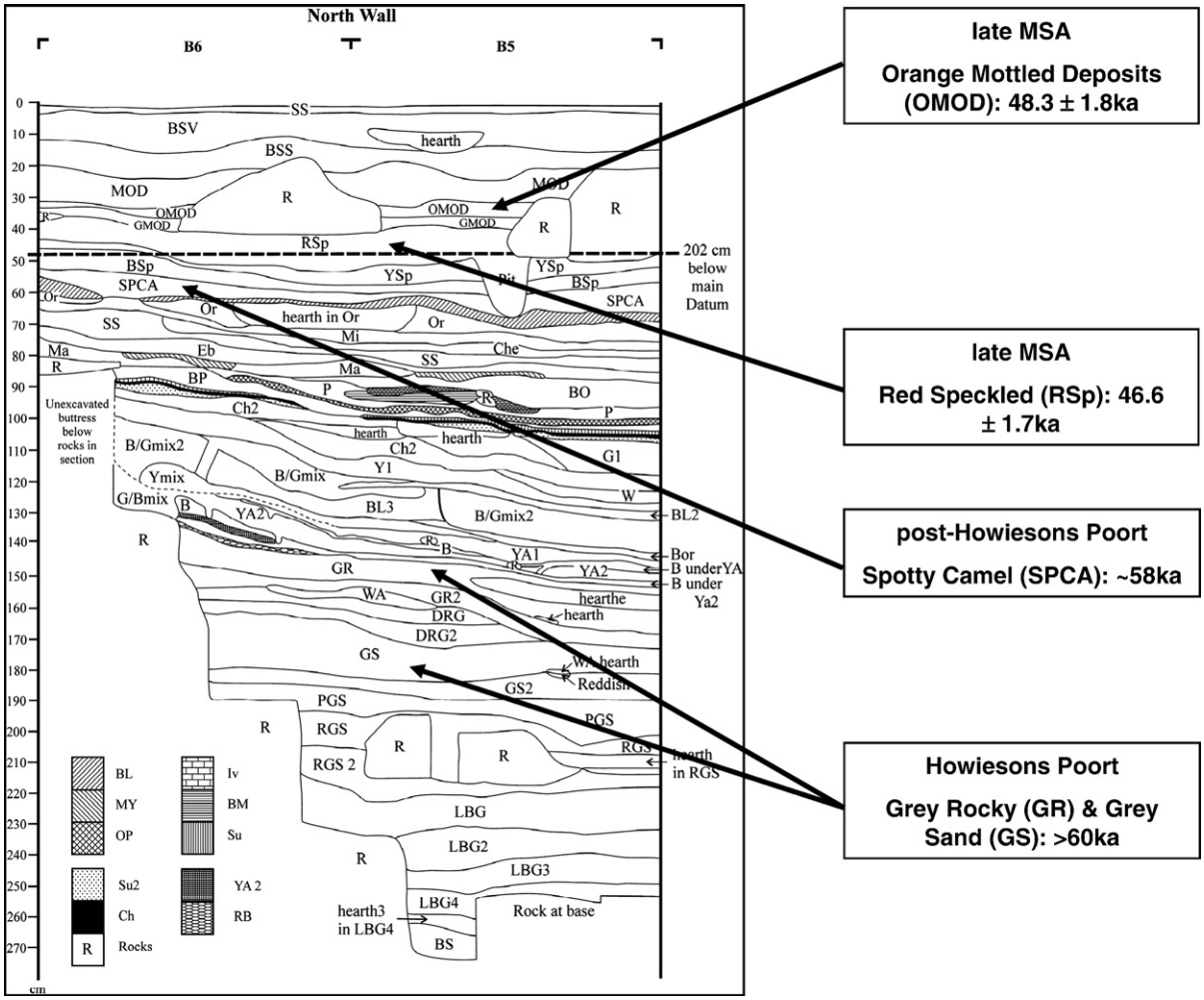

Fig. 2. Stratigraphy of the trial trench in the northern grid from Sibudu Cave. The layers and ages (Jacobs et al., in press) from where charcoal samples for this study were collected are indicated.

are referred to as the post-Howiesons Poort (post-HP), the ~48 ka assemblages as the late MSA and the ~35 ka assemblages as the final MSA. The archaeological charcoal analysed in this study was taken from the HP, the post-HP and the late MSA assemblages. No suitable charcoal samples were available from the final MSA.

A complex mosaic of habitats may always have existed near the shelter because of the influence of the Tongati River and because of the combination of shaded south-facing hill slopes and warm north-facing hill slopes. Based on recent analyses of seed (Wadley, 2004; Sievers, 2006), charcoal (Allott, 2004, 2005, 2006) and micro/macrofaunal assemblages (Plug, 2004; Cain, 2006; Glenny, 2006, 2006; Reynolds, 2006) from the site, the HP layers (GR and GS) represent a period of warm, moist conditions with a predominance of evergreen forest (dominated by *Podocarpus* spp.), probably on the southwest-facing hillside and some savanna species possibly on the north-facing slopes. During the post-HP period (SPCA) at ~58 ka, conditions were cooler and drier than present with varied habitats that included some evergreen forest (perhaps restricted in its extent), riverine forest and open woodland. There appears to have been a shift to warmer (though still cooler than present) dry conditions with bushveld and limited forest communities during the late MSA (RSp and OMOD) at ~48 ka.

