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Morphology and isotope heterogeneity of Late Quaternary pedogenic carbonates: Implications for paleosol carbonates as paleoenvironmental proxies

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Abstract

Stable isotope values and radiocarbon ages were determined for pedogenic carbonate microsamples from relict soils and palaeosols from the Rio Grande Rift region of New Mexico. Carbonate nodules and clusters were sampled from fluvial and piedmont soils and palaeosols with widely varying exposure durations (7–900 ky). Pedogenic carbonates from individual soils exhibited irregular relationships between age and depth, ranging in radiocarbon age by ≤13 ky at individual depths. $\delta^{18}O$ values, and to a lesser extent $\delta^{13}C$ values, likewise had wide ranges within soils. However, comparing the stable isotope values of carbonates with similar radiocarbon ages, within and between soils, revealed consistent trends in stable isotope values over time. $\delta^{18}O$ values of pedogenic carbonates tended to decrease with decreasing age 25–17 radiocarbon ka, and increased with decreasing age <15 radiocarbon ka, with a marked shift to more positive values at 9–6 ka. Pedogenic carbonates from the piedmont soils showed minimal variation in $\delta^{13}C$ values with either depth or age, although the oldest palaeosol piedmont carbonates (radiocarbon ages of 24.5–19.2 ka) are ≥1‰ more negative than the younger piedmont palaeosol carbonates. Pedogenic carbonates in the relict fluvial soil, which has by far the longest exposure period, showed the greatest range in $\delta^{13}C$ values. Comparing the $\delta^{13}C$ values of samples of similar radiocarbon age from the relict fluvial soil indicates a transition from a mixed C_3:C_4 ecosystem at ~11 ka to an effectively pure C_3 ecosystem at ~9 ka, followed by a return to mixed vegetation by ~5 ka. Thus, although C_4 vegetation persisted in southern New Mexico through the last glaciation, drought-resistant C_3 vegetation became dominant at ~9 ka, prior to significant strengthening of the summer monsoon. This study illustrates that the stable isotope values of carbonate nodules and clusters from relict soils and/or slowly buried palaeosols can be used for palaeoenvironmental reconstructions in the context of a detailed chronologic framework. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: stable isotopes; New Mexico; pedogenic carbonates; palaeosols; palaeoenvironment; soils

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1. Introduction

The $\delta^{13}C$ and $\delta^{18}O$ values of pedogenic carbonates within successions of rapidly buried Quaternary soils have been shown to exhibit stratigraphic trends that, when integrated with radiocarbon ages, are interpreted to record a history of significant climate variation (Amundson et al., 1994b; Cole and Monger, 1994; McDonald and McFadden, 1994; Buck and Monger, 1995; Wang et al., 1994; Wang et al., 1996; Monger et al., 1998). Such interpretations, however, require that pedogenic carbonates in individual soil horizons or palaeosols developed over a limited period of time characterized by constant climatic conditions. The assumption of a relatively rapid accumulation time for pedogenic carbonates in these soils is warranted given that duration of pedogenesis was limited by rapid burial.

In contrast, carbonate accumulation in relict (unburied) and buried soils occurs over 10^3–10^6 yr (Machette, 1985), during which time significant changes in environmental and/or climate conditions can occur. This can result in overprinting of pedogenic carbonate, a process by which early generations of carbonate are overgrown by subsequent generations with minimal recrystallization of pre-existing carbonate (Cerling, 1984; Amundson et al., 1994b; Deutz et al., 2001). Consequently, the stable isotope composition of pedogenic carbonate within individual relict and buried soils, which formed during prolonged periods of pedogenesis, is typically complex and records a history of varying soil environmental conditions and/or climate fluctuations rather than formation under constant conditions (Deutz et al., 2001). Consequently, the utility of overprinted carbonates in relict and/or slowly buried palaeosols for palaeoenvironmental and/or palaeoclimate reconstructions has been questioned (Cerling, 1984; Amundson et al., 1994b; Pendall et al., 1994).

Recent studies of Holocene to latest Pleistocene soils have demonstrated that radiocarbon dating of individual carbonate laminations on clasts holds great potential for constraining the temporal distribution of carbonate stable isotope composition within one soil or a series of stacked soils (Wang et al., 1993; Amundson et al., 1994b; Wang et al., 1996). Radiocarbon dating has thus provided a chronological framework for palaeoenvironmental reconstructions in gravel rich soils that formed over extended time periods. This approach, however, has not been successfully extended to carbonate nodules in relict and slowly and/or intermittently buried non-gravel soils. Nodules typically do not exhibit concentric zonation or distinguishable laminations for strategic microsampling and isotopic analysis of distinct generations of pedogenic carbonate.

This study of Late Pleistocene and Holocene buried and relict soils from the Rio Grande Rift region of New Mexico documents the evolution of pedogenic carbonates in soils characterized by a range of burial rates and durations of pedogenesis. Significantly, this study extends the use of radiocarbon dating to carbonate nodules and clusters that formed in fine- to medium-grained parent materials rather than carbonate laminations on pebbles in coarse-grained soils, to which previous radiocarbon studies have largely been confined. In contrast to the stable and radiogenic isotope trends observed in many rapidly buried Quaternary soils, the $\delta^{13}C$ and $\delta^{18}O$ values of pedogenic carbonates within these late Quaternary soils exhibit significant intranodule and internodule heterogeneity at any given depth, as well as a range in their radiocarbon ages at various depths throughout the soil profiles. These complex spatial distributions in stable and radiogenic isotope values are interpreted to reflect varying degrees of overprinting of the pedogenic carbonates (Deutz et al., 2001). Significantly, this study documents that strategic and thorough microsampling of pedogenic carbonates for stable isotope analysis and radiocarbon dating does permit the use of such relict and slowly buried soils as complex yet reliable proxy records for environmental and climate reconstruction.

2. Sedimentologic and climatic setting

The studied soils and palaeosols are located at four sites in the Rio Grande Rift zone of central southern New Mexico (Fig. 1). Sites 1 through 3 are developed in non-calcareous alluvial fan deposits fringing the Doña Ana Mountains; the soils at these sites are referred to as 'piedmont' soils. Sites 1 through 3 (Fig. 2) all have a soil developed in Jornada II deposits. At proximal alluvial Sites 1 and 2, these coarse-grained soils were truncated and subsequently

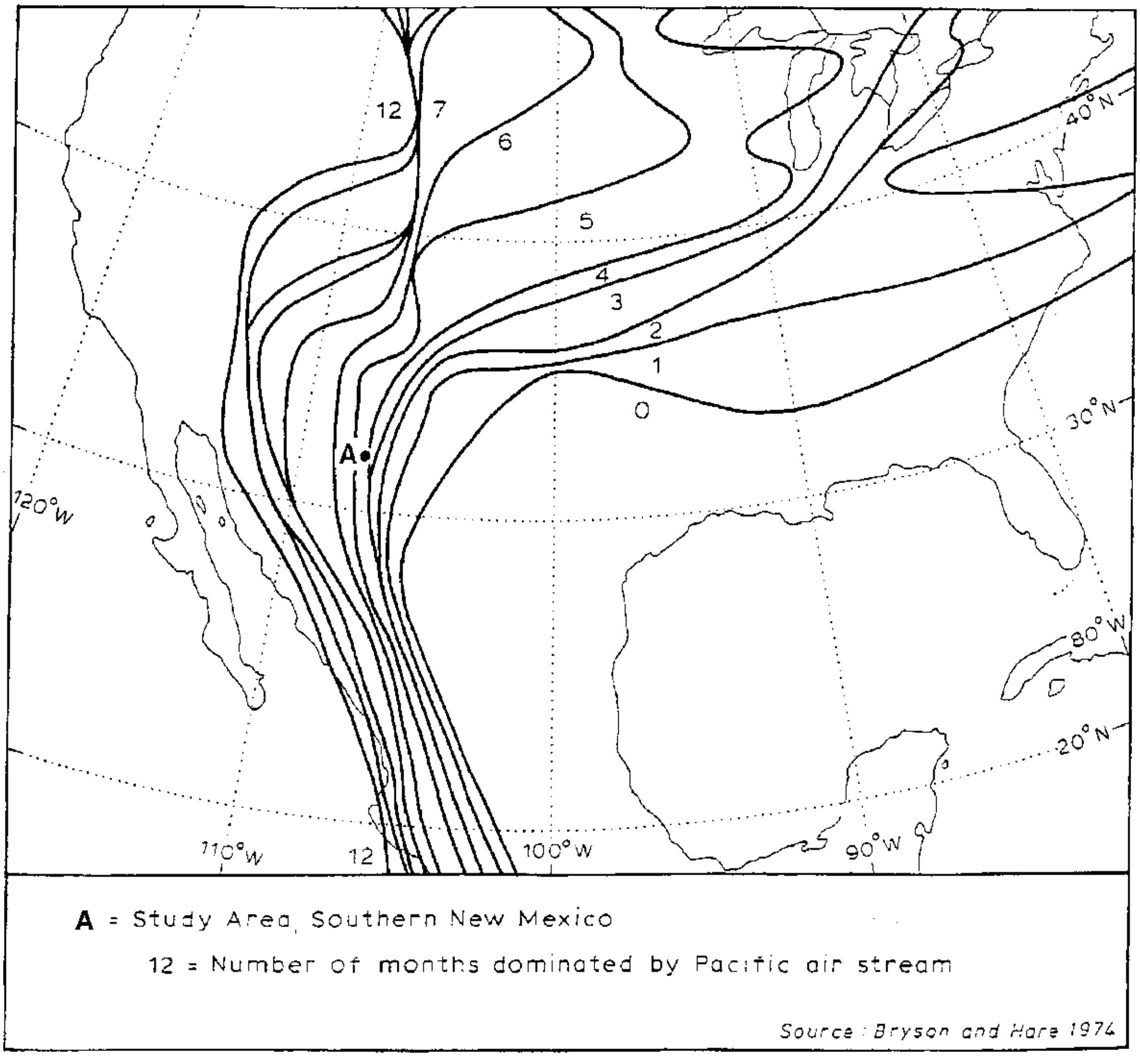

Fig. 1. Map of North America showing average number of months per year (delimited by isolines) of domination by Pacific airmasses (after Bryson and Hare, 1974). (A) Study area, southern New Mexico.

buried by Organ Alluvium and Isaacks' Ranch deposits, respectively, in which younger soils subsequently developed (Encina-Rojas, 1995; Wierenga et al., 1989; Deutz et al., 2001). At Site 3 (Fig. 2), a relict soil is developed in fine-grained sediments of the distal alluvial Jornada II deposits. At Site 4 a relict soil is developed within the Lower La Mesa geomorphic surface in fine-grained non-calcareous fluvial deposits of the Camp Rice Formation (Monger et al., 1991; Deutz et al., 2001).

