

MORPHOLOGY AND STABLE AND RADIOGENIC ISOTOPE COMPOSITION OF PEDOGENIC CARBONATES IN LATE QUATERNARY RELICT SOILS, NEW MEXICO, U.S.A.: AN INTEGRATED RECORD OF PEDOGENIC OVERPRINTING

PAULINE DEUTZ¹, ISABEL P. MONTAÑEZ², AND H. CURTIS MONGER³

¹ Department of Geography, University of Hull, Hull, HU6 7RX, U.K.

² Department of Geology, University of California, Davis, California 95616, U.S.A.

e-mail and correspondence to: montanez@geology.ucdavis.edu

³ Department of Agronomy and Horticulture, New Mexico State University, Las Cruces, New Mexico 88003, U.S.A.

ABSTRACT: This petrographic and stable ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) and radiogenic (^{14}C) isotope study of pedogenic carbonates from late Quaternary soils in the Rio Grande Rift region of New Mexico documents that carbonate formation in semiarid to arid soils (Aridisols) occurs principally by overprinting and can result in a complex petrographic and isotopic record. With increasing duration of exposure (< 7 to 900 ky) of the four studied profiles, pedogenic carbonates exhibit: (1) an increase in the degree of intraprofile $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ heterogeneity, (2) increased development of down-profile $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ trends, (3) an increase in the degree of intermorphologic and intramorphologic stable-isotope variation, commonly in samples distributed laterally within narrow depth intervals, and (4) development of covariation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. Radiocarbon ages of the carbonates permit assessment of the degree of isotope heterogeneity in *contemporaneous* carbonates and recognition of temporal isotopic trends.

The range of exposure times recorded by the studied soils are analogous to those associated with the formation of fossil soils. This makes the studied soils ideal for evaluating the origin of stable-isotope heterogeneity in paleosol carbonates and the implications of those heterogeneities for the use of stable isotopes as paleoenvironmental proxies. Specific implications of this study include the following: (1) Pedogenic carbonates that form by overprinting are a cumulative record of the soil conditions present during their accumulation; thus, isotope analysis of overprinted carbonates can result in "time averaging" of changing climatic, paleoenvironmental, and paleoecologic conditions. (2) Carbonates may record only a fraction of the duration of development of their host profile. (3) There is a high level of uncertainty associated with using the sequence of morphologic development of carbonate as a function of time or maturity in paleosols. (4) An exponential decrease in carbonate $\delta^{13}\text{C}$ values with depth in a paleosol does not imply that the carbonates are contemporaneous or accumulated under invariant soil conditions. (5) Shifts in soil and paleoclimatic conditions may be recorded by the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonates distributed within narrow depth intervals of a given soil in addition to those distributed down-profile, or even from within individual carbonate samples.

INTRODUCTION

In recent years, the stable-isotope composition and depth of accumulation of pedogenic carbonates in paleosols has been increasingly applied to reconstructions of regional paleoprecipitation and paleoatmospheric circulation patterns (Retallack 1994; Caudill et al. 1996; Amundson et al. 1998; White et al. 2001), spatial and temporal evolution of paleofloral communities (Cole and Monger 1994; Quade et al. 1995; Wang et al. 1996; Latorre et al. 1997; Monger et al. 1998; Deutz et al. 2001), and paleoatmospheric $p\text{CO}_2$ and CO_2 $\delta^{13}\text{C}$ values (Cerling 1991; Mora et al. 1996; Ekart et al. 1999). Despite the potential of pedogenic carbonates as quantitative paleoenvironmental and paleoclimate proxies, the mechanism and timing of their formation, and the influence of these on their stable-isotope compositions, remain poorly documented.

This paper integrates the macromorphologic and micromorphologic characteristics and stable ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) and radiogenic (^{14}C) isotope compositions of pedogenic carbonates from late Quaternary soils in the Rio Grande Rift region of New Mexico to document, in detail, the mechanism and timing of carbonate formation relative to the duration of pedogenesis of the host profiles. This paper builds on a previous study of these soils (Deutz et al. 2001) that defined the degree of heterogeneity in carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values within individual profiles, and used a ^{14}C chronologic framework to interpret the isotope variations as records of shifts in C_3/C_4 plant ratios and regional atmospheric circulation in the Rio Grande Rift region during the latest Pleistocene through Holocene.

The heterogeneous isotope compositions of these pedogenic carbonates, however, record "time averaged" records of environmental conditions given that the soil profiles in which they formed record a prolonged history (10s of thousands of years) of accumulation under changing soil and climatic conditions. Notably, the pedogenic carbonates from all studied profiles yield a similar range of radiocarbon ages (21 to 4 ka) despite differences of two orders of magnitude in duration of exposure (thousands to hundreds of thousands of years) of the individual profiles. This study documents a complex relationship between carbonate components and their morphologic development, depth of occurrence in the profile, and the soil age, providing a caveat for inferring paleosol maturity and sediment accretion rates in ancient alluvial sequences on the basis of genetic stage of pedogenic carbonate morphologic development. Given that the range of exposure times (10^3 to 10^5 yr) associated with the studied soils are similar to those associated with fossil soils documented throughout the Phanerozoic record (Retallack 1990; Mora and Driese 1999), the results of this study have implications for using the morphologies, intraprofile spatial distribution, and stable-isotope compositions of pedogenic carbonates for reconstructing paleo-ecosystem dynamics, paleoclimate conditions, and paleoatmospheric $p\text{CO}_2$.

GEOMORPHIC SETTING

Pedogenic carbonates from four unburied (herein referred to as "relict") soils in the Rio Grande Rift of south-central New Mexico were studied (Fig. 1). All of the soils developed in noncalcareous parent material, and under similar climatic conditions and associated vegetation (summarized in Deutz et al. 2001). Three of the soils are forming in alluvial fan ("piedmont") deposits derived from monzonites in the northern Doña Ana Mountains (Encina-Rojas 1995). Of the piedmont soils, two are developed in coarse-grained, proximal deposits of the Organ Alluvium and Isaacks' Ranch alluvium (Fig. 2A, B), whereas the third piedmont soil formed in finer-grained distal deposits of the Jornada II alluvium (Fig. 2C). The fourth soil developed in fine-grained, arkosic flood-plain sediments of the mid- to upper Pleistocene Camp Rice Formation underlying the Lower La Mesa geomorphic surface (Monger et al. 1991a) (Fig. 2D).

METHODS

A soil stratigraphic approach was utilized for describing and sampling the soils to evaluate their genesis and the origin of their carbonates. This

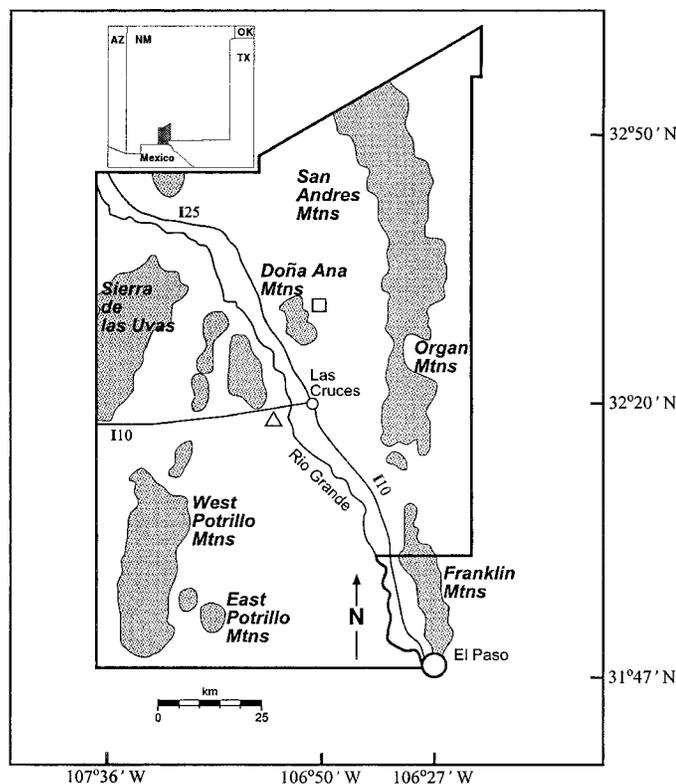


FIG. 1.—Location map of the study area in Doña Ana County, New Mexico (insert), U.S.A. Triangle = Lower La Mesa soil; square = location of the three piedmont soils. After Kottlowski (1965).

approach incorporated detailed descriptions and vertical and lateral sampling on a decimeter scale. Soil terminology and carbonate classification followed that proposed by the Soil Survey Staff (1992) and Machette (1985), respectively. Pre-excavated trenches were used; soil pit faces were dug back to provide a fresh surface for sampling. In order to provide a framework for sampling, existing field and laboratory soil descriptions for the excavated trenches were integrated with field logging of soil horizons (Wierenga et al. 1989; Monger et al. 1991a; Encina-Rojas 1995; Monger, unpublished data).

Various carbonate morphologies (nodules, filaments, carbonate clusters, and pebble coatings) were sampled, along with their surrounding matrix, for petrographic and geochemical analysis (Deutz 1997). Thin sections ($n = 53$) stained with Dickson's (1965) solution were analyzed by transmitted light and cathodoluminescence. Point counting of selected thin sections was carried out using a 50 μm spacing (minimum of 300 points per thin section or feature). Scanning electron microscopy of thin sections, grains, and nodule fragments was carried out on a Cambridge 360 SEM (Center for Electron Microscopy and Microanalysis, University of Southern California, and Dept. of Chemistry, University of Hull, U.K.). Gold-coated (2.5 minutes for grains, 30 seconds for thin sections) or carbon-coated samples (1 minute for grains) were analyzed at 5 to 15 kV.

Samples for geochemical analysis were isolated from carbonate features from which the outer 0.5 mm was previously removed to avoid contamination. Microsamples of petrographically homogeneous material (on a 500 μm scale) were collected using a binocular mounted dental drill equipped with a 0.25 mm drill bit. Multiple microsamples were taken from individual carbonate features that were considered to be, at a petrographic scale, homogeneous.

Carbonate microsamples were analyzed for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ at the University of Southern California on a V.G. Prism II mass spectrometer. Car-

bonate samples ($n = 65$) and standards were roasted at 380°C under vacuum for one hour to remove organic matter. Samples were subsequently dissolved in 100% orthophosphoric acid at 90°C. External precision (2σ) was $\pm 0.2\text{‰}$ for both carbon and oxygen. Aliquots (< 10 mg) of selected carbonate samples ($n = 19$) were analyzed for ^{14}C . Sampling strategy and details of analysis are presented in Deutz et al. 2001. The dates presented in this paper are uncalibrated "conventional" RC ages (Stuiver and Polach 1977).