3.2. Archaeological samples

The genus *Podocarpus* was selected for isotopic analyses because of its predominance in certain of the MSA layers at Sibudu Cave. *Celtis* charcoal was sampled from the same archaeological periods as the *Podocarpus* charcoal on the assumption that the different sensitivity of this genus to environmental factors might provide a more robust interpretative framework than the *Podocarpus* alone. The charcoal was identified using important wood anatomical features and a number of reference collections (Allott, 2004, 2005, 2006). The oldest layers analysed in this study, Grey Rocky (GR) and Grey Sand (GS) (Fig. 2) are still undated, but are older than 60 ka and probably younger than 70 ka (Wadley and Jacobs, 2006; Wadley, 2006). These layers are representative of the HP (>60 ka) period One hundred and twenty two charcoal sub-samples (18 fragments) identified as *Podocarpus* were obtained from the GR and GS layers. A small sample of 7 sub-samples (1 fragment) of *Celtis* charcoal was taken from GS. The next oldest layer sampled was Spotty Camel (SPCA) and has an age of ~58 ka. This layer represents the post-HP period. Twenty sub-samples (2 fragments) of *Podocarpus* and 12 sub-samples (1 fragment) of *Celtis* were taken from SPCA. It should be noted that two species of *Podocarpus* were recorded for SPCA: *P. latifolius* and *P. falcatus* (Allott, 2004, 2005, 2006). The youngest samples were taken from two layers from the late MSA. Fifteen sub-samples (1 fragment) of *Podocarpus* were from Red Speckled (RSp) which has an OSL date of 46.6±1.9 ka (Jacobs et al., in press). Thirty-six sub-samples (3 fragments) of *Celtis* were obtained from the Orange Mottled Deposit (OMOD) layer. OMOD has an OSL date of 48.3±1.8 ka (Jacobs et al., in press).

These sample sets were selected from layers considered to be representative of the different climatic and environmental conditions that occurred in the Sibudu region during Oxygen Isotope Stages 3 and 4, as indicated by published palaeoenvironmental data. These environmental shifts may be reflected in the carbon isotope composition of the archaeological charcoal, if an environmental signal has been retained.

3.3. Modern samples

Podocarpus is generally a dominant climax genus in many of the tropical and subtropical forest types in South Africa (Palmer and Pitman, 1972; Acocks, 1988; Killick, 1990; Schmidt et al., 2002b; Pooley, 2003) and their adaptability allow the genus to establish and maintain its presence. The genus is therefore potentially a good indicator of environmental change over time. The presence of *Podocarpus* implies a well-forested environment with high moisture availability. An absence or limited occurrence of the genus may imply a reduced forested environment and drier conditions and the genus may thus be restricted to sheltered and protected portions of the landscape. Archaeological charcoal from a second genus, *Celtis*, was subject to isotopic analysis. This genus has a larger distribution and the ability to adapt to a wider range of environments, particularly drier ones (Acocks, 1988; Van Wyk and Van Wyk, 1997; Coates-Palgrave 2003; Pooley, 2003).

Five specimens of *Podocarpus latifolius* (Real Yellowwood) (Van Wyk and Van Wyk, 1997; Coates-Palgrave, 2003; Pooley, 2003) were sampled from a remnant portion of Coastal Forest (Lubke et al., 1997; Low and Rebelo, 1998; Lubke and McKenzie, 1998). This section of indigenous forest has been preserved as a small suburban park, called Seaton Park, located to the north of the city of Durban, about five kilometres from the coastline. There are about 100 species of indigenous trees in a fairly densely wooded environment (Nichols and Fairall, 1992). The park is located on the lower eastern slope of a steep-sided valley and is protected

from winds originating from the coast. The *P. latifolius* trees sampled are located on a rough transect with samples from the upper region of the park down to the lower area that was at one stage a marshland (Nichols and Fairall, 1992).

Core samples (2, 3 and 4) were removed from the trunks of two *P. latifolius* specimens (B and C) for comparison with corresponding branch samples. Branch samples were cut from five selected *P. latifolius* specimens (B, C, L, M, N). The branches range in diameter from 30 to 60 mm, which falls within the size ranges currently collected by firewood harvesting communities (Abbot and Lowore, 1999; Van Wyk and Gericke, 2000; Sekhwela, 2003). In much of rural Africa, branches collected for firewood would be predominantly derived from deadwood that had either fallen to the ground or that was easily accessible. Modern ethnobotanical studies have shown that harvesting firewood is predominantly done on naturally produced, dry (dead), but not rotten, wood (Archer, 1990; Shackleton, 1998; Abbot and Lowore, 1999; Van Wyk and Gericke, 2000; Sekhwela, 2003). Some wood is cut or chopped from trees or shrubs from easy-to-reach branches and thin trunks.

An additional trunk sample of *Podocarpus falcatus* from the Baviaans Kloof area, Eastern Cape Province (Fig. 1) formed part of the modern sample set. This tree was analysed to provide a stable carbon isotope record from trees growing in a more restricted environment as a contrast to the Seaton Park trees.

A single green branch sample of a specimen of *P. latifolius* was collected from the grounds surrounding the laboratory in Pretoria and was subjected to isotopic analysis to determine the range of variability in the carbon isotope values of the products released from wood tissues during the stages of combustion.

3.4. Wood and charcoal preparation and analysis

Three discs, 15 mm thick, were cut in sequence from each branch from Seaton Park. These discs, core samples and the Baviaans Kloof sample were sanded with increasingly finer grades of sandpaper (grades P40 μm to P1200 μm) until their growth ring sequences were clearly visible. The total number of growth increments was established for each disc/core using a binocular microscope and an incident light source.

One disc from each sample set was left un-burnt; the second set was tightly double wrapped in heavy duty aluminium foil to exclude oxygen and was placed in a pre-heated muffle furnace at 450 °C for two hours. This produced charcoal under a reducing (O_2-limited) environment. The third set of discs was placed on a foil-covered grid over an open wood fire to simulate natural burning conditions and left until completely charred. This produced charcoal under oxidizing (O_2-rich) conditions. This process took less than 15 min for the largest disc (60 mm in diameter) and about five minutes for the smallest (30 mm in diameter).

Material for isotope analysis was drilled along two adjacent offset transects using a 2 mm drill bit, from the intersection of the cambium and bark with the last visible growth ring to the centre of the disc or end of the core. This method of sampling growth ring sequences has proven to be successful in a number of stable isotope studies (Woodborne and Robertson, 2000, 2001; Woodborne et al., 2003; McCarroll and Loader, 2004; Norström, 2005). Each sample was allocated to a portion of a corresponding ring or rings to allow comparison of the $\delta^{13}C$ values. The growth rings from *P. latifolius* are extremely variable in width. Between three and five samples could be taken from the widest rings, but in narrower rings only one or two samples could be removed. This precludes examining the isotopic variability on a sub-annual basis in this species, and so the $\delta^{13}C$ ratios for each core/branch were annualised.