The age of each deposit has been constrained by previous geomorphic and stratigraphic studies (Fig. 2). The Organ Alluvium soil has developed over the past 7 ky based on a radiocarbon date on charcoal (Gile, 1987). Best estimates of the age of the Isaacks' Ranch deposit ranges between 7.5 and 22 ka based on thermoluminescence measurements, radiocarbon ages of soil carbonates, estimated carbonate accumulation rates, and uranium trend dating (Harden and Taylor, 1983; Machette, 1985; Gile, 1987; Monger, unpublished data; this study). Estimated age of the Jornada II deposit varies widely with geomorphic position,

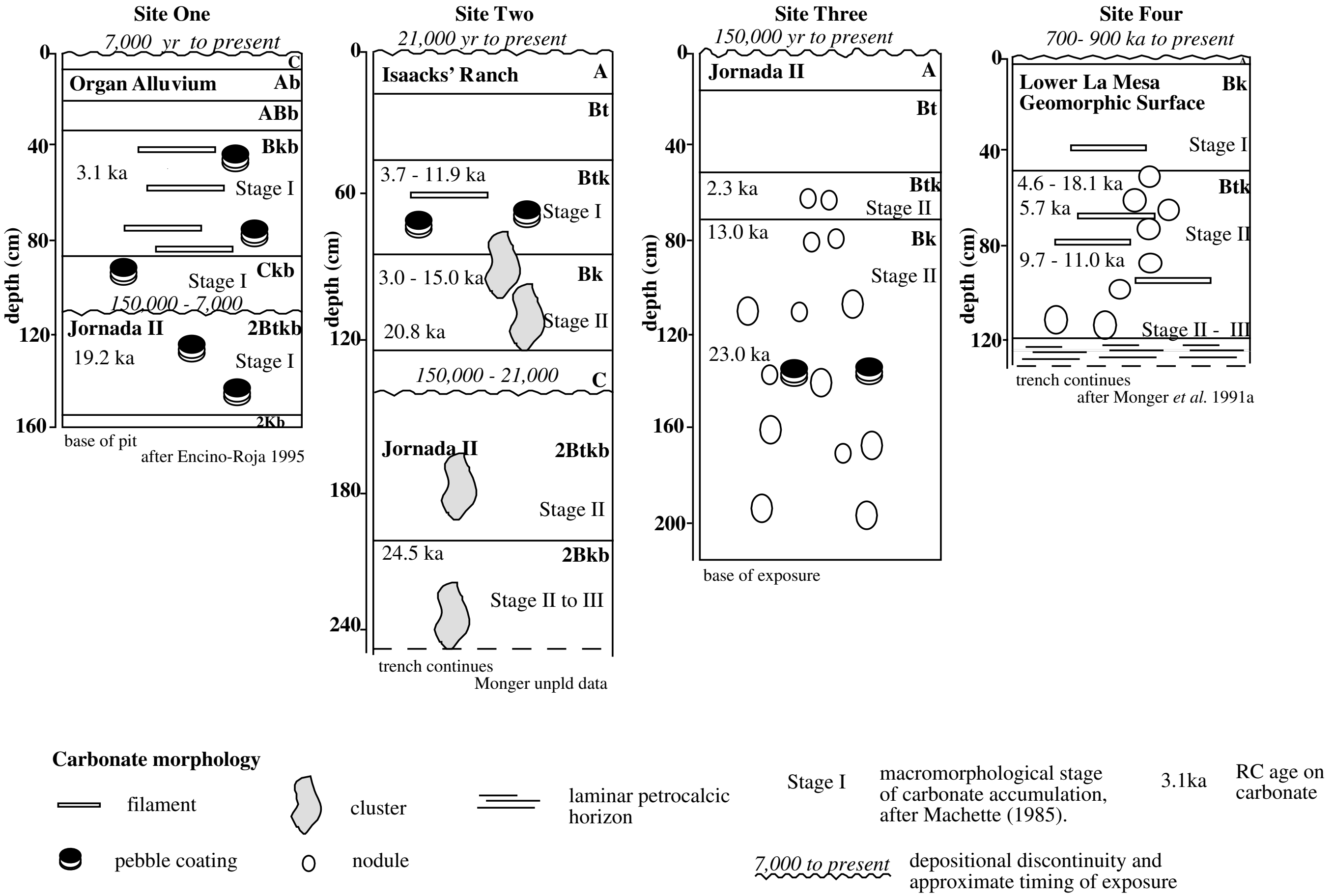

Fig. 2. Soil stratigraphy for the study region showing estimated durations of exposure, soil horizons, carbonate morphologies, stages of carbonate accumulation (after Machette, 1985), and range of carbonate radiocarbon dates obtained for given depths within each profile.

with age estimates varying from 25 to 150 ka based on geomorphic criteria (Gile, 1987) and a uranium trend date of 130 ka ± 25 ky (Machette, 1985). Based on the aforementioned age estimates, the Jornada II palaeosol at Site 1 was exposed from <150 ka to up to 7 ka, while the Jornada II palaeosol at Site 2 was exposed between <150 and 25 ka. In contrast, the Lower La Mesa relict soil has been exposed for the past 730–900 ky (Mack et al., 1993). Pedogenic carbonate in all studied soils occurs as filaments, tubules, and clusters, with nodules present only in relict soils of the Lower La Mesa and Jornada II deposits (Fig. 2; Deutz et al., 2001).

The climate in the study area is characterized by ~20 cm mean annual rainfall, a mean annual temperature of 15.6°C, and an average monthly soil temperature at a depth of 50 cm of 20°C (Gile and Grossman, 1979). The region is influenced by air movement from the Gulf of Mexico for up to 8 months per year (Bryson and Hare, 1974). Sixty eight percent of the annual precipitation typically falls during the summer monsoon (June–October) fed from the Gulf of Mexico (Bulloch and Neher, 1980). By contrast, Pacific air is dominant in southern New Mexico during November and February and (less so) in March through May (Fig. 1; Bryson and Hare, 1974). Precipitation during those months accounts for less than 20% of total annual rainfall.

Situated in the northern Chihuahuan desert, the study area has vegetation consisting of an 80:20 mix of C_3 desert shrubs (primarily creosote, tarbush and honey mesquite) and C_4 grasses (primarily black grama), but prior to the introduction of ranching 150 yr ago was predominantly C_4 grasses (Buffington and Herbel, 1965; Dick-Peddie, 1993; Reynolds et al., 1999). The piedmont sites also contain a small proportion of yucca plants (primarily *Yucca elata*; Reynolds et al., 1999), which are CAM succulents. The proportion of bare ground at local piedmont sites of similar elevation and vegetation has been estimated at ≥80% (Reynolds et al., 1999).

3. Methods

All soils were logged and sampled, both vertically and laterally, on a dm-scale for petrographic and geochemical analysis. Thin sections of all samples were studied petrographically (plane-light and cathodoluminescence). The outer ≤0.5 mm of carbonate samples was removed prior to the collection of isotope microsamples. Multiple microsamples were taken from individual nodules and carbonate clusters. Stable isotope analysis of carbonate microsamples (≥0.3 mg) was carried out at the University of Southern California following procedures outlined in Stott (1992). External precision was ±0.2‰ (2σ) for both C and O. Aliquots of selected carbonate samples ($n = 21$) were analysed for ^{14}C at the Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory. In five cases, aliquots from more than one microsample had to be combined to generate sufficient material for ^{14}C analysis. Combined microsamples have similar stable isotope values and originate either from the same macromorphological feature or from the same type of feature from a similar depth in the soil. Samples were dissolved in 85 wt% phosphoric acid at 90°C for a minimum of 1 h. The evolved CO_2 was cryogenically purified to remove water and non-condensable gases, and graphitized by reacting with H_2 at 570°C for seven hours in the presence of a cobalt catalyst.

Occluded organic matter samples ($n = 9$) were prepared according to the methods of Sinha and Stott (1994) and analysed for stable isotopes at the University of Southern California. Root fragments ($n = 14$) were analysed to determine average $\delta^{13}C$ values for C_3 and C_4 vegetation. Root fragments were rinsed in distilled water, leached overnight in 1 N HCl, rinsed three times in distilled water and dried overnight at 60°C. The carbonate-free samples were combusted at 1030°C with a silvered cobaltous cobaltic oxide scrubber, and at 650°C with Cu to extract the CO_2 for carbon isotope analysis. Analyses were carried out on an Optima stable isotope mass spectrometer at Fison Instruments. External precision was ±0.2‰ (2σ).

4. Results

4.1. ^{14}C ages of pedogenic carbonate

Recent studies (Wang et al., 1993, 1994, 1996; Amundson et al., 1994b, 1998) have shown the potential for radiocarbon (herein referred to as RC) dating of Quaternary carbonates, but not without noting its limitations. Measured RC ages are affected by the fluctuating levels of ^{14}C in the atmosphere (Faure, 1986), such that for the temporal range pertinent to this study (2–25 ka), the effect is to yield apparent RC ages that are younger by ~1–4 ky than the true depositional or pedogenic age (Bard et al., 1993). Calibration is necessary to convert RC dates into calendar dates, however, un-calibrated, 'conventional' dates (Stuiver and Polach 1977) can be used comparatively, as well as cautiously related to independently recorded events such as the transition from the Pleistocene to the Holocene (Wang et al., 1996; Monger et al., 1998).

Additionally, incorporation of ^{14}C-depleted CO_2 into soil CO_2 and subsequently into pedogenic carbonate from decaying organic matter yields erroneously old carbonate RC ages (Wang et al., 1993, 1994, 1996; Amundson et al., 1994b, 1998). Wang and colleagues (Wang et al., 1993, 1994; Amundson et al., 1994b, 1998) have developed a model to correct pedogenic carbonate RC dates for the effect of incorporation of ^{14}C-depleted carbon from decaying organic matter. However, this model cannot be applied for correction of measured RC ages of our studied soils given that several of the model assumptions are violated (cf. Monger et al., 1998). The model assumes continuous carbonate accumulation throughout pedogenesis recorded by the stratigraphic interval of interest, however carbonate accumulation in some of our studied soils was cut-off by subsequent burial. The assumption of constant temperature and carbonate accumulation at a constant rate is not reasonable given that climate in the area has varied over the past 2–25 ky (Bryson and Hare, 1974; Van Devender, 1990). Lastly, our $\delta^{13}C_{org}$ values, coupled with other studies of soil organic composition in the study region (Connin et al., 1997a), do not support the model assumption that the $\delta^{13}C$ of soil organic matter and soil respiration rates stayed constant throughout soil development. Given that soil organic matter in desert soils has a mean residence time of 10^1–10^2 yr (Parker et al., 1983; Connin et al., 1997a), measured soil carbonate RC ages presented in this paper should be at most overestimated by 10^1 and 10^2 yr due to incorporation of ^{14}C from decaying organic matter.

An additional factor contributing to erroneous overestimation of pedogenic carbonate RC ages is the incorporation of detrital, or aeolian, ^{14}C-depleted carbonate (Wang et al., 1996) into the analysed soil carbonates. Pedogenic carbonates are assumed to precipitate in an open system characterized by soil respiration rates typical of most modern soils (cf. Cerling, 1984). This implies that the stable isotope signature of soil CO_2 and soil water dominate the stable isotope signature of the precipitating pedogenic carbonate (Quade et al., 1989). The assumption of equilibrium precipitation in an open system has been extended to the radiogenic isotope composition ($\delta^{14}C$) of pedogenic carbonates (Amundson et al., 1994b). However, it is critical that unaltered detrital carbonate be avoided during analysis (Amundson et al., 1989; Wang et al., 1996). Petrographic and stable isotopic analyses of soil carbonates in this study have found minimal evidence for detrital carbonate (Deutz et al., 2001).

Alteration of pedogenic carbonates by ^{14}C-depleted groundwaters due to interaction with older carbonates or carbonate-bearing soils would also yield erroneously old RC ages. However, groundwater alteration of the pedogenic carbonates in this study is unlikely given that the current and palaeo-depth to the watertable is >100 m (King and Hawley, 1975).