SOIL PROFILES AND PEDOGENIC HISTORY

All four studied soils are classified as Aridisols on the basis of macro-morphologic and micromorphologic characteristics (Soil Survey Staff 1992). The soil developed in the proximal piedmont deposit of the Organ Alluvium is overlain by a 6-cm-thick deposit of siliciclastic alluvium ("C" horizon in Fig. 2A). Carbonates first occur at 33 cm below the surface in the Bk horizon, and include Stage I carbonate coatings and filaments. Stage I coatings extend downward into the Ck horizon, and are also present in the buried 2Btkb horizon of the underlying Jornada II paleosol. Stage II and Stage III carbonates are present in the 2Kb horizon of the underlying buried, Jornada II paleosol. An unaltered C horizon is not exposed at this site.

Carbonates in the soil developed within the proximal piedmont. Isaacks' Ranch deposits occur as Stage I filaments and coatings in the Btk horizon (42 cm below the profile surface; Fig. 2B). Stage II carbonate nodules and "clusters" (carbonate-coated pebbles surrounded by a loose fabric of disseminated carbonate grains; cf. "interpebble" carbonate of Gile and Grossman 1979) are developed in the underlying Bk horizon. A thin (15 cm) C horizon occurs at the base of the Isaacks' Ranch profile. In contrast, Stage I carbonates are absent in the soil developed in the distal piedmont Jornada II deposit. Stage II nodules are common in all horizons developed below 50 cm in the profile (Btk and Bk horizons in Fig. 2C). The level of apparent maturity and abundance of Stage II nodules increases with depth in the soil profile.

The Lower La Mesa soil (Fig. 2D) is developed to 4.5 m depth in the fine-grained fluvial deposits of the Camp Rice Formation (Monger et al. 1991a). Stage I filaments are developed throughout the Bk and Btk horizons. Stage II nodules occur at the base of the Bk horizon and in the underlying Btk horizon (Fig. 2D). Stages II and III nodules coexist towards the base of the Btk horizon. A Stage IV petrocalcic horizon consisting of an upper laminar carbonate (Bkm1 horizon) and an underlying plugged horizon (Bkm2 horizon) occurs at 1.2 m depth in the profile and overlies a Btk horizon with Stage III nodules.

Exposure History

The age of each deposit has been constrained by previous geomorphic and geochronologic studies. The youngest deposit in the study area, the Organ Alluvium, is estimated to have been deposited between 100 and 7,000 years ago with the maximum age constrained by a ^{14}C age of 6.4 ka from charcoal at the base of the deposit (Gile 1987). The Isaacks' Ranch deposit is estimated to have an age of between 8 and 15 ka on the basis of radiocarbon ages of charcoal and carbonates (Gile 1987; Monger, unpublished data). However, uranium trend dating of organic matter and carbonates in the Isaacks' Ranch deposit (Machette 1985), and an AMS ^{14}C age on pedogenic carbonate (this study) suggest a maximum age of up to 21 ka. The age of the oldest of the piedmont deposits, the Jornada II deposit, is estimated to be between 25 and 150 ka (Gile 1987), with the maximum age reflecting a uranium trend date of 130 ± 25 ka (Machette 1985). Judging from these age estimates, the soil developed in the Organ Alluvium deposit has been forming for up to the last 7 ky, the soil in the Isaacks' Ranch deposit has been forming since at least 7 ka to up to 21

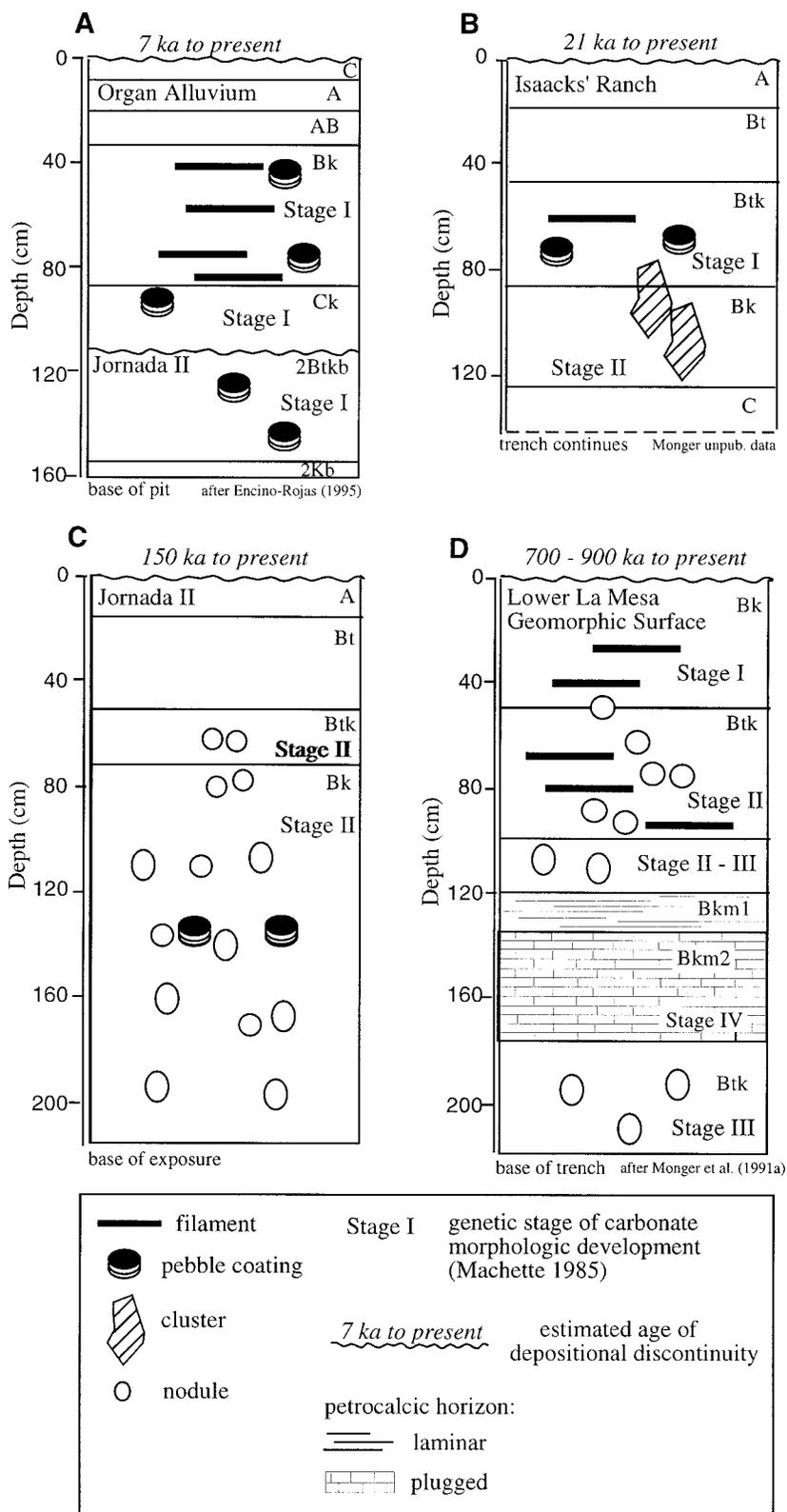


FIG. 2.—Soil stratigraphic chart of the four relict soils showing estimated exposure times, soil horizons, stage of carbonate accumulation, and the distribution of carbonate morphologies within each profile. **A)** Proximal piedmont soil developed in Organ Alluvium deposit, and underlying buried Jornada II soil, **B)** proximal piedmont soil developed in Isaacks' Ranch deposit, **C)** distal piedmont soil developed in Jornada II deposit, and **D)** soil developed in fluvial deposits under the Lower La Mesa geomorphic surface.

ka, and the unburied Jornada II soil has undergone pedogenesis since at least 25 ka and possibly since 150 ka.

The Lower La Mesa soil has been exposed at the surface over several Pleistocene glacial-interglacial climate cycles since the incision of the an-

cestral Rio Grande river between 730 to 900 ka (Monger et al. 1991a; Mack et al. 1993). Thus, at least three of the four studied soils (Isaacks' Ranch, Jornada II, and Lower La Mesa) have undergone prolonged exposure (> thousands of years) under a range of climate conditions and eco-

systems. We refer to all four soils as relict, and we consider them ideal candidates for evaluating overprinting of pedogenic carbonates.

CARBONATE MORPHOLOGIES

Five carbonate morphologies are recognized in the Rio Grande Rift relict soils. These are (1) matrix carbonate and associated filaments, (2) nodules, (3) carbonate clusters, (4) pebble coatings, and (5) a petrocalcic horizon developed within the Lower La Mesa soil. Details of the petrocalcic horizon are presented in Deutz (1997) and are not further discussed in this paper.

Matrix and Filaments

The disseminated carbonate referred to as matrix carbonate in the non-calcareous soils is interpreted to be the first stage of pedogenic carbonate accumulation rather than detrital carbonate. The presence of matrix carbonate is fundamental to the macromorphological stages of soil carbonate accumulation in noncalcareous soils (Gile et al. 1966; Wieder and Yaalon 1974, 1982). Disseminated carbonate makes up 1 to 10% of the matrix surrounding nodules in the soils (Fig. 3A). Matrix carbonate occurs as (1) peloids composed of aphanocrystalline calcite ($< 4 \mu\text{m}$ crystals) (Fig. 3B), (2) bundles or coatings composed of needle fibers, (3) isolated aphanocrystalline calcite crystals or clusters disrupting clay coatings, and (4) calcite coatings on clastic grains. Primary porosity typically makes up 9 to 12% of the total matrix. Carbonate-bearing matrix is typically less well indurated and darker in color than carbonate clusters with which it is commonly associated. Stage I carbonate filaments, which are typically associated with root hairs, occur in all of the soils.

Nodules and Transitional Carbonate

Stage II nodules can be divided into two types on the basis of the nature of their boundaries with the surrounding soil matrix. Orthic nodules (Fig. 3C) have gradational boundaries (Monger et al. 1991a; cf. Wieder and Yaalon 1974), whereas discrete nodules have distinct boundaries and thin coatings of illuvial clay (Fig. 3D) (cf. disorthic nodules of Wieder and Yaalon 1974). Nodules contain between 25 and 65% carbonate, with more highly indurated discrete nodules tending to have slightly higher carbonate contents than orthic nodules (Fig. 4). Orthic and discrete nodules are dominantly made up of subhedral to euhedral aphanocrystalline calcite (micrite) (Figs. 3D, F, 4), whereas more coarsely crystalline microspar ($> 4 \mu\text{m}$) and needle fiber calcite are generally limited to void-filling cement (Fig. 5A). Calcite crystals commonly have etched surfaces (Fig. 3F). Orthic and discrete nodules are interpreted to have formed *in situ* rather than having been reworked from older soils. This is because they contain clastic grains similar in size and mineralogy to the adjacent soil matrix, and the relative proportion of aphanocrystalline (2 to $4 \mu\text{m}$) calcite, which is interpreted to be pedogenic, increases linearly with increase in percent carbonate within individual nodules (Fig. 4).