The method used to pre-treat the wood samples was developed by Green (1963) and adapted by Loader et al. (1997). This method allows for the rapid batch processing of small wood samples for stable carbon isotope analysis. Samples were run through an ethanol/toluene Soxhlet distillation process in order to remove mobile constituents such as resins, oils and waxes. The Soxhlet process removes those materials that may not coincide with the formation of the growth rings and ensures that they are not reflected in the stable carbon isotope values obtained (Loader et al., 1997). The un-burnt wood samples were run as whole wood. A number of recent isotope studies of tree ring sequences have produced stronger climatic signals from whole wood samples than those derived from either α-cellulose or lignin (Loader et al., 1997, 2003; McCarroll and Loader, 2004).

The charcoal samples from the two burning methods were placed in Pyrex test-tubes and covered with a 1% hydrochloric acid solution. These were placed in an oven at 70 °C overnight, washed with distilled water until pH neutral and dried. The archaeological charcoal samples were pre-treated with 1% HCl overnight and washed with distilled water until pH neutral.

Aliquots of approximately 0.2 mg were combusted on-line in a Thermo Flash Elemental Analyser (1112 series) integrated via a Thermo Finnigan Con-flo III system with a Thermo Delta V Plus Isotope Ratio Mass Spectrometer, housed at the Ecosystem Processes and

Dynamics (EPD) laboratory, CSIR, Pretoria. Each sample was run in duplicate. If the precision for each sample pair was unacceptable (0.10‰ variation), an additional sub-sample was run. The average precision for the modern replicates was <0.06‰ and for archaeological samples <0.08‰.

An additional experiment was carried out using a green sample of *P. latifolius*. A 10 mm long piece of the branch was placed directly into the furnace of the elemental analyser, with no pre-treatment. The temperature of the furnace was manually increased in steps by between 5 and 15 °C and the carbon isotope composition of the released products was measured using the mass spectrometer at each temperature increment. This was done under a reducing environment until a temperature of 1000 °C was reached. Once the furnace reached 1000 °C, oxygen was introduced and carbon isotope composition of the gasses released were measured at regular intervals until the sample was completely combusted.

Two project specific standards, a C_4 grass (*Hyparrhenia hirta*) and C_3 tree (*Shorea superba*) were used. These species were selected as they each represented average carbon isotope values for C3 and C4 plants. All stable carbon isotope results were expressed in delta (δ) notation on a per mil (‰) scale. The stable carbon isotope ratios were measured as deviations from international standard reference materials and are

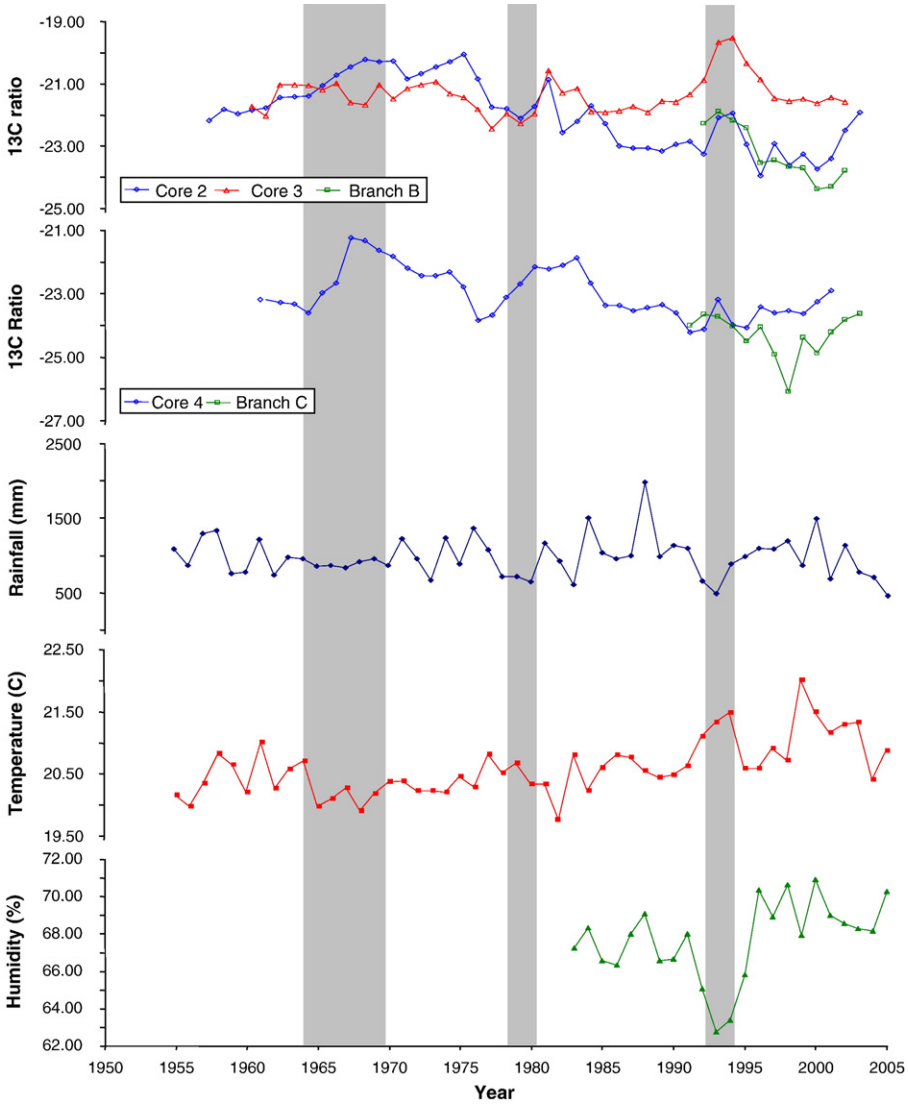

Fig. 3. Modern $\delta^{13}C$ values from two *Podocarpus latifolius* specimens from Seaton Park plotted with the corresponding average rainfall, temperature and humidity.