Lastly, carbonate accumulation in soils is a cumulative process, which can be punctuated by intervals of partial dissolution. Dissolution–reprecipitation at shallow depths (<40 cm) in soils can affect the ^{14}C content (as well as the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values) of pedogenic carbonates (Pendall et al., 1994) due to incorporation of atmospheric CO_2 in newly formed overgrowths. Thus, pedogenic carbonates that record progressive overprinting and multiple intervals of dissolution–reprecipitation yield radiocarbon ages that provide an average value of all crystals present in the sampled fraction. To that end, in this study $\delta^{14}C$, $\delta^{13}C$ and $\delta^{18}O$ analyses were carried out on the smallest obtainable microsamples (0.3–10 mg) in order to minimize the artificial homogenization of crystals of varying ages.

Additional considerations that support our assumption that the carbonate RC dates obtained in this study are reasonable estimates of the timing of their formation include: (1) palaeosol carbonates have older RC ages than carbonates from overlying relict soils; and (2) well indurated, larger nodules yield older RC ages than smaller, less well cemented nodules from the same soil profile, which presumably record shorter periods of pedogenesis than well cemented nodules.

Table 1
Stable isotope values and radiocarbon age for carbonate samples

Site and soil	Depth (cm)	Type	AMS ^{14}C age	$\delta^{13}C_{PDB}$	$\delta^{18}O_{PDB}$
Site 1					
Organ Alluvium					
OA2 I[a]	54	Filament	[b]	−1.6	−3.4
OA3	68	Filament	3120 ± 70	−1.7	−3.7
Jornada II					
JIIb9 I	114	Coating		−2.3	−6.5
JIIb9 II	114	Coating		−1.7	−5.5
JIIb7I	126	Interpebble	19210 ± 80	−1.1	−5.1
Site 2					
Isaack's Ranch					
IR5	45	Filament	3710 ± 70	−1.6	−3.96
IR1 I	50	Matrix		−1.0	−5.0
IR1 II	50	Interpebble	11870 ± 100	−1.1	−5.4
IR1 III	50	Matrix		−1.1	−5.0
IR1 IV	50	Interpebble	9390 ± 70	−1.0	−4.8
IR 7a I	85	Matrix		−1.6	−5.1
IR7a II	85	Interpebble		−1.5	−5.0
IR7b III	92	Interpebble		−1.1	−5.0
IR7b IV	92	Coating		−1.5	−5.9
IR7b Va	92	Interpebble		−1.1	−4.3
IR7b Vb	92	Interpebble	2960 ± 50	−1.0	−4.2
IR7c VI	95	Matrix		−1.1	−5.4
IR7c VIII	95	Coating	14980 ± 80	−0.7	−5.6
IR7c IX	95	Matrix		−1.2	−5.7
IR10	120	Matrix	20840 ± 110	−0.7	−4.8
Jornada II					
IR15 I	184	Interpebble		−2.9	−5.1
IR15 II	184	Interpebble		−3.1	−5.5
IR17 I	207	Interpebble	24530 ± 460	−3.1	−4.9
IR17 II	207	Interpebble		−2.9	−5.2
IR17 III	207	Interpebble		−2.3	−5.1
IR17 IV	207	Interpebble		−3.0	−4.9
Site 3					
Jornada II					
DD6 I	60	Nodule: discrete		−0.7	−3.3
DD6 II	60	Nodule: discrete	2260 ± 70	−1.2	−3.4
DD6 III	60	Matrix		−1.3	−3.7
DD7 I	70	Nodule: discrete		−1.3	−4.6
DD7 II	70	Nodule: discrete	13260 ± 70	−1.2	−4.5
DD7 III	70	Nodule: discrete		−1.2	−4.3
DD14 I	80	Pebble coating		−0.6	−5.8
DD14 IV	80	Pebble coating		−0.4	−5.1
DD16 I	100	Pebble coating		−0.2	−4.4
DD16 II	100	Pebble coating		−0.9	−5.0
DD18 I	135	Nodule: orthic	23030 ± 120	−1.1	−4.9
DD18 II	135	Nodule: orthic		−1.3	−5.2
DD18 III	135	Nodule: orthic		−1.1	−5.1
Site 4					
Lower La Mesa					
CR1aV I	48	Nodule: discrete	17640 ± 90	−4.4	−5.2
CR1aV II	48	Nodule: discrete	18010 ± 110	−2.4	−4.5

Table 1 (*continued*)

Site and soil	Depth (cm)	Type	AMS ^{14}C age	$\delta^{13}C_{PDB}$	$\delta^{18}O_{PDB}$
CR1aV III	48	Nodule: discrete		−3.7	−5.3
CR1aV IV	48	Nodule: discrete		−3.8	−5.0
CR1aV V	48	Nodule: discrete	11720 ± 160	−3.1	−4.7
CR15	50	Nodule: discrete	18070 ± 120	−4.3	−5.3
CR16 II	50	Nodule: orthic		−2.1	−2.9
CR16 IV	50	Nodule: orthic	9220 ± 60	−2.5	−3.7
CR17 I	50	Nodule: orthic		−2.0	−2.9
CR17 II	50	Nodule: orthic	4590 ± 60	−1.0	−2.1
CR17 III	50	Nodule: orthic		−1.3	−2.6
CR17 V	50	Nodule: orthic		−1.9	−3.1
CR51	50	Nodule: discrete		−2.6	−4.4
CR18 III	65	Nodule: orthic	5720 ± 50	−2.6	−3.9
CR18 V	65	Nodule: orthic		−2.5	−3.5
CR18 VII	65	Nodule: orthic		−2.0	−3.2
CR19 II	68	Nodule: orthic		−2.4	−3.4
CR23 I	80	Nodule: orthic		−3.8	−6.0
CR23 IV	80	Nodule: orthic	11020 ± 120	−3.6	−5.9
CR20 IV	82	Nodule: orthic	9700 ± 70	−3.6	−5.6
CR16 III	50	Transitional		−3.0	−4.1
CR17 IV	50	Transitional		−2.0	−3.0
CR19 I	68	Transitional		−3.2	−4.4
CR23 II	80	Transitional		−3.9	−5.7
CR20 II	82	Transitional		−4.0	−5.7
CR14	35	Matrix		−2.7	−3.7
CR16 I	50	Matrix		−3.4	−4.5
CR20 I	82	Matrix		−4.9	−6.1
CR16 V	50	Filament		−3.4	−4.4
CR18 I	65	Filament		−4.2	−5.4
CR18 II	65	Filament		−4.7	−5.9
CR20 III	82	Filament		−4.3	−6.3

[a] Letters show soil, Arabic numerals macromorphological feature, and Roman numerals microsample.
[b] Vertical lines indicate stable isotope microsamples combined for radiocarbon dating.

Measured carbonate RC ages, however, are significantly less than independently estimated ages of the deposits in which they formed. This likely reflects dissolution of previously accumulated pedogenic carbonate during increased depths of wetting in soils brought on by the last glacial maximum (21–18 ka). In this study, carbonate RC ages provide a chronologic framework for interpretation of pedogenic stable isotope trends. For comparison with independently dated events, carbonates with RC ages of >18 ka are assumed to pre-date the last glacial maximum, those with RC ages of 18–15 ka are assumed to overlap in time with the last glacial maximum, those with RC ages of <15–9 ka are assumed to be late glacial to earliest Holocene, while carbonates with RC ages ≤6 ka are assumed to be Holocene.

4.2. *Isotope composition and radiocarbon ages of pedogenic carbonates*

Pedogenic carbonates from the piedmont soils show minimal variation in $\delta^{13}C$ values (<1.5‰) with either depth or age (Table 1; Figs. 3A–C and 4). However, the $\delta^{13}C$ values (−2.3 to −3.1‰) of the oldest pedogenic carbonates (RC ages of 24.5–19.2 ka, respectively) from the buried Jornada II soil profiles (Fig. 3A and B) are 1–2.5‰ more negative than the $\delta^{13}C$ values of younger pedogenic carbonates. In contrast, the $\delta^{13}C$ values of pedogenic carbonates in the Lower La Mesa soil show a much more complex record (Fig. 3D). Firstly, the $\delta^{13}C$ values exhibit a large range at any given depth, with the range in $\delta^{13}C$ values decreasing from 3.3‰ at 50 cm to 1.3‰ at 80 cm depth.

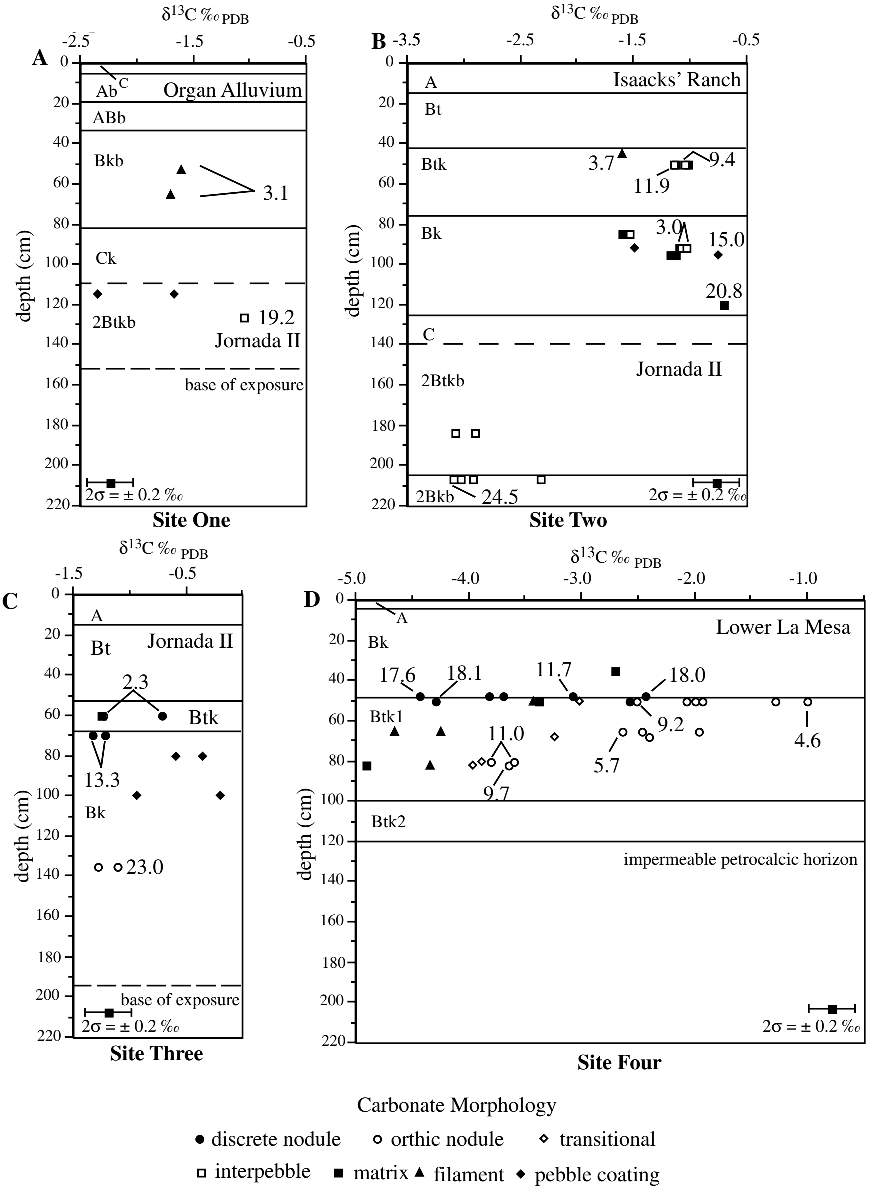

Fig. 3. Carbonate δ^{13}C values and uncorrected carbonate radiocarbon ages (in ka) plotted against depth (cm) in each soil: (A) Site 1 — Jornada II palaeosol buried by Organ Alluvium soil; (B) Site 2 — Jornada II palaeosol buried by Isaacks' Ranch soil; (C) Site 3 — Jornada II relict soil; and (D) Site 4 — Lower La Mesa relict soil. Tie lines connect measured radiocarbon date to relevant sample(s).