Transitional carbonate (Fig. 3C) defines gradational boundaries of orthic nodules, and has a carbonate content between 10 and 25%, and color intermediate between that of nodule cores and surrounding matrix. Micron-size peloids composed of submicron calcite crystals are common in transitional carbonate. Micritic coatings on terrigenous grains and needle fiber calcite are more common in transitional carbonate than in the other carbonate morphologies.

Carbonate Clusters and Carbonate-Coated Pebbles

In the proximal piedmont soils, clusters are a common pedogenic carbonate morphology (Fig. 2). Clusters contain between 20 to 45% carbonate, and similarly to nodules, are composed mainly of aphanocrystalline calcite crystals. Crystals typically are subhedral to euhedral and have rhombic terminations (Fig. 5B). Channel porosity (tens of microns to 0.5 mm in

diameter), with occasional occluded organic roots, are common in clusters (Fig. 5C). Micron-size peloids are also a common component of carbonate clusters (Fig. 5D).

Carbonate-coated pebbles (< 0.5 cm in diameter) are a primary constituent of some carbonate clusters (e.g., Organ Alluvium and Isaacks' Ranch soils). Carbonate coatings typically are < 1 mm thick, range from discontinuous to continuous over the length of their development, and occur as single to multiple laminae developed on individual pebbles.

CARBONATE ACCUMULATION IN RIO GRANDE RIFT SOILS

The extent to which the textures and geochemical compositions of pedogenic carbonates preserve a record of change in soil conditions during their accumulation depends on whether overprinting or recrystallization is the dominant process of carbonate formation. Carbonate textures in the studied relict soils suggest that carbonate formed principally by overprinting rather than by recrystallization of existing calcite. Overprinting occurs by precipitation of overgrowths on previously precipitated carbonate crystals (cf. Cerling 1984; Amundson et al. 1994). Overprinting by addition of new carbonate occurs with no effect on the textures or geochemistry of the previously precipitated crystals. However, partial dissolution of carbonate crystals prior to subsequent precipitation of younger generations of pedogenic calcite can occur (i.e., overprinting with intermittent episodes of dissolution). Etched faces on a small percentage of euhedral crystals (Fig. 5B) and nonplanar crystal boundaries in the studied pedogenic carbonates are interpreted to record intermittent periods of dissolution during overall carbonate accumulation (cf. Wright and Peeters 1989).

Alternatively, previously precipitated pedogenic carbonate may undergo single or repeated events of recrystallization without a change in mineralogy. Although the driving mechanism for low-magnesium calcite recrystallization is unclear (Wright and Peeters 1989), previous studies have interpreted various soil carbonate textures as indicative of recrystallization (Sehgal and Stoops 1972; Knox 1977; Wieder and Yaalon 1982; Calvet and Julia 1983; Solomon and Walkden 1985; Monger et al. 1991a). Rapidly precipitated, aphanocrystalline soil carbonates potentially contain microstructural irregularities or trace-element inhomogeneities that may make them susceptible to recrystallization (Monger et al. 1991b; Wright and Tucker 1991; Verrecchia and Verrecchia 1994). In contrast to the process of overprinting, recrystallization of pedogenic carbonate imparts a change in the geochemical composition (cf., Montañez and Read 1992; Kupecz et al. 1993).

Several lines of evidence argue for overprinting as the main process of carbonate formation in the studied soils. Firstly, micrite is the dominant crystal type in all carbonate morphologies (Fig. 4), suggesting that pedogenic micrite formed during all stages of carbonate accumulation rather than during specific stages of development. Secondly, the presence in several carbonate morphologies of micron-size peloids composed of submicron crystals (Fig. 5D), which would be thermodynamically unstable because of their high crystal surface area, suggests limited recrystallization. Thirdly, the lack of inverse correlation between the abundance of microspar (crystals $> 4 \mu\text{m}$) and micrite, and lack of positive correlation between the abundance of microspar with degree of carbonate cementation (Fig. 4), does not support recrystallization (i.e., aggrading neomorphism) of pedogenic micrite.

Evidence of limited recrystallization of pedogenic calcite, however, exists in the clay-rich carbonate morphologies of these soils. The occurrence of micrite in some needle fiber bundles (Fig. 3E) is interpreted to reflect recrystallization of needle fiber calcite (cf. Calvet and Julia 1983; Solomon and Walkden 1985). Additionally, a small amount of void-filling microspar and calcite spar (crystals $> 50 \mu\text{m}$) in orthic and discrete nodules shows evidence of micritization.

In summary, the carbonate textures and microfabrics of the pedogenic carbonates from the Rio Grande Rift relict soils strongly support the hy-

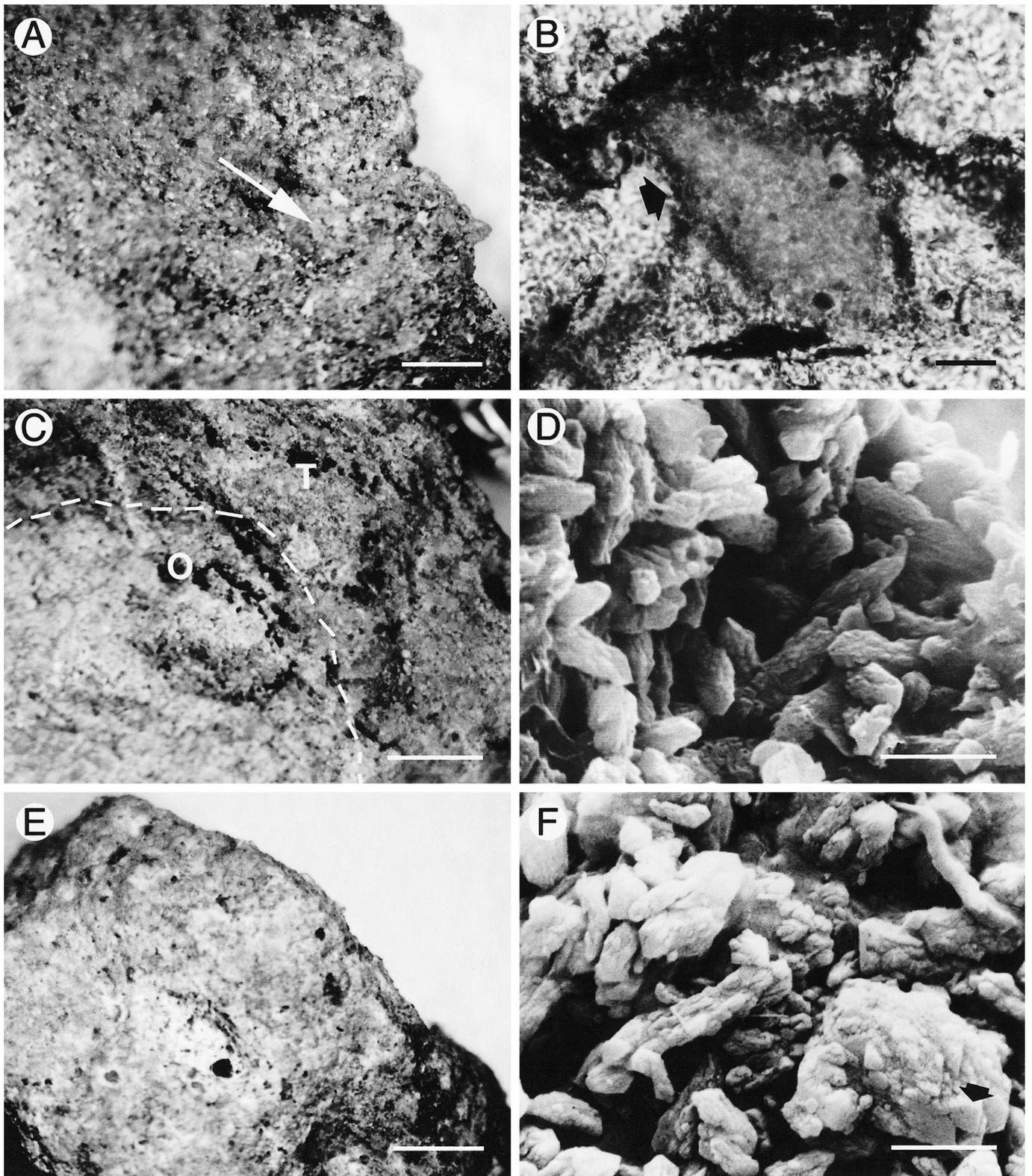


FIG. 3.—Representative carbonate morphologies. **A)** Photograph of matrix sample, Lower La Mesa soil (82 cm depth); the carbonate is visible as loose grains (arrow). Scale bar is 5 mm. **B)** Photomicrograph of micritic carbonate peloid in a matrix sample, Lower La Mesa relict soil (68 cm depth). Clay coats (arrow) surround clastic grain and peloid. Scale bar is 20 μm . **C)** Photograph of poorly indurated orthic nodule (O) and associated transitional carbonate (T), Lower La Mesa soil (80 cm depth). Scale bar is 5 mm. **D)** SEM image of euhedral to subhedral, elongate (up to 4 μm in length) calcite crystals in an orthic nodule, Lower La Mesa soil (50 cm depth). Scale bar is 2 μm . **E)** Photograph of discrete nodule, Lower La Mesa soil (48 cm depth); nodule is well indurated and has distinct boundaries delineated by a thin brown coating. Scale bar is 5 mm. **F)** SEM image of a discrete nodule in a matrix of clay-coated terrigenous grains, Lower La Mesa soil (50 cm depth). Pedogenic calcite crystals overlie the clay coatings. Rhombic calcite crystals exhibit partial dissolution (arrow). Scale bar is 2 μm .

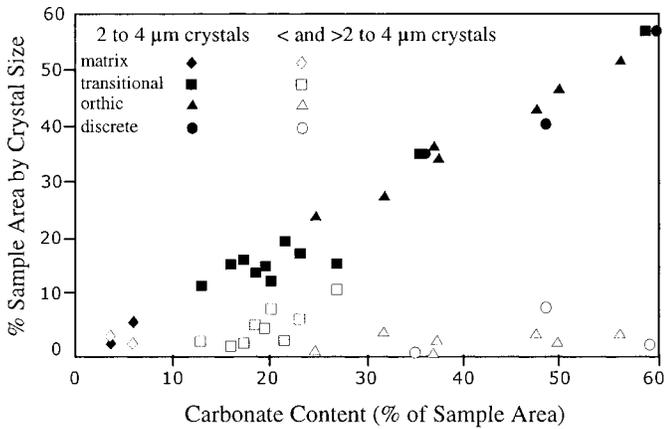


FIG. 4.—Cross-plot of the distribution of two populations of calcite crystal sizes (solid symbols = 2 to 4 μm ; open symbols = < or > 2 to 4 μm) characterized by morphology. Vertical axis is % sample area represented by crystal size population. The horizontal axis shows the total carbonate content as a percentage of sample area. All percentages were determined by point counting thin sections. Calcite crystals of 2 to 4 μm size (i.e., micrite) are dominant at all levels of carbonate cementation. The < and > 2 to 4 μm size populations, which include needle fibers as well as aphanocrystalline calcite, microspar, and spar, are most prominent in moderately cemented, transitional samples.

pothesis that carbonate in semiarid to arid soils (e.g., Aridisols) accumulates chiefly by overprinting interrupted by relatively short periods of dissolution. Notably, the spatial distribution of textures and microfabrics in the various carbonate morphologies observed in the soils does not support the idea that each carbonate texture and microfabric is characteristic of a unique stage of pedogenic carbonate accumulation. Rather, all carbonate micro-morphologies appear to have formed throughout the period of Stages I through III carbonate accumulation in the relict soils.