reported relative to the PeeDee Belemnite (PDB) standard using the following equation (Francey and Farquhar, 1982):

$$\delta_{\text{sample}} = \left(\frac{\left(R_{\text{sample}} - R_{\text{standard}}\right)}{R_{\text{standard}}}\right) \times 1000 \quad .$$
$$R = {}^{13}\text{C}/{}^{12}\text{C}$$

4. Results and discussion

4.1. Comparison of $\delta^{13}C$ values from modern trunk cores and branches

The annualised carbon isotope variability for three core samples (Core 2, 3 and 4) as well as the branch data (Branch B and Branch C) were compared with annual rainfall, temperature and humidity records for the region (Fig. 3). A striking feature of the data is that Core 2 and Core 3, despite being from the same tree, show quite substantial differences. The implication is profound. At any point in time the tree appears to have the ability to partition its resources in such a way that the isotopic signal of the wood formed in one part of the tree differs from that in another. This vital fractionation appears to remain relatively consistent through the growth of the trees, as all three cores appear to have common features that might be anticipated on the basis of the theoretical discourse on the control of carbon isotope values in trees. During three periods of multi-year below average rainfall (1963–1968, 1978–1980, and 1992–1993) the isotope values in the trees become progressively more positive. During intervening years the results tend in a negative direction.

There is a degree of redundancy between the environmental datasets (although the comparison is limited to last 23 years in the case of humidity) and so a statistical regression approach was adopted to determine which of the environmental variables best correlates with the isotope data. A summary is presented in Table 1. *P*-values are representative of statistical significance and correlation values represent the correlation coefficient, indicating the extent to which the data sets co-vary. Core 2 correlates with both temperature and humidity at the >99 % and >95% confidence levels, but core 3, from the same tree, only correlates with humidity at the >99% confidence level. The diachronic comparability of these cores has already been noted as evidence for the synchronic partitioning of resources between the sampling points. That this is partially the result of temperature suggests a localised effect and may relate to the temperature at which the wood is formed. This temperature differential may be systematic if it relates to the aspect of the sun, but other micro-environmental factors may apply. Core 4 is also correlated with temperature (>99% confidence) but not humidity nor rainfall. Both of the branch samples have weak correlations with rainfall and humidity, and none with temperature.

Table 1
Statistical relationships and correlations between modern core and branch $\delta^{13}C$ values and local rainfall, temperature and humidity

Sample	*n*	r^2	*P*-value	Correlation
Core 2				
Rainfall	47	0	0.3	−0.16
Temperature	47	0.29	<0.000001	−0.55
Humidity	21	0.25	0.01	−0.53
Core 3				
Rainfall	43	0.07	0.05	−0.3
Temperature	43	0	0.33	0.15
Humidity	20	0.41	0	−0.66
Branch B				
Rainfall	11	0.29	0.05	−0.6
Temperature	11	−0.09	0.77	−0.1
Humidity	11	0.81	<0.000001	−0.91
Core 4				
Rainfall	41	0.01	0.22	−0.2
Temperature	41	0.27	0	−0.54
Humidity	19	−0.01	0.4	0.2
Branch C				
Rainfall	13	0.28	0.04	−0.58
Temperature	13	−0.03	0.44	0.23
Humidity	13	0.22	0.06	−0.53

P-values indicate the statistical significance of the relationships between isotope values and climatic data. Correlation values refer to the correlation coefficient indicating the extent to which the isotope and climate data co-vary.

The correlation between carbon isotopes and humidity appears to be common to all the samples with the exception of Core 4. This may be a result of the position of this tree within a riparian zone. The persistence of water availability at the roots of this tree may mean that it is not water limited and that the control of photosynthesis in then by temperature (possibly as a proxy for sunlight).

4.2. Charcoal experiments

Two factors that produce variation in charcoal isotope signatures are the formation temperature and the isotopic value of the original wood. During combustion certain moieties will volatilize and others will concentrate. The rate at which the combustion temperature increases will affect the amount of secondary reaction products formed (Gundale and DeLuca, 2006). Secondary products may