Secondly, the δ^{13}C values of pedogenic carbonates in the Lower La Mesa relict soil exhibit a weak trend of decreasing values with increasing depth. Thirdly, the range in δ^{13}C compositions of similar age carbonates (RC ages of ± 0.5 ky) in the Lower La Mesa soil is smaller (≤ 2.0‰) than the range of δ^{13}C values exhibited by all pedogenic carbonates in the soil. Lastly, the δ^{13}C values of carbonates of similar radiocarbon ages in the Lower La Mesa soil define a trend of decreasing values with increasing depth.

Although the δ^{18}O values of pedogenic carbonates from all of the studied soils exhibit a large range

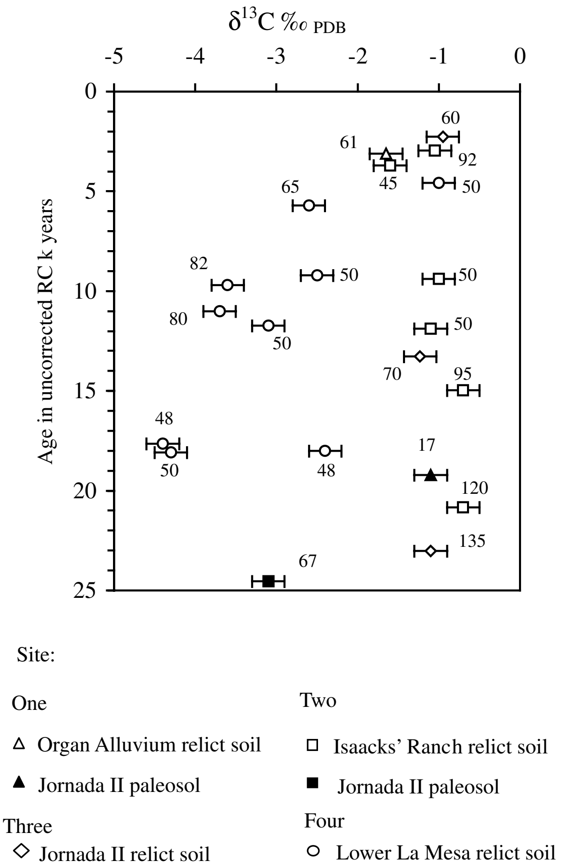

Fig. 4. Carbonate $\delta^{13}C$ values plotted against uncorrected carbonate radiocarbon dates for all soils. Numbers indicate the depth (cm) of accumulation of carbonate in the soils. For palaeosols from Sites 1 and 2, the depth is a minimal estimate due to truncation of soils prior to burial. Error bars indicate ± 2 standard deviations for $\delta^{13}C$ values.

(-6.5 to -2‰ in the Lower La Mesa relict soil; Table 1; Fig. 5D), the $\delta^{18}O$ compositions of similar age carbonates within and between soils exhibit a smaller range in values (1–2.3‰) (Figs. 5 and 6). Moreover, the $\delta^{18}O$ values of pedogenic carbonates with radiocarbon ages of <15 ka define a trend of increasing $\delta^{18}O$ values with decreasing age, whereas the $\delta^{18}O$ values of pedogenic carbonates with radiocarbon ages between 25 and 15 ka show a weaker trend of decreasing $\delta^{18}O$ values with decreasing radiocarbon age (Fig. 6).

Pedogenic carbonates in the Lower La Mesa (Fig. 5D) and Jornada II relict (Fig. 5C) soils show weak trends of decreasing $\delta^{18}O$ values with depth. The proximal piedmont relict soils and palaeosols (Fig. 5A and B) do not display similar trends within individual soil profiles, although $\delta^{18}O$ values of carbonates in the Organ Alluvium soil are more positive than $\delta^{18}O$ values of carbonates in the underlying Jornada II palaeosol (Fig. 5A). This trend of decreasing $\delta^{18}O$ values with increasing depth in part reflects the distribution of oldest carbonates at greater depth than the youngest carbonates. However, at any given depth in individual soil profiles, there is a significant range in carbonate $\delta^{18}O$ values (<1–3.3‰) and radiocarbon ages (up to 13.5 ky). Moreover, the $\delta^{18}O$ values of carbonates of similar radiocarbon ages (± 0.5 ky) decrease with increasing depth; this trend is best developed in the Lower La Mesa relict soil (Fig. 5D).

4.3. Isotope composition of organic matter

Occluded organic matter from Sites 2, 3, and 4 were analysed for their $\delta^{13}C$ composition (Table 2), but not for their ^{14}C content. The $\delta^{13}C$ values of occluded organic matter from Site 2 decrease with increasing depth; $\delta^{13}C$ values of -15.1 to -16.7‰ at <85 cm depth decrease to $\delta^{13}C$ values of -20.5 to -22.4‰ at >95 cm depth. A single sample of occluded organic matter from the Jornada II relict soil (Site 3) has a $\delta^{13}C$ value of -14.2‰. A single sample from 80 cm in the Lower La Mesa relict soil has a $\delta^{13}C$ value of -20.5‰.

C_3 roots ($n = 5$) from the Isaacks' Ranch soil (Site 2) have an average $\delta^{13}C$ value of -25.08‰ ($\sigma = 2.46$), whereas C_3 roots ($n = 4$) from the Lower La Mesa soil have an average $\delta^{13}C$ value of -23.95‰ ($\sigma = 1.25$) (Table 2). C_4 roots ($n = 5$) from the unburied Jornada II soil (Site 3) have an average $\delta^{13}C$ value of -12.88‰ ($\sigma = 0.49$).

5. Discussion

5.1. Soil carbonate carbon isotope palaeoenvironmental proxies

5.1.1. Factors controlling the $\delta^{13}C$ composition of carbonates in desert soils

The $\delta^{13}C$ value of soil carbonates reflects the $\delta^{13}C$ composition of total soil CO_2, which in turn reflects the relative proportion of associated C_3:C_4 vegetation, the soil respiration rate, and the $\delta^{13}C$ value of atmo-

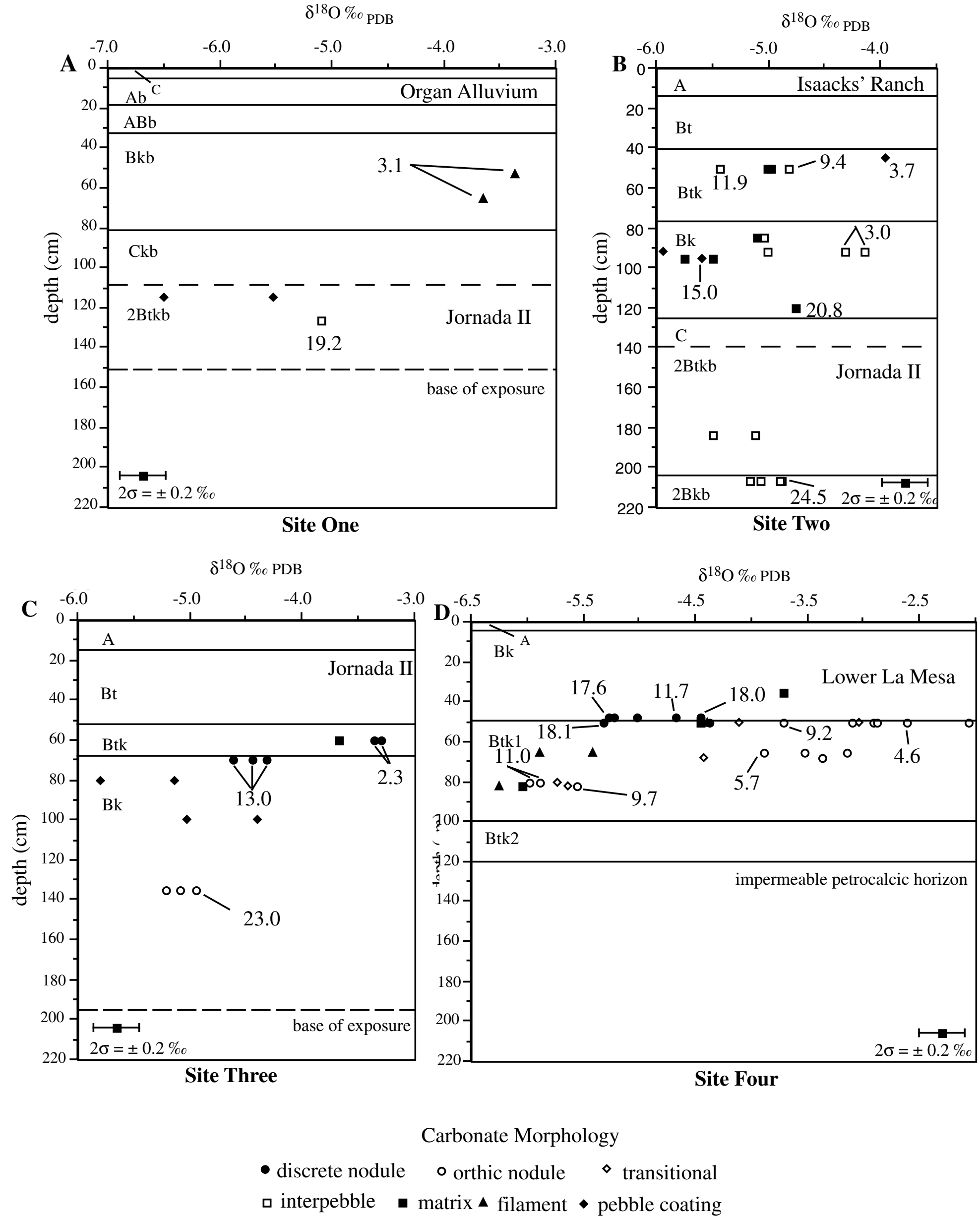

Fig. 5. Carbonate $\delta^{18}O$ values and uncorrected carbonate radiocarbon ages (in ka) plotted against depth (cm) in each soil: (A) Site 1 — Jornada II palaeosol buried by Organ Alluvium soil; (B) Site 2 — Jornada II palaeosol buried by Isaacks' Ranch soil; (C) Site 3 — Jornada II relict soil; and (D) Site 4 — Lower La Mesa relict soil. Tie lines connect measured radiocarbon date to relevant sample(s).

spheric CO_2 (Cerling, 1984; Amundson et al., 1988; Quade et al., 1989, 1995; Latorre et al., 1997). C_4 vegetation is associated with high light intensity and moisture stress and warm season precipitation (Cerling and Quade, 1993). Conversely, C_3 vegetation can indicate cool temperatures and winter precipitation. However, some C_3 species are more tolerant of drier and/or hotter conditions than C_4 vegetation (Ehleringer et al., 1991). Thus low elevation vegetation in semi-arid to arid climates, such as the southern