STABLE ISOTOPE (C, O) RESULTS

In the proximal piedmont Organ Alluvium soil (≤ 7 ky of exposure) and underlying buried Jornada II paleosol (exposed between 7 and 150 ka), the $\delta^{13}\text{C}$ values of pedogenic carbonate are generally invariant (avg. of -1.7‰ ; 1σ of $\pm 0.3\text{‰}$) regardless of morphology (Fig. 6; see also Acknowledgments). In contrast, the carbonate $\delta^{18}\text{O}$ values (avg. of -3.6‰ ; 1σ of $\pm 0.2\text{‰}$) in the Organ Alluvium soil are more positive by 1.4 to 3.1 ‰ than those of the underlying Jornada II paleosol (avg. of -5.7‰ ; 1σ of ± 0.6). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonates in these soils show no correlation.

The $\delta^{13}\text{C}$ values of pedogenic carbonates in the proximal piedmont Isaacks' Ranch soil (≤ 21 ky of exposure) have an average value of -1.2‰ (1σ of $\pm 0.3\text{‰}$), and exhibit little variation ($< 1\text{‰}$) with depth in the profile or between carbonate morphologies (Fig. 7A). The $\delta^{18}\text{O}$ values (avg. of -5.0‰ ; 1σ of ± 0.5) exhibit a greater variation (2 ‰) with depth in the profile although no down-profile trend in $\delta^{18}\text{O}$ values is apparent (Fig. 7B). Variation in $\delta^{18}\text{O}$ values of laterally coexisting pedogenic carbonates ranges from less than the analytical uncertainty to up to 1.8 ‰ . At any given depth in the profile, the variation in $\delta^{18}\text{O}$ values within a given carbonate morphology ("intramorphologic" variation) is $\leq 0.9\text{‰}$, whereas there is minimal intranodule variability. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values show no correlation.

The $\delta^{13}\text{C}$ values of pedogenic carbonates (avg. of -1‰ ; 1σ of $\pm 0.4\text{‰}$) from the Jornada II soil (≤ 150 ky of exposure) define a slightly larger range ($< 1.3\text{‰}$) than exhibited by carbonates in the Organ Alluvium and Isaacks' Ranch soils (Fig. 8A). As with the other piedmont soils, the $\delta^{13}\text{C}$ values do not exhibit a down-profile trend. The $\delta^{13}\text{C}$ values of all carbonate morphologies overlap with minimal intramorphologic variation at any given

depth (0.3 to 0.8 ‰). The $\delta^{13}\text{C}$ values of pebble coatings, however, exhibit the most positive $\delta^{13}\text{C}$ values (-0.9 to -0.2‰). Similarly to the Isaacks' Ranch soil, the $\delta^{18}\text{O}$ values in the Jornada II soil exhibit a greater variation with depth in the profile ($\sim 3\text{‰}$) than the corresponding $\delta^{13}\text{C}$ values. The $\delta^{18}\text{O}$ values of all carbonate morphologies overlap and average -4.6‰ (1σ of $\pm 0.7\text{‰}$). However, the $\delta^{18}\text{O}$ values, especially of nodules, show a down-profile trend of decreasing values with increasing depth (Fig. 8B). Maximum variation in $\delta^{18}\text{O}$ values between (internodule) and within (intranodule) individual nodules at any given depth is $\leq 0.3\text{‰}$ (Fig. 8B), whereas intrapebble coating variation in $\delta^{18}\text{O}$ values ranges up to 0.7 ‰ . There is no correlation between the carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values.

In contrast to the piedmont soils, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of pedogenic carbonate in the Lower La Mesa soil (≤ 900 ky of exposure) decrease with increasing depth (Fig. 9A, B). These trends are defined mainly by the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonates from within the top 1 m of the soil and are best exhibited by the isotope composition of samples from within individual carbonate morphologies (e.g., discrete nodules). At any given depth in the Lower La Mesa soil profile, matrix samples typically have the most negative $\delta^{13}\text{C}$ values, filaments and transitional samples have intermediate $\delta^{13}\text{C}$ values, and nodules exhibit the highest $\delta^{13}\text{C}$ values. There is a less consistent relationship between carbonate morphology and $\delta^{18}\text{O}$ values, although orthic nodules tend to have higher $\delta^{18}\text{O}$ values than other carbonate morphologies at a given depth. The petrocalcic carbonate has the lowest $\delta^{13}\text{C}$ (-5.4 to -3.2‰) and $\delta^{18}\text{O}$ (-7.9 to -5.1‰) values in the profile. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of all carbonate morphologies from the Lower La Mesa soil show significant covariation (Fig. 10).

Significantly, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of nodules from the Lower La Mesa soil exhibit considerable intranodule and internodule variation within narrow depth intervals in the soil (Fig. 9). The degree of internodule heterogeneity in $\delta^{13}\text{C}$ values, at a given depth, decreases with increasing depth, from 3.3 ‰ at 50 cm depth to 0.2 ‰ at 80 cm depth. The intranodule variation in $\delta^{13}\text{C}$ values ranges from less than the analytical uncertainty ($\pm 0.2\text{‰}$) to as much as 2 ‰ . Notably, two microsamples drilled from the same 1 mm by 1 mm area on a nodule exhibit a difference in $\delta^{13}\text{C}$ values of $> 0.6\text{‰}$. The $\delta^{18}\text{O}$ values of nodules from the Lower La Mesa relict soil show internodule variation of up to 3.2 ‰ . The maximum intranodule variation in $\delta^{18}\text{O}$ values is 0.8 ‰ , significantly less than the maximum intranodule variation in $\delta^{13}\text{C}$ values (2 ‰) in this soil.

In summary, the carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from the Rio Grande Rift relict soils exhibit the following trends with increasing duration of exposure and potential pedogenesis: (1) an increase in the range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of all pedogenic carbonates within a profile, with $\delta^{18}\text{O}$ values typically exhibiting a larger range than corresponding $\delta^{13}\text{C}$ values, (2) development of down-profile trends in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, (3) an increase in degree of intermorphologic and intramorphologic heterogeneity in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, commonly in samples distributed laterally within narrow depth intervals in the soil, (4) increasing intranodule variation in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, and (5) a shift from no correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values to significant correlation.

^{14}C Ages of Soil Carbonates

Recent studies (Wang et al. 1993, 1994; Wang et al. 1996; Amundson et al. 1994; Amundson et al. 1998) demonstrate both the potential and the limitations of radiocarbon (RC) dating of Quaternary pedogenic carbonates. The reliability of the RC ages of pedogenic carbonates in this study is supported by the following factors, which are discussed in greater detail by Deutz et al. (2001). Firstly, inheritance of ^{14}C -depleted HCO_3^- from groundwaters is unlikely given the > 100 m estimated depth of the modern and paleowater tables (King and Hawley 1975). Secondly, detrital carbonate, which could be a source of inherited C, is a very minor to missing component of the analyzed pedogenic carbonates. Thirdly, the short mean residence time of soil organic matter in desert soils (10^1 to 10^2 yr; Parker

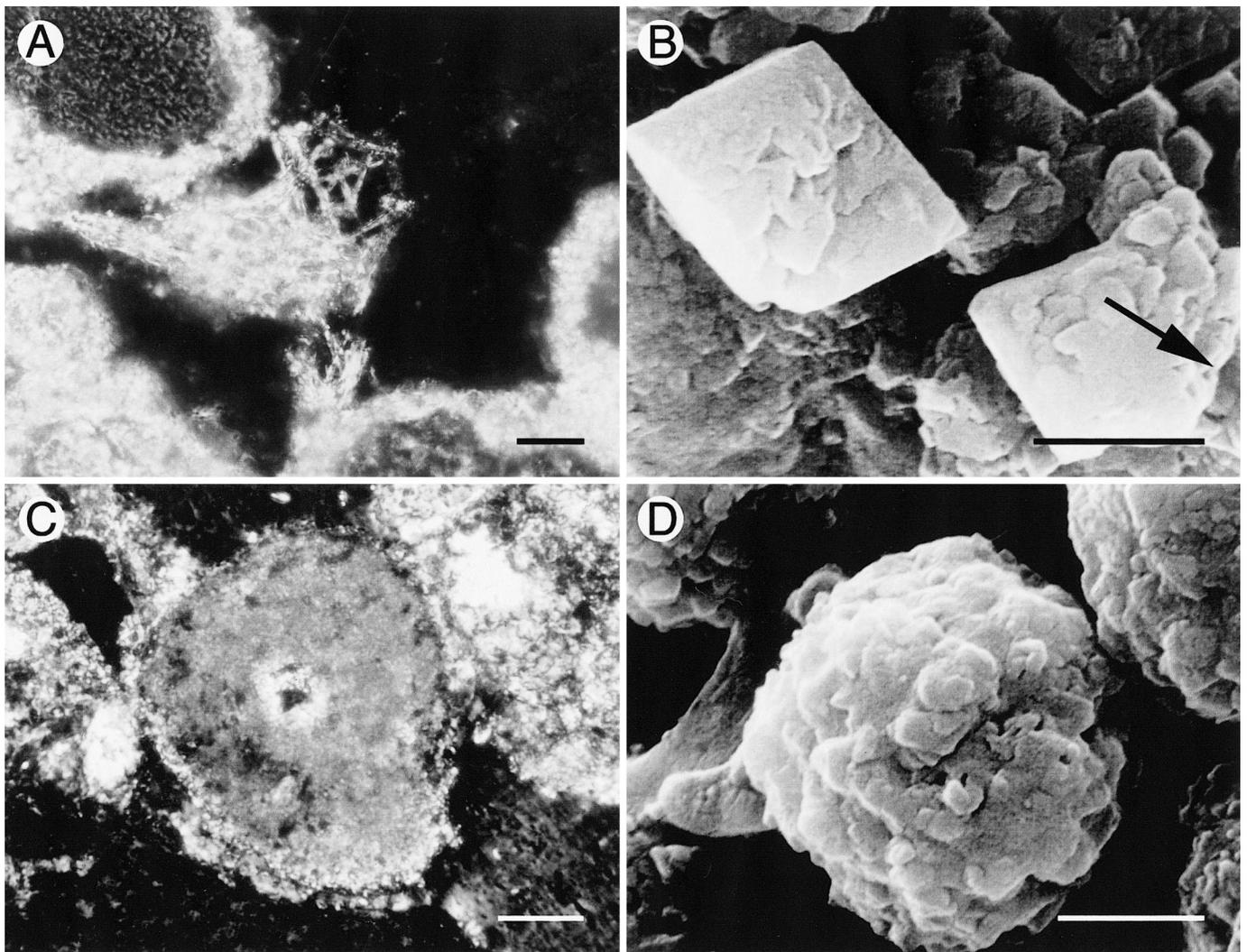


FIG. 5.—Representative carbonate morphologies. **A**) Photomicrograph of needle fiber calcite partially occluding a void in a discrete nodule, Lower La Mesa soil (48 cm depth). Micrite in the carbonate cluster may have formed by needle fiber recrystallization. Scale bar is 10 μm . Crossed polars. **B**) SEM image of rhombic calcite crystals from a carbonate cluster, Isaacks' Ranch soil (85 cm depth). Note partial dissolution of a euhedral calcite crystal (arrow). Scale bar is 1 μm . **C**) Photomicrograph of micritic peloid in a carbonate cluster, Isaacks' Ranch soil (90 cm depth). Central void in peloid is likely a former root channel. Scale bar is 60 μm . **D**) SEM image of a μm -scale peloid in a carbonate cluster, Isaacks' Ranch relict soil (85 cm depth). Scale bar is 1 μm .