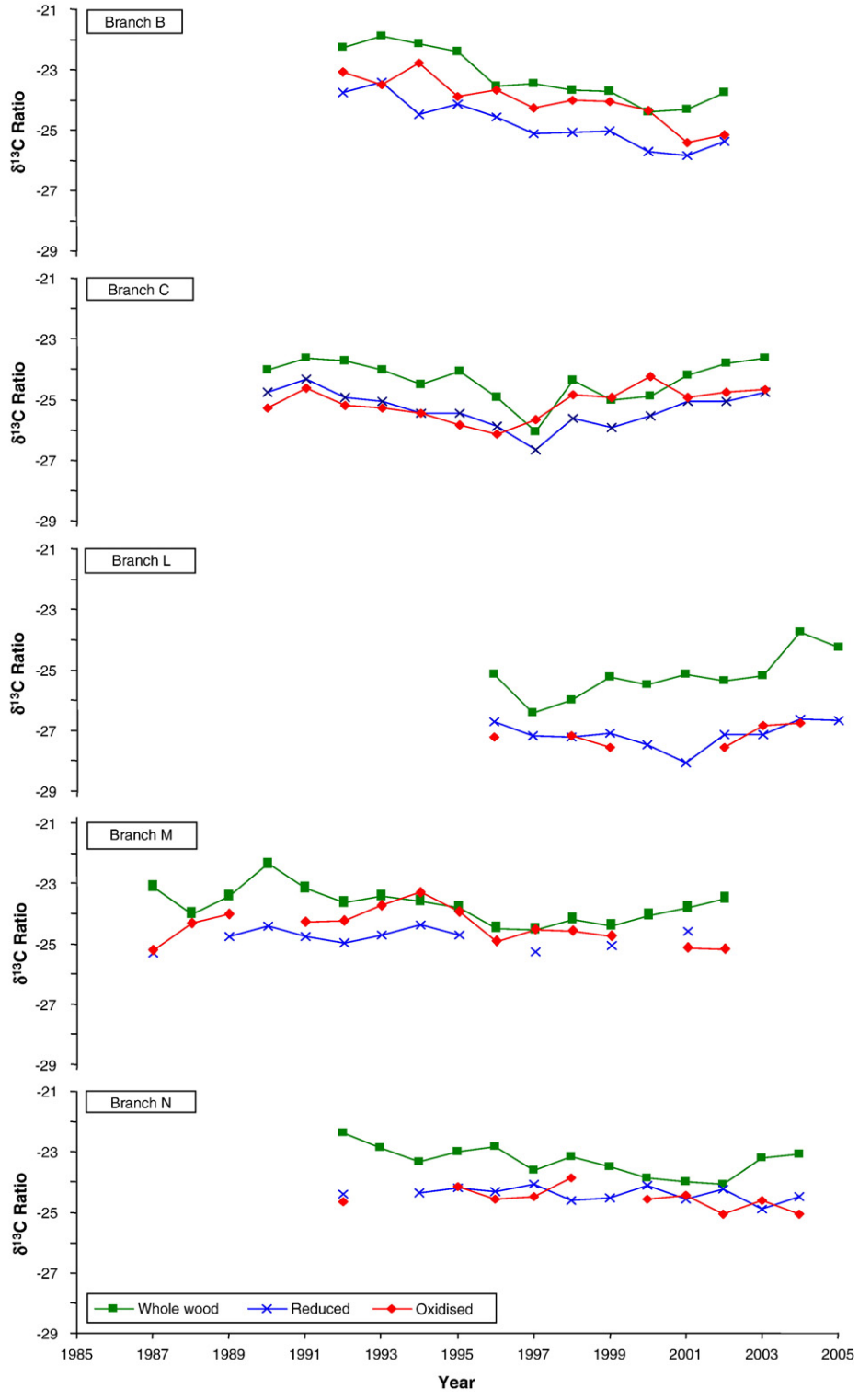

Fig. 4. $\delta^{13}C$ values for five *P.latifolius* branch samples showing values for whole wood and charcoal produced under reducing and oxidizing conditions.

be more thermally stable and persist for a longer period within the source material. With respect to the source material different plant tissues contain different chemicals (e.g. lignin, cellulose) and have different physical properties. Therefore different woody species will produce different qualities of charcoal. In the case of archaeological charcoal, it will be derived from woody species that burn slowly and produce a large amount of long-lasting charcoal. These species would have been selected by the original inhabitants of an archaeological site. Since fuel wood is generally collected in the form of branches rather than tree trunks (Archer, 1990; Shackleton, 1998; Abbot and Lowore, 1999; Van Wyk and Gericke, 2000; Sekhwela, 2003), the charcoal from archaeological sites will likely be derived from branches burnt as fuel. It remains to be demonstrated that branch $\delta^{13}C$ values preserve the environmental signal during the process of charcoal formation.

The $\delta^{13}C$ values for the charcoal experiment in which disks from each of 5 branches were subject to different charcoal formation protocols are presented in Fig. 4. Under both reducing and oxidizing conditions the overall isotopic trends are similar to that seen in the whole wood $\delta^{13}C$ values. In all five branch samples the $\delta^{13}C$ values for charcoals produced under both a reducing and oxidizing environment show depleted isotopic values relative to the whole wood (Fig. 4). These results are consistent with the majority of findings from previous combustion experiments (see Section 2) where the products of combustion had $\delta^{13}C$ values that were more negative with respect to the C_3 source material (Bird and Gröcke, 1997; February, 1997; Ballentine et al., 1998; Turekian et al., 1998; Czimczik et al., 2002; Steinbeiss et al., 2006; Turney et al., 2006). There were occasional exceptions to this trend. In branch C, $\delta^{13}C$ values from three rings showed