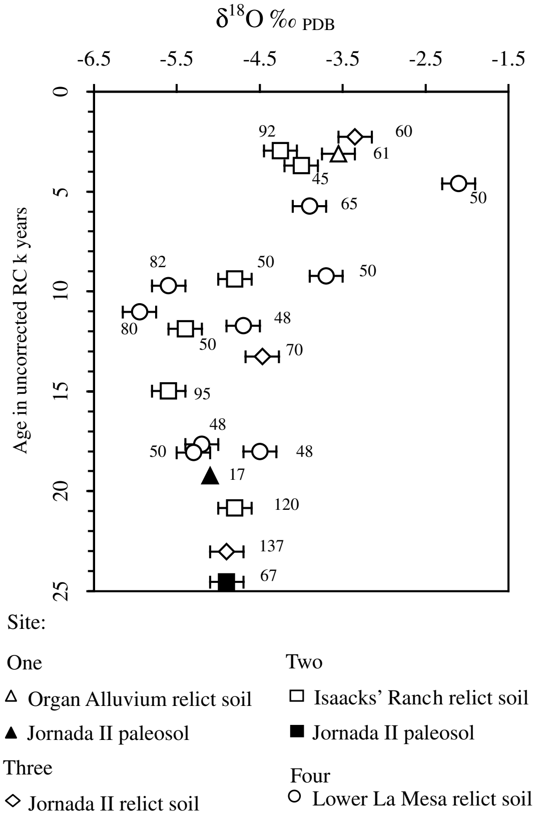

Fig. 6. Carbonate $\delta^{18}O$ values plotted against uncorrected carbonate radiocarbon dates for all soils. Numbers indicate the depth (cm) of accumulation of carbonate in the soils. For palaeosols from Sites 1 and 2, the depth is a minimal estimate due to truncation of soils prior to burial. Error bars indicate ± 2 standard deviations for $\delta^{18}O$ values.

New Mexico region, is dominated by C_3 desert shrubs, despite predominantly summer rainfall. In addition, some succulent desert plants follow the CAM photosynthetic pathway and have $\delta^{13}C$ values intermediate between those of C_3 and C_4 plants (Cerling and Quade, 1993).

The low plant density and consequently low respiration rate associated with desert shrub vegetation can result in a significant component of atmospheric CO_2 to total soil CO_2, especially at shallow depths in desert soils (Amundson et al., 1988; Quade et al., 1989; Cerling and Quade, 1993; Wang et al., 1996). Consequently, carbonates that precipitate in semi-arid to arid desert soils may have more positive $\delta^{13}C$ values than would be expected if the total soil CO_2 were dominated by soil-respired CO_2, as is common in C_4-dominated soils. Respiration rates in desert soils, however, vary considerably, reflecting both seasonal changes in plant behaviour (Parker et al., 1983), and the low vegetation density (5–20%: Quade et al., 1989; Reynolds et al., 1999). Any spatial variability in the $\delta^{13}C$ composition of soil CO_2 will be reflected in the $\delta^{13}C$ values of the soil carbonates that precipitate in desert soils.

Observed down-soil changes in the $\delta^{13}C$ values of soil carbonates can be described using Cerling's diffusion-reaction model (1984, 1991), which predicts an exponential decrease in the $\delta^{13}C$ value of total soil CO_2 and of soil carbonates with depth. Variations in measured carbonate $\delta^{13}C$ values with depth can thus be used to model soil respiration rates and the $\delta^{13}C$ composition of soil-respired CO_2, which presumably governed the down-soil profile in measured carbonate $\delta^{13}C$ values. However, this application requires that the soil carbonates are contemporaneous, or that climatic conditions and/or associated vegetation remained constant throughout carbonate accumulation (Cerling, 1984; Cerling et al., 1989). Where soil carbonates from various depths in a given soil are close enough in age that unchanging climatic conditions is a reasonable assumption ('penecontemporaneous'), we can qualitatively estimate trends through time in soil respiration rate and use this to inform our estimate of the C_3:C_4 composition of the associated vegetation. A quantitative estimate of likely soil respiration rates during carbonate accumulation and the C_3:C_4 composition of the associated vegetation can also be attempted using Cerling's (1991) diffusion-reaction model.

Two additional factors can compromise the use of the $\delta^{13}C$ values of pedogenic carbonates from desert soils as palaeoenvironmental proxies. These include: (1) a contribution to soil CO_2 by CAM plants; and (2) some species of desert shrubs (notably *Atriplex* species) use the C_4 metabolic pathway and thus contribute a component of CO_2 to total soil-CO_2 that is indistinguishable from grassland respired-CO_2 (Monger et al., 1998). In the study region, CAM vegetation makes up a minor component of the present-day ecosystem of the piedmont soils, and is effectively absent from the Lower La Mesa site (Dick-Peddie, 1993; Peters et al., 1997; Reynolds et al., 1999). Furthermore, the presence of yucca plants (a CAM succulent) at the piedmont sites is an indicator of a recent transition from a grass to

Table 2
$\delta^{13}C$ values of organic samples

Site and soil	Depth (cm)	Type	$\delta^{13}C_{PDB}$
Site 2			
Isaacks' Ranch			
IR I	50	Occluded organic matter	−15.5
IR I dup	50	Occluded organic matter	−15.1
IR II	50	Occluded organic matter	−15.5
IR 7a II	85	Occluded organic matter	−16.7
IR 7c IX	95	Occluded organic matter	−20.5
IR5	45	Root	−23.8
IR1 I	50	Root	−23.0
IR1 II	50	Root	−29.5
IR1 IV	50	Root	−23.1
IR7 VI	95	Root	−26.0
Average ($\pm\sigma$)		Root	−25.08 (±2.46)
Jornada II			
IR15 III	184	Occluded organic matter	−21.9
IR17 V	207	Occluded organic matter	−22.4
Site 3			
Jornada II			
DD7a IV	70	Occluded organic matter	−14.2
DD6a I	60	Root	−12.4
DD6a II	60	Root	−13.2
DD7a	70	Root	−12.4
DD7a I	70	Root	−13.5
Average ($\pm\sigma$)		Root	−12.88 (±0.49)
DD7a II	70	Root	−16.4
Site 4			
Lower La Mesa			
CR23 III	80	Occluded organic matter	−20.5
CR17 I	50	Root	−26.1
CR17 I	50	Root	−23.2
CR17 II/III	50	Root	−23.1
CR16 I	50	Root	−23.4
Average ($\pm\sigma$)		Root	−23.95 (±1.25)

shrub-dominated ecosystem (Dick-Peddie, 1993). *Atriplex* shrubs are not characteristic of the Chihuahuan desert flora of southern New Mexico, but are more typical of the Great Basin desert flora, as found in northern New Mexico (Dick-Peddie, 1993).

5.2. Palaeoenvironmental reconstructions from soil carbonate $\delta^{13}C$ values

5.2.1. Piedmont soils

Radiocarbon dates indicate that carbonate accumulation in the piedmont soils occurred over at least 18 ky, far too great a period to assume constant climatic conditions. The largest temporal variation in carbonate $\delta^{13}C$ values over the extended period of carbonate accumulation in the piedmont soils is recorded by the distribution of $\delta^{13}C$ values in the buried Jornada II soil at Site 2 (Fig. 3B). Soil carbonates with the most negative $\delta^{13}C$ values (−3.1 to −2.3‰) and oldest radiocarbon age (24.5 ka) occur in the buried Jornada II palaeosol. A shift (2‰) in carbonate $\delta^{13}C$ values occurs across the discontinuity developed between the Jornada II palaeosol and the Isaacks' Ranch soil, which buried the Jornada II soil prior to 21 ka (Fig. 3B). This shift to more positive soil carbonate $\delta^{13}C$ values between 24.5 and 21.0 ka can be interpreted as either an increased component of C_4 vegetation to the local flora or a lowering of soil respiration rates due to decreased density of desert vegetation (C_3-dominated) overlying the soils. The lack of two or more penecontemporaneous samples from different depths precludes an assessment (e.g. using Cerling's diffusion-reaction model) of the soil respiration rate and the $\delta^{13}C$ value of soil respired CO_2 immediately before or after the observed transition in soil carbonate $\delta^{13}C$ values.

Nevertheless, several lines of evidence suggest that the shift in carbonate $\delta^{13}C$ values at Site 2 reflects an increased component of C_4 vegetation to the local flora. Firstly, the shift to more positive carbonate $\delta^{13}C$ values is recorded in the Isaacks' Ranch soil that overlies the Jornada II soil (Fig. 3B). The Jornada II soil was truncated prior to the deposition of the Isaacks' Ranch deposit, consistent with a low vegetation density (and low respiration rate) towards the end of the period of exposure of the Jornada II soil (<150 ka to ~21 ka) (cf. Gustavson and Holliday, 1999; Reynolds et al., 1999). Conversely, the Isaacks' Ranch deposit has been accumulating over the last ≤21 ky, implying sufficient vegetation cover to prevent erosion and to sustain soil respiration rates. Secondly, the lack of preservation of carbonates in the upper 50 cm of the Isaacks' Ranch soil indicates that soil moisture levels did not drop sufficiently to minimize near-surface carbonate dissolution and decrease vegetation density over the soils (cf. Quade et al., 1989). Thirdly, variations in carbonate $\delta^{13}C$ values with depth in the Isaacks' Ranch soil are much less than expected in desert soils characterized by low respiration rates (range of <1‰ in $\delta^{13}C$ values, compared to ≤10‰ in Quade et al., 1989). Lastly, the $\delta^{13}C_{org}$ values of occluded organic matter in the soil carbonates from Site 2 show a 1.4‰ positive shift between the Jornada II palaeosol and the overlying Isaacks' Ranch relict soil indicating a probable increase in C_4 vegetation. An even larger shift (3.8‰) in $\delta^{13}C_{org}$ values in the lower Isaacks' Ranch soil (between 95 and 85 cm depth) may record an even larger-scale increase in C_4 vegetation, potentially with a CAM component.

There is marked variation between the $\delta^{13}C$ values of soil carbonates developed in Jornada II palaeosol at Site 2 (buried at ~21 ka; Fig. 3B) and those of the Jornada II palaeosol at Site 1 (buried at ~7 ka) and the Jornada II relict soil at Site 3 (Fig. 3A and C). This marked variation in carbonate $\delta^{13}C$ values is interpreted to record, in part, spatial and temporal variations in the proportion of C_4 vegetation between the different piedmont soils. The $\delta^{13}C$ values of soil carbonates in the relict Jornada II soil (−1.4 to −0.2‰) and the Jornada II palaeosol (−2.3 to −1.1‰) buried by the much younger (≤7 ka) Organ Alluvium deposit, suggest that vegetation at piedmont Sites 1 and 3, in contrast to Site 2, had a large component of C_4 plants throughout the period of carbonate accumulation over the last 23 ky. Given the uncertainty associated with the carbonate radiocarbon dates, and a radiocarbon age of >20 ka for only one carbonate sample in these two soils, it is possible that the $\delta^{13}C$ values of the carbonates in these piedmont soils formed after the initial shift (24.5–21 ka) to increased C_4 vegetation identified at Site 2. The vegetation at all piedmont sites appears to have retained a large component of C_4 plants from the time of the initial shift in vegetation C_3:C_4 through to the end of accumulation of the youngest soil carbonates (4–3 ka).