et al. 1983; Connin et al. 1997) should minimize incorporation of ^{14}C -depleted carbon from decaying older soil organic matter (cf., Wang et al. 1993, 1994; Wang et al. 1996; Amundson et al. 1994; Amundson et al. 1998). Finally, very small samples of minimum size were used for AMS ^{14}C analysis (≤ 0.3 to 10 mg) in order to minimize the effects of mixing of calcite of varying ages.

The RC ages of Stages I and II pedogenic carbonates in the Rio Grande Rift soils span a time period of ~ 23 to 3 ka, thus recording a total duration of carbonate accumulation in each soil of between 13 to 20 ky (Figs. 6–9). Notably, the duration of carbonate accumulation is significantly shorter than the interval of soil exposure (from < 7 ky to ≤ 900 ky), and is of the same magnitude and absolute time span in three of the four soils despite an order-of-magnitude difference in exposure times associated with the soil profiles. The finite period of apparent carbonate accumulation (23 to 3 ka) and the observed lack of covariance between genetic stages of carbonate morphologic development and RC ages in the Rio Grande Rift soils could be interpreted as evidence for open-system behavior with respect to C. Open-system isotope behavior could have occurred during calcite recrystallization or because of incorporation in pedogenic overgrowths of

“young” ^{14}C introduced through microfractures. Open-system C isotope behavior is, however, not supported given the textural evidence for limited carbonate recrystallization and the lack of petrographic evidence for microfractures in the carbonate components. The observed consistent temporal trends in carbonate $\delta^{13}\text{C}$ values (and $\delta^{18}\text{O}$ values) defined by the RC ages in all of the studied soils further argues against open-system isotope behavior. This reflects that a small amount ($< 10\%$) of modern ^{14}C contamination would result in measured RC ages that are too young by 1000s to 10,000 years but would not produce a concomitant shift in carbonate $\delta^{13}\text{C}$ values. Rather, the finite range of carbonate RC ages observed in all four studied soils likely records dissolution of pedogenic carbonates older than 23 ka during the latest Quaternary pluvial period, prior to the progressive Holocene shallowing of the zone of wetting in the soil profiles.

In general, the RC ages of Stages I and II carbonates in the three piedmont soils tend to increase with depth in the profile (Figs. 6–8); however, carbonates from within narrow depth intervals exhibit a large range in RC ages (e.g., 12 ky range defined by samples from 90 cm depth in Isaacks' Ranch soil; Fig. 7). The RC ages of pedogenic carbonates from the three piedmont soils define temporal trends in stable-isotope compositions. Car-

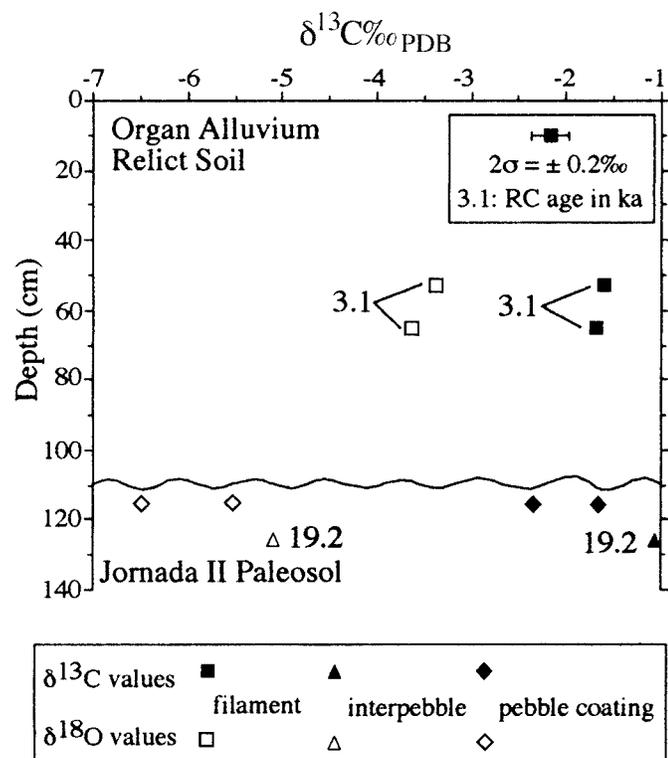


Fig. 6.— $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of pedogenic carbonates plotted against depth for the Organ Alluvium soil and underlying buried Jornada II paleosol. ^{14}C age in ka is shown by the numbers associated with plotted carbonate samples. Tie lines between RC ages and samples indicate that multiple stable-isotope samples were combined for ^{14}C analysis. Analytical uncertainty (2σ) for all data is shown by the horizontal bar in the legend.

bonate $\delta^{13}\text{C}$ values in the piedmont soils are either invariant throughout the time period represented by RC ages of dated carbonates (Organ Alluvium and Jornada II soils) or exhibit a weak trend of increasing $\delta^{13}\text{C}$ values with increasing age (Isaacks' Ranch soil). Conversely, within all piedmont soils, for carbonates with RC ages ≤ 15 ka the $\delta^{18}\text{O}$ values exhibit an inverse trend of decreasing value with increasing age. Significant temporal variation in $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ values of pedogenic carbonates from the Isaacks' Ranch soil are recorded by samples collected laterally from narrow depth intervals.

A down-profile trend in RC ages is not defined by carbonates in the Lower La Mesa soil. Of note, the largest range in carbonate RC ages observed in the Lower La Mesa soil occurs within samples from one narrow depth interval (45 to 50 cm depth in Fig. 9). Moreover, microsamples drilled from a single nodule exhibit a range in RC ages of greater than 6 ky. In contrast to the piedmont soil carbonates, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonate nodules in the Lower La Mesa soil define overall trends of decreasing values with increasing RC age (Fig. 9). This trend is best developed, however, in carbonates from within narrow depth intervals rather than by the down-profile distribution of carbonates (Fig. 9). For samples with RC ages within ~ 1 ky of each other it is reasonable to assume accumulation under effectively constant climate conditions (Deutz et al. 2001). Four sets of "contemporaneous" samples (11.7 to 11.0 ka; 9.7 to 9.2 ka; and 5.7 to 4.6 ka in Fig. 9) exhibit a range in stable-isotope values from less than analytical uncertainty (0.2‰) to up to $\sim 2\%$. In three cases, the contemporaneous samples occur over a broad depth range, thus allowing for evaluation of down-profile trends in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values; in these sets, the samples found at the greatest depth invariably have the lowest isotope values.

DISCUSSION: ORIGIN OF STABLE ISOTOPE HETEROGENEITY

The aforementioned trends and large range in carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values observed in the studied soils can be interpreted to record any of several regional paleoenvironmental or local soil-specific processes. These include: (1) carbonate precipitation from soil CO_2 evolved from soil organic matter with a wide range of $\delta^{13}\text{C}$ compositions, (2) a significant contribution of detrital carbonate to pedogenic carbonates, (3) variable mixing with atmospheric CO_2 , (4) the effects of variable infiltration of meteoric water and evaporation on soil-water $\delta^{18}\text{O}$ values, and (5) overprinting of pedogenic carbonate due to changing climate and soil vegetation. The following sections discuss each of these processes and consider the extent to which they apply to this study.

Heterogeneity of Soil Organic Matter

Heterogeneity in the $\delta^{13}\text{C}$ compositions of soil CO_2 and soil carbonates has been interpreted to reflect heterogeneity in the $\delta^{13}\text{C}$ composition of living and decaying organic matter in soil profiles ($\delta^{13}\text{C}_{\text{org}}$) at any given period of soil formation (Pendall et al. 1991). However, pedogenic carbonates that formed in rapidly buried semiarid to arid soils (Amundson et al. 1988; Quade et al. 1989; Pendall and Amundson 1990; Cole and Monger 1994) do not display heterogeneity in $\delta^{13}\text{C}$ values of the magnitude or on the spatial scale (intranodule) of those observed in the Lower La Mesa relict soil. The observed small range in carbonate $\delta^{13}\text{C}$ values in those previously studied semiarid to arid soils indicates a low degree of heterogeneity in $\delta^{13}\text{C}_{\text{org}}$, which in turn likely reflects the relatively rapid burial rates of those soils and their limited duration of pedogenesis. In contrast, Deutz et al. (2001) documented a large range in the $\delta^{13}\text{C}$ values of soil organic matter ($\delta^{13}\text{C}_{\text{org}}$ of -25 to -13%) in the Rio Grande Rift relict soils. They used the range in $\delta^{13}\text{C}_{\text{org}}$ values, coupled with numerical modeling (Cerling 1991) and carbonate RC ages, to suggest that the large degree of heterogeneity in carbonate $\delta^{13}\text{C}$ values from the Lower La Mesa soil is better interpreted as a record of shifts in the C_3/C_4 plant ratio throughout the period of carbonate accumulation (RC age range of 13.5 ky) than as a product of contemporaneous heterogeneity in $\delta^{13}\text{C}_{\text{org}}$ values and in the $\delta^{13}\text{C}$ composition of soil CO_2 .

Influence of Detrital Carbonate

The range and covariation in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of carbonate nodules from the Lower La Mesa soil could potentially be explained by a detrital carbonate component. Several lines of evidence argue, however, against a detrital carbonate component in these soils. Firstly, the presence of thermodynamically unstable textures such as needle fiber calcite, micritic coats on siliciclastic grains, and micrite embedded in clay "skins" in matrix carbonate argues for *in situ* precipitation. Secondly, the small range in $\delta^{13}\text{C}$ values of pedogenic carbonates in the piedmont soils and the lack of correlation between their $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values do not support the presence of a detrital carbonate component in the studied soils (cf., Cerling and Quade 1993).