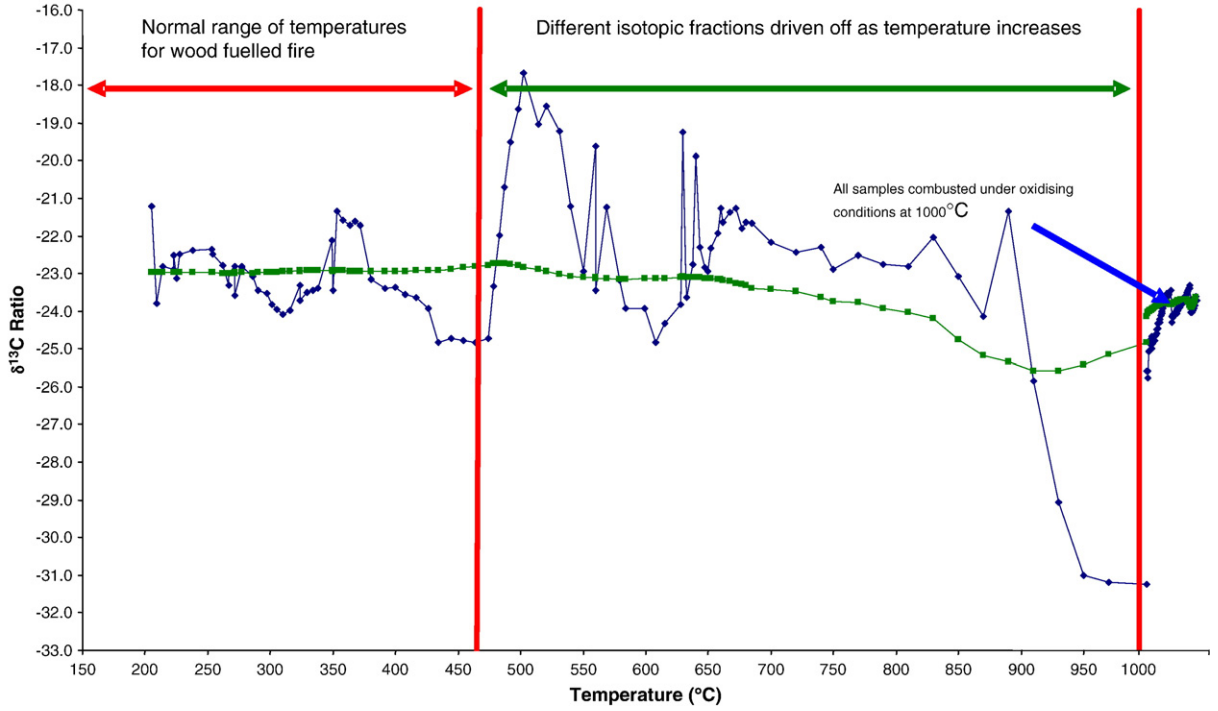

Fig. 5. Elemental analyser experiment: In order to determine the isotopic value of the volatile compounds that are driven off during charcoal formation a small, fresh sample of *P.latifolius* was heated in an elemental analyser by pulsed heating (heating and cooling cycles with a progressive temperature increment of 5–10 °C) under reducing conditions. Volatile fractions continued to be produced up to 1000 °C and the isotopic values for the different fractions showed a large range of variability (diamonds). When no further CO_2 was produced (at 1000 °C) the oxygen cycle in the elemental analyser was used and the remaining carbon was oxidised. Using the mass spectrometer peak integral, the isotopic contribution of the CO_2 pulses were integrated to approximate the isotopic value of the "remaining carbon fraction" at any point in the heating experiment (squares). Isotopically light volatile fractions driven off up to approximately 650 °C make up a relatively small proportion of the overall carbon, but above this temperature the "remaining carbon fraction" shows progressively more negative values because of a substantial and very negative compound evolved between 900–1000 °C. The isotopic values for the specific volatile compounds that are driven off during burning comprise both isotopically light and heavy fractions, and the seemingly erratic fractionation observed during charcoal formation experiments is likely to relate to the presence of the different (unidentified) volatile compounds.

enrichment relative to the whole wood values and one ring from branch M also produced an enriched $\delta^{13}C$ value. This occasional enrichment seen in these two branches may be as a result of the presence of different chemical compounds in those particular growth rings. Overall the depletion ranges between −0.02‰ and −3.00‰. Branch L produced $\delta^{13}C$ values with the greatest depletions relative to its corresponding whole wood values. This branch was collected in a live state and had a higher concentration of ^{13}C enriched volatile compounds or simple saccharides that were released during combustion resulting in more ^{13}C depleted charcoal. The other branches were collected in a dry (dead) state and would have lost the more easily released volatile compounds. The $\delta^{13}C$ values of the reduced charcoals (mean=−1.4‰) are slightly more negative than the oxidized charcoals (mean=−1.2‰).

The apparent differences in $\delta^{13}C$ between whole wood and the oxidised and reduced BC products imply that a selective pyrolitic distillation takes place during charcoal formation. The elemental analyser combustion experiment provides an indication of the sequential loss of different macromolecules and associated secondary products from the wood on the basis of their strength and degree of cross-linking. The degree of isotopic depletion or enrichment of the remaining charcoal will depend on the extent to which fractions are driven off during combustion, the compound specific isotope value and the absolute abundance of these fractions. Ideally each fraction could be identified and the $\delta^{13}C$ related back to the physiological process involved in its formation. However our approach is limited to an empirical quantification of the sequential process of carbon isotope fractionation in charcoal formation in *Podocarpus*. Further research is required to identify the precise chemical makeup of the pyrolitic distillation products.

The initial measurements during the elemental analyser combustion experiment were done without the addition of oxygen by the instrument. The evolution of CO_2 implies that volatile carbon containing molecules are driven from the wood and that oxygen is simultaneously made available. Under reducing conditions it is clear that the combustion temperature has a significant effect on the carbon isotope fractions driven off. Initially $\delta^{13}C$ values are more positive, probably due to the loss of simple saccharides and ^{13}C enriched volatiles that are not thermally stable. After 200 °C they are generally more negative. A second stage of more positive fractions is

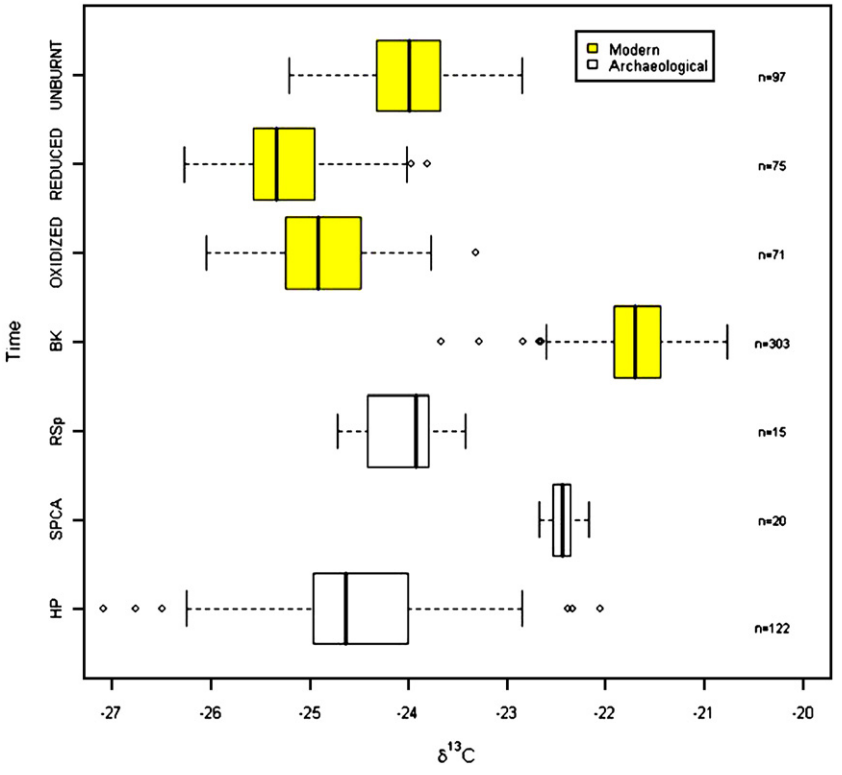

Fig. 6. The relationship between $\delta^{13}C$ values of modern *Podocarpus latifolius* whole wood and charcoal from Seaton Park, KwaZulu-Natal and Baviaans Kloof (BK), Eastern Cape and archaeological *Podocarpus* charcoal from three MSA layers at Sibudu Cave.