5.2.2. Lower La Mesa relict soil

Radiocarbon dating of the Lower La Mesa soil carbonate samples documents that they are not contemporaneous but rather record carbonate precipitation over a period of at least 13 ky duration (~18–4.5 ka) (Fig. 3). Similarly to the piedmont soils, it is a poor assumption to assume invariant climatic conditions over this time period. The carbonate $\delta^{13}C$ values from the Lower La Mesa relict soil (Site 4) exhibit a trend towards overall more positive $\delta^{13}C$ values during the period of carbonate accumulation (~18–4.5 ka) (Fig. 4). This trend implies either an increase in C_4 contribution to the local flora or a decrease in C_3 vegetation density and associated decreased soil respiration rates during the latest Pleistocene through mid-Holocene. Significantly, this temporal trend in soil carbonate $\delta^{13}C$ values is recorded by laterally equivalent samples at various depths down to 90 cm. The contribution of atmospheric CO_2 to total soil CO_2, and thus the effect on the $\delta^{13}C$ values of soil carbonates has been shown to be minimized at depths below 20–40 cm in desert soils (Quade et al., 1989; Cerling and Quade, 1993). Thus, an increase in C_4 contribution to the local ecosystem as the source of increased carbonate $\delta^{13}C$ values in the Lower La Mesa soil through the latest Pleistocene–Holocene period is favoured. This palaeoecologic reconstruction parallels that drawn from the $\delta^{13}C$ values of carbonates and organic matter in the piedmont soils.

Radiocarbon dating of the Lower La Mesa soil carbonates allows us to identify penecontemporaneous sets, where the assumption of near constant soil conditions may be more valid. There are three sets of penecontemporaneous soil carbonates (carbonate radiocarbon ages within 700 yr of each other) from various depths in the Lower La Mesa soil, which can be used to assess the validity of this palaeoecologic reconstruction. The set of oldest soil carbonates (18.1–17.6 ka) formed at a similar depth (48–50 cm) in the Lower La Mesa soil and thus cannot be used to quantitatively model respiration rate. However, a 2‰ range in $\delta^{13}C$ values between contemporaneous samples from one carbonate nodule (Table 1) suggests that there was a significant component of atmospheric CO_2 at their depth of formation. The floral composition during this period cannot be constrained by the $\delta^{13}C$ values of the oldest soil carbonates beyond suggesting that: (1) it could have contained up to 100% C_3 plants with a variable contribution of atmospheric CO_2 due to varying vegetation density on the Lower La Mesa soil; or (2) it could have contained up to a 55% component of C_4 vegetation if the oldest soil carbonates with the most negative $\delta^{13}C$ values represent equilibrium fractionation with soil-respired CO_2 (assuming soil temperature present levels, and average $\delta^{13}C$ values for C_3 and C_4 vegetation in the study area — Table 2).

The two younger sets of penecontemporaneous carbonates (12–11 and 10–9 ka) offer samples from various depths in the Lower La Mesa soil (Fig. 3D). The intermediate-age carbonates (11.7–11.0 ka) are considered here to be statistically distinguishable in age from the younger set of penecontemporaneous carbonates (9.7–9.2 ka) given that the difference in their corrected average chronological ages (13.3 and 10.9 ka, respectively using methodology of Bard et al., 1993) is greater than the difference in their average measured radiocarbon ages (11.4 and 9.5 ka). Furthermore, correcting the measured carbonate radiocarbon ages for a contribution of ^{14}C-depleted CO_2 from decaying organic matter in the soil (Wang et al., 1996) would minimally impact the difference in the ages of the two penecontemporaneous sets given the mean residence times of organic matter (10^2 yr) measured in other contemporaneous soils from southern New Mexico (Connin et al., 1997a).

The difference in $\delta^{13}C$ value between penecontemporaneous samples from different depths is greater between the 10–9 ka set of samples (1.1‰) than the 12–11 ka sample set (0.6‰). This suggests a considerable decrease in soil respiration rate between the periods of accumulation of the two sets of samples. Thus the shift to more positive $\delta^{13}C$ values between 12 and 9 ka may not reflect a shift to increasingly C_4 dominated vegetation, but rather a shift to C_3 desert shrub vegetation, with an associated decrease in respiration rates. This conclusion is also indicated by the results of the application of Cerling's model to each of the two sample sets.

Cerling's model (1991) was used to delineate the best-fit model curves to the $\delta^{13}C$ values of the 12–11 and 10–9 ka sets of penecontemporaneous carbonates, and thus address to what degree changes in the C_3:C_4 vegetation ratio or variations in floral density and soil respiration rates governed the temporal trends defined by the $\delta^{13}C$ values of these soil carbonates (Fig. 7). The flux and $\delta^{13}C$ value of soil-respired CO_2 is derived from the curve that most closely fits the measured $\delta^{13}C$ values of each set of penecontemporaneous carbonates; a constant rate of soil-respired CO_2 production with depth is assumed. In modelling soil respired CO_2 $\delta^{13}C$ values and soil respiration rates we have taken into account the ± 0.2‰ analytical uncertainty of the measured soil carbonate $\delta^{13}C$ values, resulting in large and overlapping estimates of the ranges of possible %C_4 vegetation (Table 3). These ranges, however, overestimate the probable range of conditions throughout the period of accumulation of the carbonates, given that they are delimited by the statistically unlikely extremes of the analytical uncertainty of the carbonate $\delta^{13}C$ values. The bulk of the modelled values indicate a transition from an ecosystem with a significant proportion of C_4 vegetation at 12–11 ka (11–43% C_4) to effectively a pure C_3 ecosystem at 10–9 ka (based on average C_3 and C_4 vegetation $\delta^{13}C$ values for the study area; Table 2). A comparable shift to a

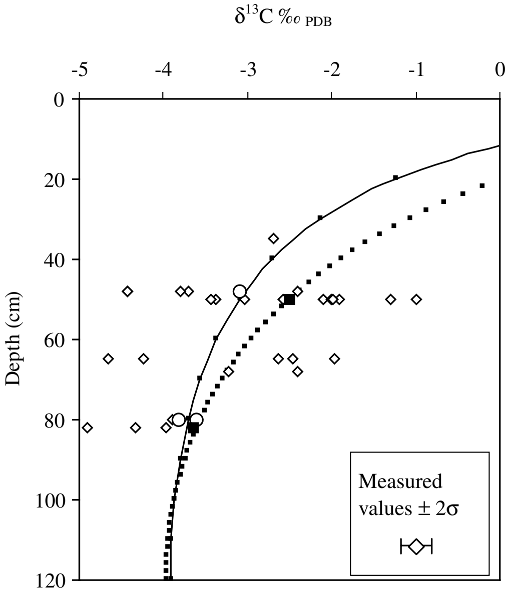

Fig. 7. Model results for the Lower La Mesa soil. Measured carbonate $\delta^{13}C$ values are shown as open diamonds, except for model input values. 12–11 ka carbonates: modelled values = solid line, measured values = open circles. 10–9 ka carbonates: modelled values = dotted line, measured values = closed squares. See Table 3 for input parameter values.

nearly pure C_3 ecosystem is not recorded by the carbonates $\delta^{13}C$ values of the piedmont soils.

A fourth set of Lower La Mesa soil carbonates differ in radiocarbon age by 1.1 ka (RC ages of 5.7 and 4.6 ka). If conditions remained effectively constant over the period of accumulation of these samples, the 1.6‰ difference in carbonate $\delta^{13}C$ values over a depth interval of only 15 cm would imply an extremely low respiration rate and an ecosystem dominated by C_3 desert vegetation. However, using Cerling's model to define a best-fit model curve for the measured $\delta^{13}C$ values of these youngest carbonates requires unrealistic input values for both production rate and $\delta^{13}C$ value of soil-respired CO_2 (<0.015 mmol/m^2/h and <-40‰, respectively). This may reflect a rapid shift to C_4 vegetation within the period of accumulation of these dated carbonates. This interpretation is supported by the >1‰ range in the $\delta^{13}C$ values of microsamples from one carbonate nodule in this set (Table 1). If the most negative $\delta^{13}C$ values of microsamples from the nodules containing the 5.7 and 4.6 ka microsamples are modelled (Table 1), then the best fit curve indicates $\delta^{13}C$ values of soil-respired CO_2 of -24.0 to -22.5‰, which implies an ecosystem of 0–23% C_4 vegetation overlying the Lower La Mesa soil between ~6 and 4.5 ka (Table 3).

In summary, the $\delta^{13}C$ values of carbonates in the Lower La Mesa soil can be interpreted to record an evolving associated ecosystem that: (1) at ~18 ka was C_3-dominated ($\ll 55\%$ C_4 plants); (2) likely evolved through the period to ~12–11 ka to include a larger component of C_4 vegetation (11–43% C_4); (3) underwent a subsequent shift to a near complete C_3 flora at ~10–9 ka; and (4) potentially returned to a C_3:C_4 mix (up to 23% C_4) at 6–4.5 ka. This interpreted palaeoecologic history for the Lower La Mesa soil is more complex than the trend defined by the carbonates from the piedmont soils.

5.2.3. Comparison of carbonate $\delta^{13}C$ proxy records

The carbonate $\delta^{13}C$ values exhibit relatively little difference between piedmont soils compared to the difference between the piedmont soils and the Lower La Mesa soil. Other studies of late Quaternary soil carbonates in southern New Mexico (Cole and Monger, 1994; Monger et al., 1998; Buck and Monger, 1999) have found comparable variations in carbonate $\delta^{13}C$ records between sites, both within and between different geomorphic settings. Monger and others (1998) observed maximum temporal variability in carbonate $\delta^{13}C$ values in mid-piedmont soils, and minimal variability in distal piedmont soils. These observations are analogous to the trends observed in the buried (proximal) and relict (distal) soils of this study. The lack of any recorded shift in C_3:C_4 vegetation at distal piedmont sites could reflect that soil conditions at distal piedmont settings fluctuated less than at middle to proximal piedmont settings. This view is supported by pollen studies, which suggest that vegetation at the distal piedmont sites was less variable than at the proximal piedmont soils (Monger et al., 1998).

The $\delta^{13}C$ values of previously studied Quaternary soil carbonates in southern New Mexico record a long-term trend that is similar to that defined by the pedogenic carbonates in the studied piedmont soils: (1) the oldest soil carbonates (>21 ka) record minimum values; and (2) a shift to more positive $\delta^{13}C$

Table 3
Best-fit input values for modelling soil carbonate $\delta^{13}C$ values

Age range of samples (ka)	Carbonate sample depth (cm)	$\delta^{13}C$‰$_{PDB}$ of soil carbonate ($\pm 2\sigma$)	Soil temp (°C)	Atmospheric pCO_2[a] (ppmV)	Respiration rate (range)[b] (mmol/m^2/h)	$\delta^{13}C$‰$_{PDB}$ soil respired CO_2 (range)[b]	%C_4 (range)[c]
12–11	50	−3.1 ($\pm 2\sigma$)	15–27	230–250	0.7–0.4 (0.1 to 1.4)	−21.1 to −20.2 (−24.3 to −18.0)	11–43 (0–8 to 40–54)
	80	−3.7 ($\pm 2\sigma$)					
10–9	50	−2.5 ($\pm 2\sigma$)	15–27	245–255	0.1 to 0.15 (0.02 to 0.15)	−25.3 to −24.9 (−39.9 to −20.5)	0–2 (0 to 21–40)
	82	−3.6 ($\pm 2\sigma$)					
6–4.5	50	−2.0 ($\pm 2\sigma$)	15–27	250–270	0.14 (<0.01 to 0.8)	−24.0 to −22.5 (<−40 to −17.6)	0–23 (0 to 49–64)
	65	−2.6 ($\pm 2\sigma$)					

[a] From ice core measurements of pCO_2 (Barnola et al., 1987), using calibrated RC ages (as in Bard et al., 1993); calculated from elevation of Lower La Mesa (1240 m) above sea level.