Lastly, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of matrix carbonate, which would be the morphology type with the largest detrital component in the studied soils, do not support a detectable detrital component in the analyzed pedogenic carbonates. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of matrix carbonate are typically more negative than the values of other carbonate morphologies from the same depth, suggesting that a detrital component would have a more negative $\delta^{13}\text{C}$ composition than authigenic carbonate. However, wind-blown carbonate eroded from the soils and paleosols, or from regionally exposed Late Paleozoic marine limestones in the study region, has $\delta^{13}\text{C}$ values similar to or significantly more positive (up to $+5\%$) than those of the studied pedogenic carbonates. Moreover, the down-profile decrease in $\delta^{13}\text{C}$ values of all carbonate morphologies would reflect a decreasing frac-

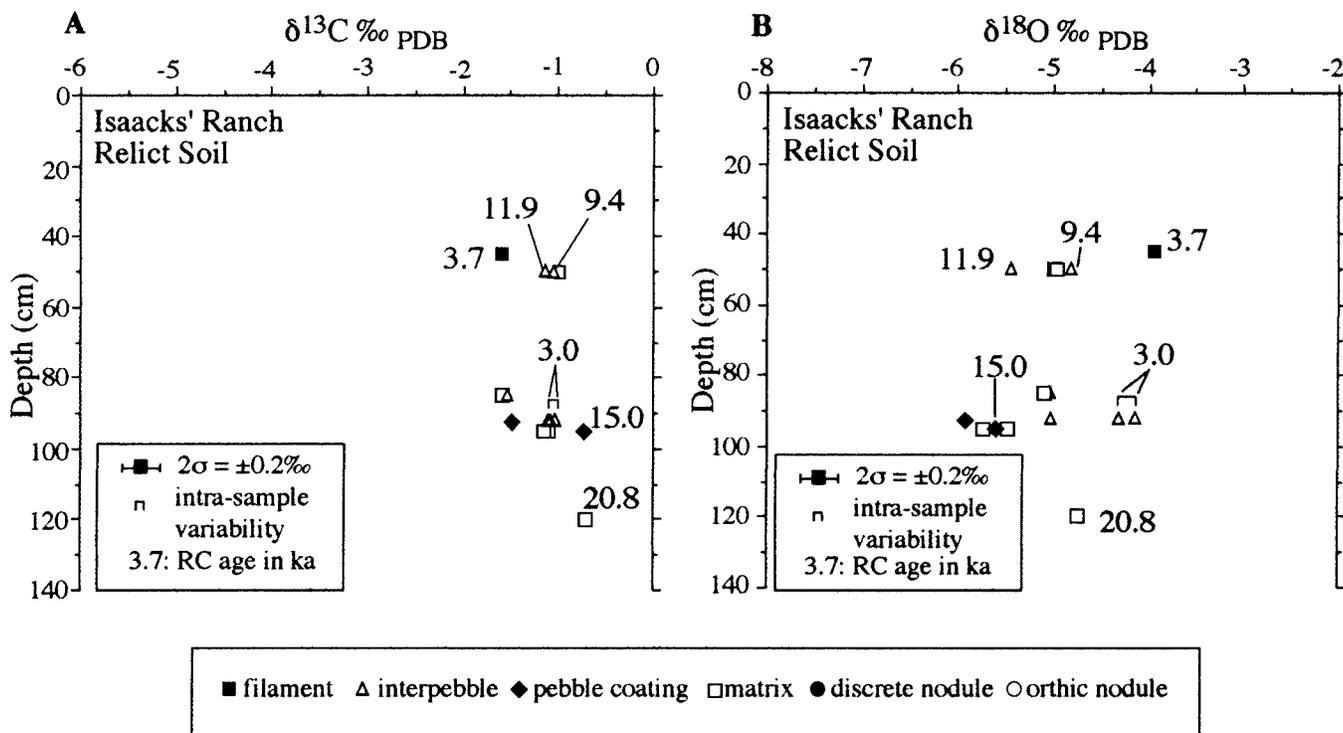


FIG. 7.— $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and ^{14}C ages in ka of pedogenic carbonates plotted against depth for the Isaacks' Ranch soil. Note change in use of symbols from Figure 6. A) $\delta^{13}\text{C}$ values; data illustrate that although pedogenic carbonates in this soil exhibit minimal variation in $\delta^{13}\text{C}$ values, they yield a considerable range in RC ages (e.g., a variation of 12 ky in RC ages of two samples at ~ 90 cm). B) $\delta^{18}\text{O}$ values; between ~ 50 and 90 cm depth values become more positive with decreasing age. Tie lines between RC ages and samples as in Figure 6. Analytical uncertainty (2σ) for all data shown by the horizontal bar in the legend.

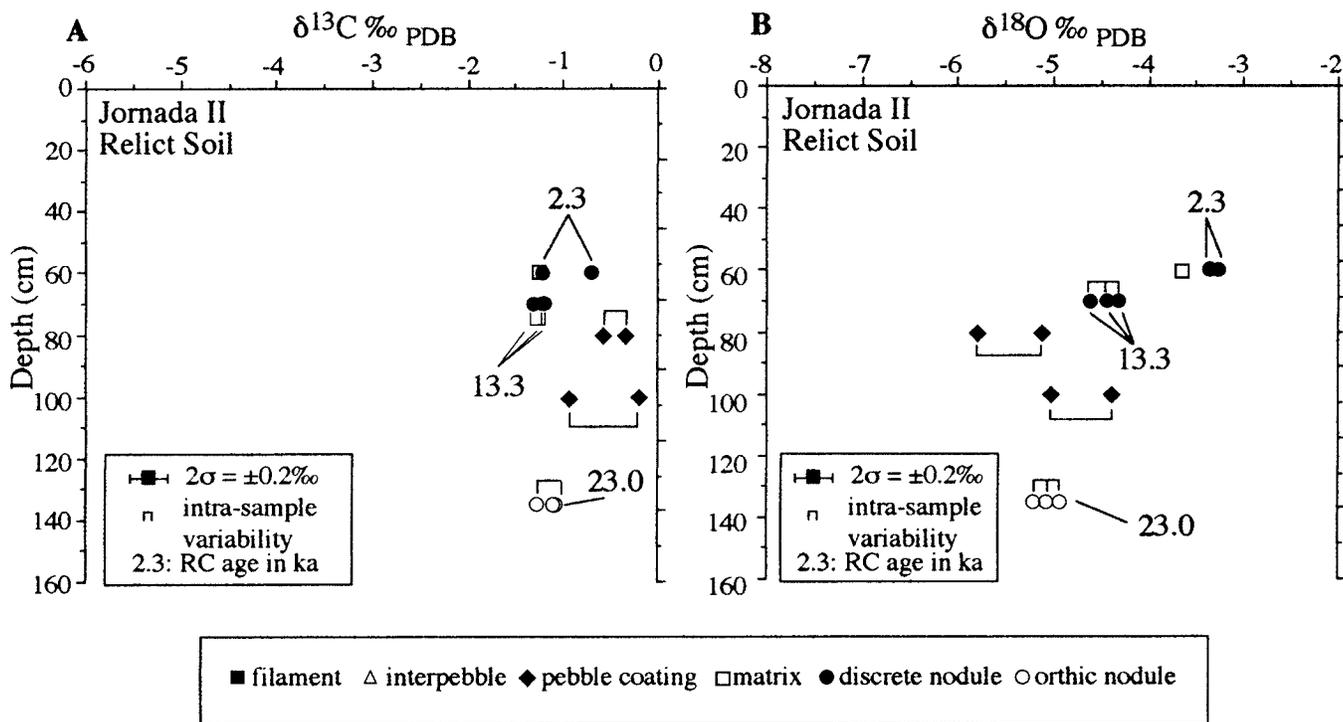


FIG. 8.— $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and ^{14}C ages in ka of pedogenic carbonates plotted against depth for the Jornada II soil. A) $\delta^{13}\text{C}$ values; B) $\delta^{18}\text{O}$ values. Tie lines between RC ages and samples are as in Figure 6. Analytical uncertainty (2σ) for all data shown by the horizontal bar in legend.

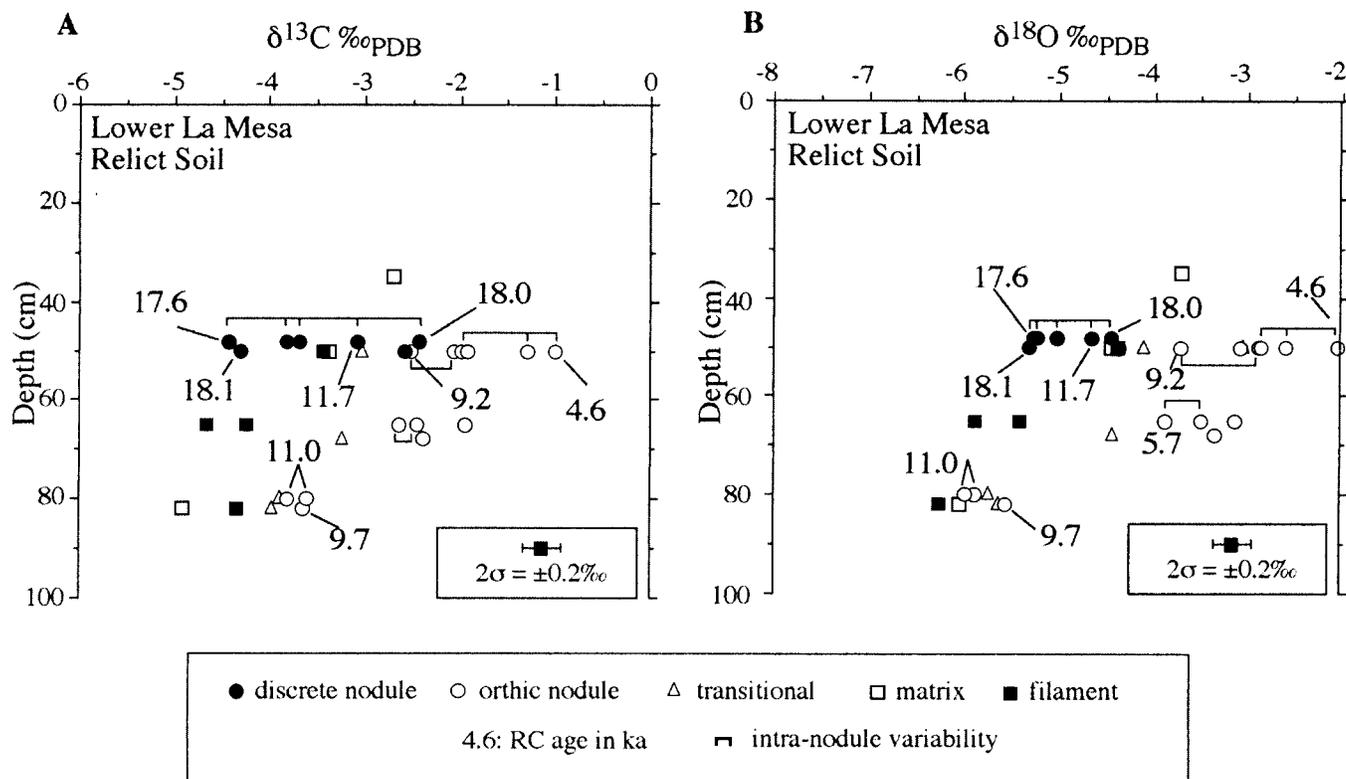


FIG. 9.— $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and ^{14}C ages in ka of pedogenic carbonates plotted against depth from above the petrocalcic horizon in the Lower La Mesa soil. A) $\delta^{13}\text{C}$ values; B) $\delta^{18}\text{O}$ values. A 3.4‰ range in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from nodules at 50 cm depth corresponds to an ~ 13 ky range. Three groups of samples from different depths in the soil are defined by their RC ages of ~ 11.5 ka, ~ 9.5 ka, and ~ 5 ka. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonates in all three groups become more negative with depth. Tie lines between RC ages and samples are as in Figure 6. Analytical uncertainty (2σ) for all data is shown by the horizontal bar in the legend.

tion of detrital carbonate with depth in the profiles, the opposite of trends observed in all modern carbonate-bearing soils (Cerling 1984).