released at about 350 °C. Between 100 °C and 475 °C, the average temperature range for a normal wood-fuelled fire, $\delta^{13}C$ values of released compounds are more negative with respect to the source material. The $\delta^{13}C$ values between 475 °C and 1000 °C (Fig. 5) show a large range of variation, with extremely positive values (−17.0‰) and very negative values (−31.0‰). This extreme variability may be a result of secondary products breaking down at higher temperatures.

When the incremental increases in temperature failed to produce further CO_2, the elemental analyser was reprogrammed to inject oxygen in order to oxidise any remaining (black) carbon. At this point the range of variability in $\delta^{13}C$ values was greatly reduced.

The result of the controlled charcoal experiment demonstrates that the potential for fractionation of the carbon isotope signal in wood during charcoal formation is high, but that this will offset the former data set relative to the latter. The elemental analyser experiment suggests that this mechanism involves the release of particular compounds, and that the consistency of the offset will likely be linked to the temperature of the fire in which the charcoal was formed. Provided the offset during charcoal formation is consistent, the results suggest that archaeological charcoal may be a source of palaeoenvironmental proxy data.

4.3. Comparison of modern and archaeological $\delta^{13}C$ values

Grouped modern and archaeological *Podocarpus* charcoal $\delta^{13}C$ values are presented in the form of box and whisker plots (Fig. 6). The HP (>60 ka) data corresponds well with the modern *P.latifolius* charcoal data from Seaton Park and it is likely that the Coastal Forest found in Seaton Park provides a good analogue for environmental conditions during the HP period. Botanical and faunal assemblages from the HP levels indicate that the environment around Sibudu was predominantly evergreen forest with cool, moist and humid conditions (Schiegl et al., 2004; Wadley, 2004, 2006; Plug, 2004, 2006; Allott, 2004, 2005, 2006; Cain, 2006; Glenny, 2006; Herries, 2006; Pickering, 2006; Renaut and Bamford, 2006; Reynolds, 2006; Schiegl and Conard, 2006; Sievers, 2006).

The post-HP (SPCA) stands out clearly within the archaeological sample set because of the mean isotopic value and also because it has the smallest standard deviation, sample variance and range. Furthermore the isotopic values are derived from two different species of *Podocarpus*, identified by Allott (2005, 2006) (Table 2). This cannot be explained by the analogous modern isotopic data from Seaton Park. The SPCA charcoals had to have been produced in the same way as the other archaeological charcoals and the material did not appear to be any less burnt than that from the late MSA and HP. Therefore the $\delta^{13}C$ values for the SPCA charcoals must represent an isotopic record of markedly different environmental conditions compared to those of the HP period. The current proxy environmental data from Sibudu Cave (see Section 3.1) indicate that conditions were cold and dry with restricted forested areas and an increase in open grass and woodland faunal and floral communities. Forest communities would have been limited to sheltered areas along the riverside where moisture levels were sufficiently high for *Podocarpus* to

Table 2
Summary statistics for the mean modern (Seaton Park and Baviaans Kloof) *Podocarpus* carbon isotope data and mean archaeological *Podocarpus* and *Celtis* charcoal carbon isotope data from Sibudu Cave

Modern	Seaton Park Branches			Baviaans
	Whole wood	Reduced	Oxidised	Whole wood
Period	Modern	Modern	Modern	Modern
Age	2005	2005	2005	~1994
Mean	−24	−25.23	−24.86	−21.70
Median	−23.92	−25.04	−24.68	−21.66
Std dev.	0.95	0.97	1.01	0.69
Variance	0.9	0.95	1.03	0.47
Range	4.55	4.65	4.92	5.25
Minimum	−26.44	−28.07	−27.92	−25.32
Maximum	−21.89	−23.42	22.8	−20.07
N	97	75	71	303

Archaeological	*Podocarpus*			
	RSp	SPCA	GR	GS
Lithic designation	late MSA	post-HP	HP	HP
Age	46.6±1.9 ka	~58 ka	>60 ka	>60 ka
Mean	−24.06	−22.44	−24.62	−24.39
Std dev.	0.42	0.13	1.11	0.59
Variance	0.18	0.02	1.23	0.35
Range	1.30	0.50	5.03	2.17
Minimum	−24.72	−22.68	−27.08	−25.07
Maximum	−23.42	−22.17	−22.06	−22.90
N	15	20	57	65

	Celtis		
	OMOD	SPCA	GS
Lithic designation	late MSA	post-HP	HP
Age	48.3±2.0 ka	~58 ka	>60 ka
Mean	−24.27	−23.24	−24.47
Std dev.	0.46	0.53	0.13
Variance	0.21	0.28	0.02
Range	2.11	2.09	0.40
Minimum	−25.67	−24.86	−24.72
Maximum	−23.56	−22.77	−24.32
N	36	12	7