[b] Extremes of ranges come from modelling shallower sample $\delta^{13}C$ value +0.2‰ with the deeper sample $\delta^{13}C$ value −0.2‰, and vice versa.

[c] Reconstructed using average $\delta^{13}C$ values ($\pm\sigma$) for local C_3 and C_4 vegetation (Table 2). Other inputs: atmospheric pressure (0.85 atm) calculated from elevation of Lower La Mesa (1240 m) above sea level. $\delta^{13}C$ value of atmospheric CO_2 (−6.5‰$_{PDB}$) is the pre-industrial value (Friedli et al., 1986). CO_2 production depth (120 cm) is the depth to the impermeable petrocalcic horizon in the Lower La Mesa soil. Porosity range (0.4–0.5) estimated for medium to fine grained desert soil (Brady, 1990; Cerling, 1991).

values prior to 17 ka (Monger et al., 1998; Buck and Monger, 2000). Moreover, a subsequent shift to negative $\delta^{13}C$ values (by up to 6–10‰) which began between 18 and 8 ka and reached minimum $\delta^{13}C$ values between 10.8 and 4 ka is recorded by some Quaternary soils in the study region (Cole and Monger, 1994; Monger et al., 1998; Buck and Monger, 2000). This negative shift in $\delta^{13}C$ values coincides with the discontinuity between the Isaacks' Ranch or Jornada II palaeosols and the overlying Organ Alluvium soil (<7 ky old). The negative $\delta^{13}C$ shift is interpreted to record a transition from C_4 grasses to C_3 desert shrub vegetation, with a consequent decrease in plant density. This negative $\delta^{13}C$ shift in carbonate $\delta^{13}C$ values is not recognized in the studied piedmont soils (Fig. 4), but an analogous negative shift in soil CO_2 $\delta^{13}C$ values is suggested by best-fit model results of Lower La Mesa soil carbonates with of RC ages 10–9 ka (Fig. 7; Table 3). The variability in duration and timing of the negative shift in $\delta^{13}C$ values recorded by previously studied carbonates and by the Lower La Mesa carbonates may reflect the existence of more than one negative shift in $\delta^{13}C$ values in response to fluctuations in vegetation over the period from >12–4 ka (cf. Smith and McFaul, 1997; Gustavson and Holliday, 1999). Resolution of this issue is limited by the fact that a considerable portion of this temporal interval (>12–4 ka) is typically incorporated in the stratigraphic discontinuity between the Isaacks' Ranch or Jornada II palaeosols and the overlying Organ Alluvium soil.

The potential return to a component of C_4 vegetation in the local floral ecosystem, which is tentatively documented in the Lower La Mesa soil between 6 and 4.5 ka is recognized in studies of other Quaternary carbonates and organic matter from southern New Mexico soils (Cole and Monger, 1994; Connin et al., 1997a; Monger et al., 1998; Buck and Monger, 1999).

5.3. Secular climate variations reconstructed from the soil carbonate oxygen isotope record

5.3.1. Factors controlling the $\delta^{18}O$ composition of carbonates in desert soils

Previous studies have suggested that the $\delta^{18}O$ composition of pedogenic carbonate can be used as a proxy for the $\delta^{18}O$ composition of local meteoric water (Cerling, 1984; Cerling and Quade, 1993; Liu et al., 1995; Amundson et al., 1994a, 1996, 1998; Hsieh et al., 1998a). This interpretation must be applied with caution, however, given that the $\delta^{18}O$ values of pedogenic carbonates can record the effects on the $\delta^{18}O$ composition of soil water of diffusion of atmospheric CO_2, evapotranspiration, elevated soil temperatures, and re-equilibration due to dissolution–reprecipitation (Pendall et al., 1994; Liu et al., 1995; Amundson et al., 1996, 1998; Hsieh et al., 1998a,b). Furthermore, the major factors affecting the $\delta^{18}O$ values of soil carbonates (e.g. air temperature, soil temperature, distance from moisture source, precipitation seasonality, elevation) can combine to produce a minimal net change in soil carbonate $\delta^{1818}O$ value in response to significant climate change (Liu et al., 1996; Monger et al., 1998).

The pedogenic carbonate $\delta^{18}O$ values in the study area define two trends: (1) a broad distribution of values at shallow depths that is interpreted to record evaporation of soil waters; and (2) decreasing $\delta^{18}O$ values of penecontemporaneous carbonates with depth (Fig. 5). Studies of Quaternary soils from the Mojave Desert (Quade et al., 1989; Amundson et al., 1996) that formed under similar climatic conditions indicate that the degree of evaporative enrichment, however, may be minor at depths >50 cm in desert soils. The clustering of $\delta^{18}O$ values of penecontemporaneous carbonates from depths >50 cm in the studied soils suggests that they reflect bulk soil water $\delta^{18}O$ compositions. We suggest that the most negative $\delta^{18}O$ values of sets of penecontemporaneous carbonates from depths of >50 cm in the soils can be used to estimate temporal variations in the $\delta^{18}O$ composition of meteoric water in the region throughout the period of carbonate accumulation. Moreover, the range in the $\delta^{18}O$ values of penecontemporaneous carbonates from different depths in a given soil provides an indication of the extent of evaporative enrichment of soil water in each soil.

5.3.2. Palaeoenvironmental reconstructions from soil carbonate $\delta^{18}O$ values

The $\delta^{18}O$ values of carbonates in the studied soils exhibit a high degree of homogeneity between soils from different geomorphic positions regardless of the duration of pedogenesis. Carbonates from discrete horizons in the Isaacks' Ranch and Lower La Mesa soils exhibit similar temporal trends in $\delta^{18}O$ values (Fig. 5). This reflects the lack of correlation between age and depth of pedogenic carbonates in the studied soils. The $\delta^{18}O$ values of the piedmont soil carbonates are generally more negative than penecontemporaneous carbonates from the Lower La Mesa soil. This likely reflects the significantly higher permeability and coarser grained parent material of the piedmont soils in comparison to the Lower La Mesa soil, which would have promoted shorter residence times of soil waters in the piedmont soils (Liu et al., 1995).

The $\delta^{18}O$ values of pre-glacial maximum carbonates (RC ages > 18 ka) at all depths in all studied soils are tightly clustered. This suggests soil waters underwent minimal evaporation and thus the carbonate $\delta^{18}O$ values are a reasonable proxy of the $\delta^{18}O$ composition of local meteoric water. A low level of evaporation is consistent with reduced temperature during the period preceding the glacial maximum. The $\delta^{18}O$ values of carbonates from the piedmont soils that formed near the last glacial maximum (RC ages of 18–15 ka) are slightly more negative than those of pre-glacial maximum carbonates; $\delta^{18}O$ values reach minimum values in soil carbonates with RC ages of 15–9 ka (Fig. 6). This shift to slightly more negative carbonate $\delta^{18}O$ values may reflect an increase in temperature during deglaciation. In contrast, the overall more positive $\delta^{18}O$ values of carbonates from the Lower La Mesa soil and the large range in $\delta^{18}O$ values of penecontemporaneous carbonates most likely record variable evaporation of soil waters rather than the $\delta^{18}O$ composition of the meteoric water.

The increasing difference between the $\delta^{18}O$ values of penecontemporaneous samples from multiple depths in the Lower La Mesa soil provides an indication that evaporation (and by implication temperature) increased between 12 and 9 ka (Fig. 6). A trend of decreasing carbonate $\delta^{18}O$ values with depth in a soil could be interpreted to record the deeper penetration of ^{18}O-depleted winter precipitation into soils than that of summer precipitation (Quade et al., 1989; Liu et al., 1995). This is an unlikely explanation for the present study region, given that the ^{18}O-enriched summer rainfall in the study region currently penetrates soils to a greater depth than the ^{18}O-depleted winter precipitation, which is less abundant (Gile and Grossman, 1979; Parker et al., 1983). A past reversal of this situation would be an indication of a change in dominant moisture source.

There is a pronounced shift to less negative $\delta^{18}O$ values between carbonates with RC ages 9 and 6 ka. The shift to more positive $\delta^{18}O$ values in the youngest soil carbonates (RC ages of <6 ka) may indicate the continuation of the warming trend interpreted from the $\delta^{18}O$ values of carbonates of RC ages 12–9 ka. Alternatively, the 9–6 ka shift in $\delta^{18}O$ values may indicate that the glacial and late glacial meteoric water in New Mexico had an isotopic signature distinct from modern meteoric water. Gulf of Mexico-sourced summer precipitation currently has a $\delta^{18}O$ value ~10‰ higher than that of Pacific-sourced winter precipitation in central New Mexico (Pendall, unpublished data, cited in Connin et al., 1997b). If a comparable isotopic distinction between the two moisture sources were present throughout the time of accumulation of these carbonates, a shift in the seasonality and/or source of precipitation would have had a marked effect on their $\delta^{18}O$ value.

5.3.3. Comparison with other soil carbonate $\delta^{18}O$ proxy records

Soil carbonate $\delta^{18}O$ records over the past 18 ky for the North American Southwest are characterized by a generally low degree of variation in $\delta^{18}O$ values (Cole and Monger, 1994; Liu et al., 1996; Monger et al., 1998; Buck and Monger, 1999). However, a few soil profiles from other studies show parallel temporal trends in carbonate $\delta^{18}O$ values to those presented here. Carbonates from rapidly buried soils in the Hueco Mountains, New Mexico record a shift to more negative $\delta^{18}O$ values sometime between 19 and 11 ka followed by a shift to more positive $\delta^{18}O$ values throughout the Holocene (Monger et al., 1998). Other soils from southern New Mexico that do not record a $\delta^{18}O$ minimum between 15 and 9 ka do exhibit a progressive shift towards more positive $\delta^{18}O$ values after 6 ka (Buck and Monger, 1999). However, none of these studies have identified the trend illustrated by the $\delta^{18}O$ record in this study of increasing evaporation and/or temperature in samples of late glacial age.

Discrepancies between this and other soil carbonate studies from the desert Southwest may reflect differences in the types of soils sampled and sampling resolution. Firstly, this study minimised the size of stable and radiocarbon isotope samples, and sampled in conjunction with a detailed petrographic study (Deutz et al., 2001). Previous work is based on standard ^{14}C dates (Cole and Monger, 1994; Monger et al., 1998; Buck and Monger, 1999), whereas the use of AMS ^{14}C dates in this study enabled the minimisation of ^{14}C sample size. Thus crystals combined in an AMS ^{14}C sample likely accumulated over a much shorter time interval than the greater number of crystals required for standard ^{14}C dating. Moreover, Liu and others' (1996) did not directly date carbonate samples, but assumed them to be similar in age to the deposits in which they were found. Secondly, in this study detailed sampling of individual soil profiles identified irregular relationships between carbonate age and depth and in particular identified penecontemporaneous samples from multiple depths in a given soil. This revealed a trend towards increasing evaporation, and therefore temperature, in the Late Wisconsinan. Thirdly, this study included relict soils exposed to carbonate accumulation over an extended period (<900 ky). Although rapid burial of a soil can preserve a pedogenic carbonate record that has not been overprinted geochemically (Buck and Monger, 1999), burial can be preceded by soil truncation, producing a hiatus in the record (cf. Liu et al., 1996; Monger et al., 1998). Carbonates in relict and slowly buried soils may thus provide a more complete palaeoenvironmental and/or palaeoclimate record given that prolonged exposure allows for the continuous accumulation of pedogenic carbonates so long as the soil moisture balance remains favourable to carbonate precipitation. Interpretation of complex stable isotopic trends in such soils, however, requires a high-resolution chronologic framework, such as the radiocarbon age framework used in this study.