Openness to the Atmosphere: Influence of Atmospheric CO_2

Diffusion of atmospheric CO_2 (pre-industrial $\delta^{13}\text{C}$ value of -6.5‰ ; Friedli et al. 1986) into desert soils is typically limited to the shallowest portions of the profile given that at high soil-respiration rates, plant-derived soil CO_2 ($\delta^{13}\text{C}$ values of -35 to -12‰ ; Cerling et al. 1993) dominates at depths > 50 cm. The result is an exponential down-profile decrease in soil- CO_2 $\delta^{13}\text{C}$ values; $\delta^{13}\text{C}$ values below the depth of significant penetration of atmospheric CO_2 are generally invariable (Cerling 1984, 1991; Quade et al. 1989). In turn, the $\delta^{13}\text{C}$ values of pedogenic carbonates exhibit a parallel exponential down-profile trend, with minimal variation in carbonate $\delta^{13}\text{C}$ values below the depth of significant penetration of atmospheric CO_2 . Deep penetration of atmospheric CO_2 into a soil due to a low soil-respiration rate (or atmospheric $p\text{CO}_2$ levels higher than present-day) would result in a more gradual rate of decrease in soil $\delta^{13}\text{CO}_2$ values with depth in the profile.

In the Lower La Mesa soil, the large-scale heterogeneity in $\delta^{13}\text{C}$ values of pedogenic carbonates from narrow depth intervals coupled with the large internodule and intranodule $\delta^{13}\text{C}$ variation could record a significant component of atmospheric CO_2 at greater depths into the soil than observed in most carbonate-bearing modern soils. Significantly, the three sets of contemporaneous carbonates in the Lower La Mesa soil display a decrease in $\delta^{13}\text{C}$ values of varying rate and depth at which the carbonate $\delta^{13}\text{C}$ values become invariant (Fig. 9; Deutz et al. 2001). This suggests that temporal fluctuation in the depth of significant penetration of atmospheric CO_2 in the Lower La Mesa soil may be a source of the observed heterogeneity in carbonate $\delta^{13}\text{C}$ values. In contrast, more homogeneity in carbonate $\delta^{13}\text{C}$

values from the younger piedmont soils does not support deep penetration of atmospheric CO_2 in these soil profiles.

Influence of Meteoric Water and Evapotranspiration

Carbonate $\delta^{18}\text{O}$ values in Holocene desert soils are typically highly variable at shallow depths, tending to decrease and become less variable with increasing depth (Quade et al. 1989). These trends record the processes governing influx, transportation, and loss of water in soil profiles and their effect on soil-water $\delta^{18}\text{O}$ composition. Water loss in a soil profile occurs by evaporation in the shallow portions of the profile and by transpiration at greater depths. Water loss by evaporation results in oxygen isotope fractionation and ^{18}O enrichment of soil water relative to the $\delta^{18}\text{O}$ values of the local meteoric water (Hsieh et al. 1998). Stable-isotope studies of soil carbonates and soil waters indicate that the depth to which the influence of evaporation extends in a soil profile is related to the annual precipitation level (Amundson et al. 1996; Hsieh et al. 1998). In a desert, with high insolation and low vegetation cover, a greater degree and depth of evaporative enrichment of soil water would be expected than under more temperate conditions. Studies of desert Holocene soils, similar to those of the study region, indicate that volumetrically significant evaporative enrichment is limited to depths of ≤ 50 cm (Quade et al. 1989; Amundson et al. 1996).

Water loss below the depth of influence of evaporation in the profile is, however, governed by transpiration. Transpiration is non-fractionating, thus the soil-water $\delta^{18}\text{O}$ values at depth should approach those of the local meteoric water source. The combined effects of evaporation and transpiration produce a down-profile decrease in $\delta^{18}\text{O}$ values of soil water and authigenic carbonates. The shape of the down-profile trends and the depth of influence of evaporation on soil-water $\delta^{18}\text{O}$ values reflects in part the

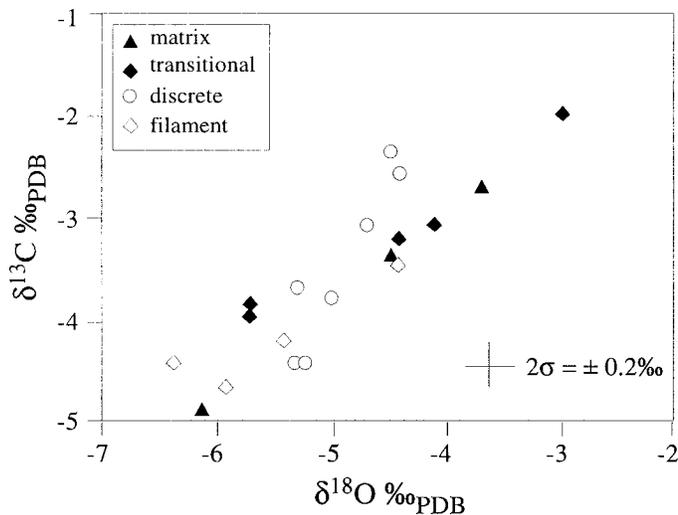


FIG. 10.—Cross plot of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for carbonate morphologies from above the petrocalcic horizon in the Lower La Mesa soil. Correlation coefficients were calculated for the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of all discrete nodules ($r^2 = 0.89$) and for a subset of orthic nodules from 50 to 68 cm depth in the soil ($r^2 = 0.92$). The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of matrix carbonate and filaments follow the trend defined by the orthic nodules.

rate at which water migrates down through the profile (Liu et al. 1995). Soils with low matrix permeability are typically characterized by exponential decreases in $\delta^{18}\text{O}$ values of soil water and authigenic carbonates with depth. Conversely, soils of high matrix permeability permit rapid infiltration of meteoric water through the profile to depths where nonfractionating transpiration is the dominant mode of water loss. This results in a rapid down-profile decrease in $\delta^{18}\text{O}$ values and a shallower depth of evaporation.

Other factors that can influence the $\delta^{18}\text{O}$ composition of soil water and pedogenic carbonates in the shallow portions of soil profiles (down to 20 to 50 cm depth) include seasonal variation in the $\delta^{18}\text{O}$ composition of local precipitation, the length of duration between precipitation events, the degree of mixing of meteoric water with antecedent soil water, and variable degrees of evaporative enrichment of soil water due to heterogeneous matrix permeability and porosity (Liu et al. 1995; Hsieh et al. 1998). These factors can result in highly variable soil water and carbonate $\delta^{18}\text{O}$ compositions in the upper portions of profiles.

The two youngest piedmont soils (Organ Alluvium and Isaack's Ranch) exhibit minimal changes in carbonate $\delta^{18}\text{O}$ values with depth. This likely reflects the permeable nature of these proximal piedmont soils, allowing for rapid downward infiltration of precipitation and minimal evaporative enrichment. In addition, restriction of evaporative enrichment of soil water to the shallowest portions of the proximal piedmont profiles is also indicated by the small internodule and intranodule variation in their carbonate $\delta^{18}\text{O}$ values. Although the $\delta^{18}\text{O}$ values of pedogenic carbonates in the oldest piedmont soil (Jornada II alluvium) do decrease with depth, the lack of contemporaneous samples precludes evaluation of down-profile trends and the influence of evapotranspiration on carbonate $\delta^{18}\text{O}$ values.

In contrast to the piedmont soils, the large internodule and intranodule $\delta^{18}\text{O}$ heterogeneity in the Lower La Mesa soil reflects the significant influence of evaporative enrichment of soil waters down to depths of at least 50 cm in this profile that developed in fine-grained fluvial deposits. Moreover, the variability in slope of the down-profile $\delta^{18}\text{O}$ trends defined by contemporaneous samples in the Lower La Mesa soil (Fig. 9) suggest that the depth of the zone of evaporation and the degree of evaporative enrichment in this profile varied throughout the duration of carbonate accumulation.

Overprinting

In the Rio Grande soils, the increased heterogeneity in stable-isotope values within a given soil profile with increasing duration of pedogenesis from less than thousands of years (Organ Alluvium) to up to hundreds of thousands of years (Lower La Mesa) provides the strongest support for overprinting of the analyzed pedogenic carbonates. The range in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of pedogenic carbonates within each soil, the degree to which down-depth $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ trends are developed, and the level of internodule and intranodule stable-isotope variation all increase with increasing exposure time. This stable-isotope evidence for overprinting is strengthened by the textural evidence for precipitation of overgrowths. Additional support for overprinting is the strong correlation between internodule and intranodule $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of most pedogenic carbonates in the Lower La Mesa soil (Fig. 10). Covariation between isotope values in a population of soils across a wide geographic area has previously been interpreted as a record of carbonate accumulation under a range of different climatic conditions (Quade et al. 1989; Cerling and Quade 1993). In the Lower La Mesa soil, the well-developed observed covariation between the carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values is interpreted to be a proxy record of changes in soil conditions throughout the duration of carbonate accumulation (Deutz et al. 2001). Portions of this proxy record may, however, be missing because of intermittent periods of carbonate dissolution.

We argue that the textural and stable-isotope evidence best supports overprinting as the dominant process governing the observed stable-isotope and textural heterogeneity in the pedogenic carbonates from the Rio Grande Rift soils. The RC ages of pedogenic carbonates provide further evidence for overprinting. The youngest carbonate samples (RC ages of 2.3 to 3.7 ka) from all three piedmont soils, including the Organ Alluvium profile, which has been exposed for less than a few thousands of years, have overlapping stable-isotope compositions. This suggests that the youngest carbonates in these profiles record formation under similar climate and vegetation with minimal overprinting. The effects of overprinting, however, are recorded by the $\delta^{18}\text{O}$ values of the older carbonates in all four studied soils. For carbonates with RC ages spanning 4 to 23 ka, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values show complex yet consistent temporal trends that have been shown to record changing climatic and ecosystem conditions throughout the evolution of the soils, which are consistent with independent reconstructions of regional climate (Deutz et al. 2001).