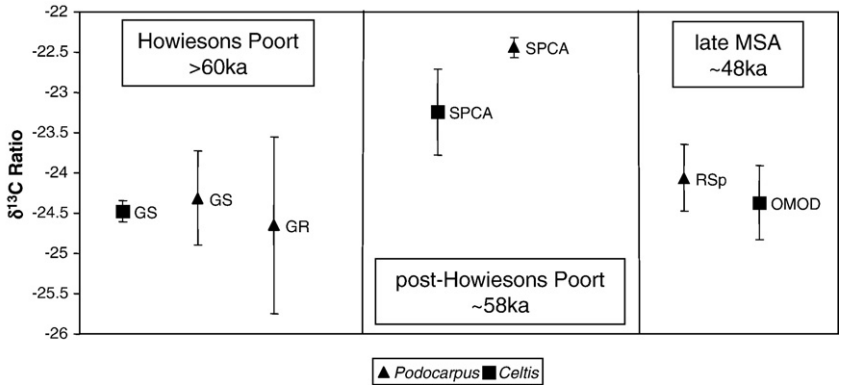

Fig. 7. Mean carbon isotope values for *Podocarpus* and *Celtis* archaeological charcoal showing changes in carbon isotope values over time. Error bars represent the standard deviation for each sample set.

grow (Allott, 2006; Sievers, 2006; Wadley, 2006), but overall conditions were dry resulting in more positive $\delta^{13}C$ values. Positive excursions in the isotope values of the modern *Podocarpus* specimens are correlated with reduced rainfall and humidity, or with an increase in temperature. Since the independent proxies suggest that temperatures were colder than at present we conclude that the isotope evidence points towards a dryer environment. Here the Baviaans Kloof may present an analogous environment. Although there is no data for burnt material from the Baviaans Kloof, based on our burning experiments, estimated $\delta^{13}C$ values for carbonised material from Baviaans Kloof would be depleted by −2‰ to −3‰. The $\delta^{13}C$ values for SPCA would fall into the variability seen in the Baviaans Kloof carbon isotope values, but comparing the variability it may imply an even drier environment.

Further research will elucidate the significance of the low variance in the SPCA carbon isotope values for *Podocarpus*, but it is possible that this reflects the degree to which the full adaptive response of the genus to variance in rainfall/humidity was possible. Such a scenario may apply if conditions were sufficiently dry that the forest could only perpetuate in refugia such as river valleys (similar to the Baviaans Kloof). The environmental constraint on growth would imply highly reduced inter-annual variability in the rainfall/humidity response of the trees because of the persistence of riparian water, but with a possibly over-riding dry response.

The isotopic evidence from the late MSA (RSp) layer is consistent with a warm (cooler than present) and dry environment. Proxy environmental data (see Section 3.1) from RSp suggests that a major environmental shift occurred. This resulted in a warmer mosaic environment of grassland, woodland and savanna communities with riverine forest along the Tongati River providing a number of potential locations for *Podocarpus* to establish (Allott, 2006; Glenny, 2006; Sievers, 2006; Wadley, 2006).

A similar trend of isotopic variation is seen in the mean $\delta^{13}C$ values of *Celtis* charcoal from the same periods (Fig. 7). The *Celtis* $\delta^{13}C$ values from the post-HP (SPCA) period are also markedly more positive than those from the HP. This suggests that this genus was responding in a similar manner as *Podocarpus* to drier conditions during the post-HP. As two very different genera are showing similar trends in their isotopic composition over time, it is very likely that an environmental signal of local conditions is preserved in their charcoal. It is also interesting to note that the variability in the *Celtis* results from the Grey Sand level is very small (based on a small sample of 7) and that the adaptive strategy of this genus might have been limited at this time in much the same way that *Podocarpus* was during the deposition of layer SPCA. The evidence for a moist, evergreen forest environment suggests that *Celtis* was at the wet limit of its adaptive capability.

5. Conclusions

A two-step process by which the carbon isotopic composition changes during combustion manifests at temperatures below 150 °C to 200 °C, when isotopic values can either become more enriched (Czimczik et al., 2002) or more depleted (Schleser et al., 1999), while above 150 °C to 200 °C, the tendency is for $\delta^{13}C$ values to become more negative. This has been linked to a pyrolitic distillation of chemical compounds within the wood, but the chemical changes that take place in a branch during drying must also be considered. When a branch dies

certain volatile and labile compounds are easily removed as the branch dries out. Charcoal formation takes place under reducing combustion, during which less volatile components and labile compounds are removed. During oxidizing combustion, oxygen from outside the wood will eventually oxidize and remove the majority of material, resulting in the formation of ash, provided the temperature remains high enough. In the case of an anthropogenic fire, charcoal will only form in the centre regions of the fire where there is no outside oxygen available (reducing environment).

The main factor affecting the isotope composition of charcoal is therefore the combustion temperature. Normal wood-fuelled fires burn at an average temperature of 450 °C to 500 °C and although overall $\delta^{13}C$ values are depleted, this temperature range does not obscure the environmental signals originally recorded in the wood tissue. Accordingly it is possible to obtain environmentally meaningful carbon isotope values from archaeological charcoal, but it is necessary to establish modern equivalents from a number of different environments to determine the full range of possible adaptive strategies available to that particular species. The comparison of modern wood and charcoal, and archaeological charcoal carbon isotope values has shown that branches and carbonised wood of *Podocarpus* and *Celtis* preserve a record of local environmental conditions and it is therefore possible to use $\delta^{13}C$ data from archaeological charcoal as a palaeoenvironmental proxy.

The environmental changes reflected in the isotopic data from the archaeological charcoal from Sibudu Cave are supported by additional proxy environmental evidence indicating that conditions changed from warm and moist in the Howiesons Poort to cooler and drier in the ~58 ka (SPCA) period and then slightly warmer again during the ~48 ka late MSA (RSp) (Schiegl et al., 2004; Plug, 2004, 2006; Wadley, 2004, 2006; Allott, 2004, 2005, 2006; Cain, 2006 Glenny, 2006; Herries, 2006; Pickering, 2006; Renaut and Bamford, 2006; Reynolds, 2006; Schiegl and Conard, 2006; Sievers, 2006). These changes in environmental conditions affected the adaptive responses of *Podocarpus* species and these responses are shown in the carbon isotope ratios of the identified archaeological charcoal. The *Podocarpus* and *Celtis* species growing during the HP and late MSA periods had a wider range of adaptive responses than those growing around Sibudu Cave during the post-HP period. This limited adaptive response around 58 ka was due to the expansion of an open grassland environment and the restriction of evergreen forests to the river valley during drier conditions.

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