5.4. Comparison of $\delta^{18}O$ and $\delta^{13}C$ records

The initial transition to an ecosystem with a significant component of C_4 vegetation appears to have occurred prior to 21 ka and continued thereafter in some soils. This initial shift in $\delta^{13}C$ values was not accompanied by a shift in $\delta^{18}O$ values. Between 12 and 9 ka the Lower La Mesa soil (Site 4) recorded a transition to effectively 100% C_3 vegetation, with a low respiration rate characteristic of desert soils. A change in climate producing increased temperatures and evaporation likely drove the transition to drought resistant C_3 vegetation. This is suggested by the soil carbonate $\delta^{18}O$ values, which indicate a trend towards progressively increasing temperatures and evaporation of soil waters during the period 12–9 ka.

The significant shift in carbonate $\delta^{18}O$ values recorded in all the soils in this study between 9 and 6 ka precedes a shift to less negative carbonate $\delta^{13}C$ values observed in this and other studies in carbonates with RC ages 6–3 ka (Cole and Monger, 1994; Connin et al., 1997a; Monger et al., 1998; Buck and Monger, 1999). The interpreted increasing proportion of C_4 vegetation in the local flora, with its requirement for summer moisture, suggests that the shift in carbonate $\delta^{18}O$ values between 9 and 6 ka most likely reflects a transition from glacial precipitation patterns to the present pattern with predominantly summer precipitation sourced from the Gulf of Mexico.

5.5. Comparison with non-carbonate environmental records

Allowing for the uncertainty associated with the measured carbonate radiocarbon ages, the oldest soil carbonates (25–17 ka) likely formed during Middle to late Wisconsinan glaciation. Glacial-age vegetation in the study region, based on the packrat midden record, consisted of piñon–juniper woodland, with a minor component of C_4 grass, rather than the present desert shrub-C_4 grassland flora (Van Devender and Spaulding, 1979; Van Devender, 1995). In contrast, this and previous studies of carbonate and herbivore tooth $\delta^{13}C$ values have documented a significant increase in the amount of C_4 vegetation in the North American Southwest during the glacial and late glacial (Cole and Monger, 1994; Liu et al., 1996; Monger et al., 1998; Connin et al., 1998; Buck and Monger, 1999). This discrepancy in the carbonate, tooth enamel and packrat records likely reflects the selective diets of herbivores (grass) and packrats (woody plants) coupled with their formation at different elevations (Van Devender, 1995; Connin et al., 1998; Buck and Monger, 1999).

The tight clustering of carbonate $\delta^{18}O$ values (RC ages > 18 ka) and lack of a transition in soil carbonate $\delta^{18}O$ values in this study to accompany the initial (pre-21 ka) transition in $\delta^{13}C$ values may be accounted for by ice core evidence that the temperature minimum associated with Wisconsinan glaciation occurred at approximately 25 ka, preceding maximum glaciation (21–18 ka) by several ky (Johnsen et al., 1992). Van Devender's (1990) study of packrat middens in southern New Mexico suggests that the climate in the study area was cooler than present-day for several ky prior to the last glacial maximum. The reduced summer temperatures, which appear to have characterised glacial times (Bryson and Hare, 1974; Van Devender, 1990), would have dampened the intensity of, or eliminated, the thermally induced summer monsoon fed by Gulf of Mexico waters (Tang and Reiter, 1984). In addition to the effects of decreased air and soil temperatures and, a potentially decreased influence of Gulf moisture on the $\delta^{18}O$ values of the oldest soil carbonates, their $\delta^{18}O$ values may reflect that the $\delta^{18}O$ composition of surface seawater was ~1‰ more positive than at present from 32 to 13 ka (oxygen isotope stage 2; Shackleton and Opdyke, 1976).

The inferred increase in C_4 vegetation prior to 21 ka is difficult to reconcile with the decrease in summer precipitation inferred from the packrat midden record during this time period (Van Devender, 1995; Connin et al., 1998). The increase in C_4 vegetation may have been influenced by a decrease in atmospheric pCO_2, which would advantage plants utilising the C_4 photosynthetic pathway over those utilising the C_3 photosynthetic pathway (Ehleringer et al., 1997). Nevertheless, a source of summer moisture would have been required to support C_4 vegetation. The reduction of monsoonal intensity, coupled with strengthening of westerly mid-latitude atmospheric circulation in response to growth of the Laurentide ice sheet, would have enhanced the potential for Pacific moisture to reach the study region (Kutzbach and Wright, 1985). Pacific-sourced storms currently characteristic of the winter months may have commenced earlier in the autumn and continued later in the spring than under present-day conditions (Van Devender and Spaulding, 1979; Pendall et al., 1999). Significantly, spring precipitation influences C_4 productivity under present climate conditions (Peters et al., 1997). The decrease in surface temperatures, and decreased soil water evaporation inferred from carbonate $\delta^{18}O$ values in this study as well as the packrat midden record (Van Devender, 1990) suggest that glacial age summers may have had a greater effective moisture than present, despite reduced summer precipitation. Conversely, tropical storms, currently originating off the southwest coast of Mexico, have been proposed as a possible non-monsoonal source of summer moisture for the North American Southwest (Connin et al., 1998). These storms do not currently reach New Mexico, but changes in atmospheric circulation associated with the glacial could potentially have drawn associated moisture from the Pacific into New Mexico (Connin et al., 1998; cf. Reyes and MejÍa-Trejo, 1991).

The 15–9 ka carbonates likely accumulated during the Late Wisconsinan to the very earliest Holocene. A decrease in mesic vegetation (e.g. decline in piñon pine relative to juniper) in late glacial packrat midden samples has been interpreted as an indication that winter precipitation decreased and temperature increased by ~11 ka before the establishment of the monsoon brought an increase to summer precipitation (Van Devender and Spaulding, 1979; Van Devender, 1990).

Soil carbonate $\delta^{13}C$ records from this and other studies (Cole and Monger, 1994; Liu et al., 1996; Monger et al., 1998; Buck and Monger, 1999) indicate a shift to C_3 vegetation and decrease in soil respiration rate at some sites at the Pleistocene–Holocene boundary. This shift in vegetation along with widespread soil truncation and burial proximal to the Pleistocene–Holocene boundary (Monger et al., 1998; Buck and Monger, 1999) suggests that desert shrub plants had replaced woodland as the C_3 component of vegetation by the earliest Holocene at the sites studied. Although both the packrat midden records and soil carbonate $\delta^{13}C$ records indicate decreasing effective moisture during the late glacial, the different records record this shift in C_3 vegetation to variable degrees (e.g. the piedmont soil carbonates do not record a shift to desert shrub vegetation between 12 and 9 ka). This likely reflects the variable levels of aridity associated with different elevations and soil types. Furthermore, the $\delta^{18}O$ record presented by this study is also in accordance with packrat midden and pollen studies indicating that regional temperature had started to increase and effective moisture levels decrease by 11 ka (e.g. Van Devender and Spaulding, 1979; Van Devender, 1990). The $\delta^{18}O$ values of the ≤ 12 ka samples may also reflect a negative shift in the $\delta^{18}O$ composition of surface seawater ~13 ky ago towards modern seawater values ($\delta^{18}O_{SMOW} = 0‰$) (Shackleton and Opdyke, 1976).

Regional ecosystem and palaeoclimate reconstructions based on pack-rat middens (Van Devender, 1990), pollen (Vierling, 1998), the δD values of tree cellulose (Friedman et al., 1988) and climate modelling (Bartlein et al., 1998) indicate that the present monsoonal circulation was established by ~10–8 ka in response to increased summer surface temperatures with the onset of deglaciation (Van Devender, 1990). The packrat midden records suggest that grasslands appeared in southern New Mexico at 8 ka, earlier than the post-6 ka timing indicated by this and other soil carbonate studies (Buck and Monger, 1999). The apparent difference in timing may reflect actual differences in the timing of vegetation change at packrat midden sites versus soil sites or may be an artefact resulting from: (1) greater temporal resolution of the packrat midden record; (2) imprecision in radiocarbon dating of packrat midden samples and/or soil carbonates; and/or (3) a hiatus in the carbonate record (owing to soil truncation and burial noted above). However, the shift to more positive carbonate $\delta^{18}O$ values observed in this study between 9 and 6 ka is compatible with the shift in precipitation source inferred from the packrat midden record.

In summary, the carbonate $\delta^{13}C$ record presented in this and previously published soil studies in the New Mexico region records a glacial to late glacial increase in C_4 vegetation, in contrast to the packrat midden record. The pronounced late Pleistocene–earliest Holocene aridity and the re-appearance of C_4 plants after 6 ka inferred from this and other studies using the carbonate $\delta^{13}C$ record are broadly in accordance with the packrat midden record. Overall the carbonate $\delta^{18}O$ record in conjunction with the packrat midden and other plant fossil records indicates: (1) Pacific-sourced precipitation during the glacial maximum and late glacial; (2) increasingly xeric conditions at the late Pleistocene–Holocene boundary; and (3) a transition to Gulf of Mexico-sourced summer precipitation between 10 and 8 ka.

6. Conclusions

This study of Late Pleistocene and Holocene buried (palaeosols) and relict soils from the Rio Grande Rift region of New Mexico documents the evolution of pedogenic carbonates in soils characterized by a range of burial rates and durations of pedogenesis. Several of the soils presented in this paper are associated with geomorphic surfaces that have been stable for a prolonged period of time. Changes in environmental and climatic conditions during their prolonged exposure periods have resulted in moderate to extensive isotopic overprinting of the soil carbonates. Coupled high-resolution radiocarbon dating and stable isotope analysis of carbonate nodules and clusters in these fine-grained soils illustrates their complex stable isotope records but also documents the potential of carbonates in relict and slowly buried soils as reliable proxies of palaeoecologic and palaeoclimate change. Thus, in regions characterized by a paucity of other palaeoecologic and palaeoclimate proxies, high-resolution stable and radiogenic isotope studies of carbonates such as the one presented here do allow for palaeoenvironmental reconstructions of temporal resolution comparable to that provided by other independent proxy records.

Soil carbonate $\delta^{13}C$ values in the studied soils are interpreted to record: (1) an increase in C_4 vegetation during glaciation and prior to deglaciation; (2) desert flora (C_3 predominantly) was established in the study region by ~10–9 ka; and (3) the C_4 component of local vegetation increased after 6 ka. Soil carbonate $\delta^{18}O$ values record: (1) a progressive increase in aridity beginning at ~12 ka; and (2) a change in moisture source and/or seasonality between 9 and 6 ka. This study presents a soil carbonate $\delta^{18}O$ record compatible with the plant fossil derived climate record in conjunction with a soil carbonate $\delta^{13}C$ record in accordance with other recent $\delta^{13}C$ records which indicate a significant presence of C_4 vegetation during the glacial and late-glacial.

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