PEDOGENIC CARBONATE AS A PALEOENVIRONMENTAL PROXY: IMPLICATIONS OF ISOTOPE HETEROGENEITY

Significantly, the range in exposure times and duration of pedogenesis (10^3 to 10^5 ky) recorded by the Rio Grande Rift soils are analogous to those of paleosols used to reconstruct paleoclimate, paleofloral ecology, and paleo-atmospheric $p\text{CO}_2$. This study of late Quaternary Aridisols documents that pedogenic carbonate in fossil paleosols that formed under analogous semiarid to arid conditions as Aridisols likely accumulated through overprinting accompanied by a small amount of recrystallization. The isotopic composition of such overprinted pedogenic carbonates is likely a cumulative record of soil, climate, and ecosystem conditions, and potentially of changes in atmospheric $p\text{CO}_2$ and CO_2 $\delta^{13}\text{C}$ values, that developed throughout accumulation. The textural and geochemical record of overprinting can vary on a submicron scale. Thus, even microsampling of carbonate nodules and rhizoliths for stable-isotope analysis can result in "time averaging" of important climatic, paleoenvironmental, and paleoecological information.

The heterogeneity in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the pedogenic carbonates from the Rio Grande soils are shown, through the use of RC ages, to record the combined effects of changes in the vegetation type and density, and magnitude of the atmospheric CO_2 component to total soil CO_2 of each soil, as well as the effects of overprinting. Without geochronologic con-

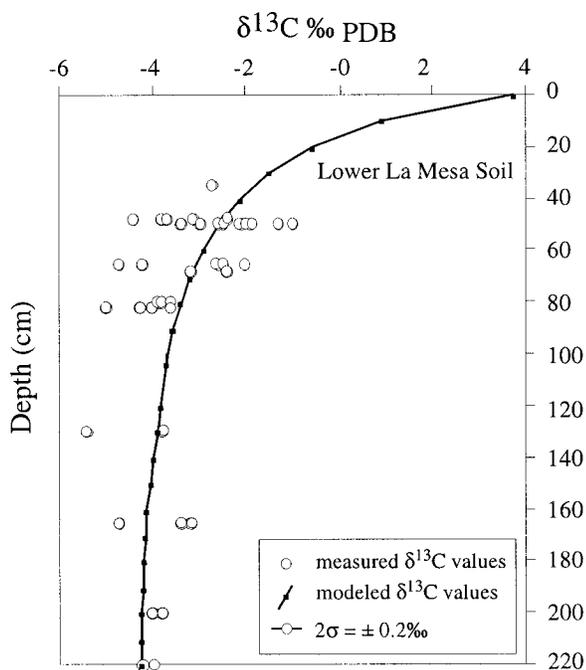


FIG. 11.—Modeled $\delta^{13}\text{C}_{\text{carb}}$ curve for the Lower La Mesa soil. The curve fitted to artificially homogenized values was obtained by averaging all measured $\delta^{13}\text{C}$ values (open circles) from within narrow depth intervals in the soil. See text for details.

straints in which to identify contemporaneous samples in paleosols, however, it is not possible to distinguish between the effects of various local soil-specific and regional paleoenvironmental processes that influence the stable-isotope composition of pedogenic carbonates. This may compromise the utility of some paleosol carbonates as paleoenvironmental proxies. Application of the isotopic composition of pedogenic carbonates for paleoenvironmental reconstruction thus requires careful assessment of the degree of intrasample and intersample isotopic heterogeneity within individual soils as well as between soils. The degree of isotopic heterogeneity can in turn be used to constrain the temporal resolution over which climate, ecosystem, and atmospheric $p\text{CO}_2$ and CO_2 $\delta^{13}\text{C}$ reconstructions should be made (or “time averaged”), as well as for constraining the level of uncertainty associated with modeled values.

The large range in stable-isotope compositions of pedogenic carbonates in the Lower La Mesa soil, and the down-profile trends defined by their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, illustrate the level of uncertainty that can be associated with interpreting stable-isotope compositions of temporally unconstrained carbonates. Figure 11 exhibits a best-fit model curve for the average value of all measured $\delta^{13}\text{C}$ values of carbonates from within narrow depth intervals in the Lower La Mesa soil. These artificially homogenized average carbonate $\delta^{13}\text{C}$ values approximate those values that would be anticipated from whole-rock sampling or from limited microsampling of the Lower La Mesa soil carbonates. The model curve, which was produced using Cerling’s model (1991) and input parameters constrained by measured values at the Lower La Mesa soil, exhibits the typical exponential profile with depth that would be anticipated for carbonates that formed contemporaneously in a soil profile. This implies that the down-profile distribution of the whole-rock $\delta^{13}\text{C}$ values can be interpreted to record a *unique* set of soil conditions, and suggests that the Lower La Mesa carbonates could be contemporaneous or have accumulated over a period of prolonged climatic stability (i.e., invariant soil conditions), and thus not be affected by overprinting. Notably, the pedogenic carbonates in this profile record a period of $\sim 20,000$ years of carbonate accumulation. This period

TABLE 1.—Modeled atmospheric $p\text{CO}_2$ contents for observed range of pedogenic carbonate $\delta^{13}\text{C}$ values and estimated respiration rates.

Respiration Rate (mmol/m ² /hr)	Measured carbonate $\delta^{13}\text{C}$ value (‰) ¹			
	-4.4	-3.1	-2.4	-1.0
0.1	35 ppmV	70 ppmV	100 ppmV	175 ppmV
0.3	100 ppmV	210 ppmV	300 ppmV	525 ppmV
1	330 ppmV	700 ppmV	1000 ppmV	1750 ppmV
2	660 ppmV	1430 ppmV	2000 ppmV	3500 ppmV

¹ Range of soil-respiration rates were chosen on the basis of modeled values for the Lower La Mesa soil (Deutz et al. 2001), and reflect the uncertainty associated with estimation of paleo-respiration rates from paleosols. Other input parameters include mean annual soil temperature (20°C), atmospheric pressure (0.85 atm), production depth (120 cm), and atmospheric $\delta^{13}\text{C}_{\text{CO}_2}$ (-6.5‰).

² Carbonate $\delta^{13}\text{C}$ values are for multiple microsamples taken from three nodules at 50 cm depth in Lower La Mesa relic soil.

of time has been shown independently to have been characterized by significant shifts in climate and vegetation (summarized in Deutz et al. 2001). The occurrence of an exponential profile with depth defined by the carbonate $\delta^{13}\text{C}$ values from one paleosol thus does not necessarily indicate that soil carbonates in the profile are either contemporaneous or that they accumulated under constant environmental conditions. Furthermore, estimating C_3/C_4 plant ratios, soil conditions, or $p\text{CO}_2$ from the $\delta^{13}\text{C}$ values of such overprinted carbonates would be associated with large error given that the reconstructions are based on a “time averaged” paleoenvironmental record.

Although the reconstruction of paleo-atmospheric $p\text{CO}_2$ contents is conventionally carried out at the scale of millions to tens of millions of years (Mora et al. 1996; Mora and Driese 1999; Ekart et al. 1999), the degree of heterogeneity present in the measured $\delta^{13}\text{C}$ values of pedogenic carbonates from paleosols should be used to constrain the level of uncertainty associated with $p\text{CO}_2$ estimates. The morphologic characteristics of the Lower La Mesa soil (e.g., well-drained, upper horizons leached of carbonate, presence of a Bt horizon overlying the carbonate-bearing horizons) are analogous to those observed in carbonate-bearing paleosols, which have been used to estimate paleo-atmospheric $p\text{CO}_2$ levels. Modeling the 3.4‰ range in carbonate $\delta^{13}\text{C}$ values observed in nodules from the Lower La Mesa soil suggests two orders of magnitude variation in $p\text{CO}_2$ (35 to 3500 ppmV) during the latest Pleistocene to Holocene period of carbonate accumulation if the assumption is made that the carbonate $\delta^{13}\text{C}$ heterogeneity solely reflects changes in paleo-atmospheric CO_2 content (Table 1). This range of estimated $p\text{CO}_2$ assumes C_3 vegetation ($\delta^{13}\text{C}_{\text{org}}$ of -20.5‰ based on analyzed C_3 organic matter in the Lower La Mesa soil), and a range of soil-respiration rates representative of those found in modern carbonate-bearing soils and inferred for fossil soils (Cerling 1992; Ekart et al. 1999). This range of modeled $p\text{CO}_2$ estimates derived from one carbonate nodule differs significantly from more direct estimates of latest Pleistocene to Holocene atmospheric $p\text{CO}_2$ (200 to 280 ppmV; Friedli et al. 1986; Barnola et al. 1987), and illustrates the need for characterizing the degree of isotopic heterogeneity in paleosol carbonates prior to applying their $\delta^{13}\text{C}$ values to paleo-atmospheric $p\text{CO}_2$ reconstructions.

Alternatively, recent studies have used the $\delta^{13}\text{C}$ values of terrestrial minerals and organic matter to document changes in atmospheric $p\text{CO}_2$ and CO_2 $\delta^{13}\text{C}$ at the scale of thousands to 100,000 years (Koch et al. 1995; MacLeod et al. 2000; Hesselbo et al. 2000; Jahren et al. 2001). These rapid changes in atmospheric $p\text{CO}_2$ and CO_2 $\delta^{13}\text{C}$ may be recorded by individual paleosols or stacks of paleosols (cf. Koch et al. 1995; MacLeod et al. 2000). Given that this study documents that intraprofile heterogeneity in carbonate $\delta^{13}\text{C}$ values can result from the combined effects of several local soil-specific processes as well as more regional or global paleoenvironmental factors, characterizing the intraprofile $\delta^{13}\text{C}$ heterogeneity of pedogenic carbonates should be an integral component of reconstructing high-resolution records of paleo- $p\text{CO}_2$ levels from paleosols.

This study elucidates several additional considerations with regard to the application of paleosol carbonates as paleoenvironmental proxies. First,

there is a high level of uncertainty associated with estimating relative ages of carbonates in a given soil on the basis of either the overall maturity of the pedogenic carbonates or the age of the deposit in which the soil is forming. In the studied soils, only Stage I morphologies are present in the youngest piedmont soil (Organ Alluvium) as compared to the occurrence of Stages I to II carbonates in the older piedmont soils (Isaacks' Ranch and Jornada II), and up to Stage IV carbonates in the oldest soil (Lower La Mesa). This carbonate distribution appears to record the correlation between carbonate morphologic development and soil age previously observed in Quaternary soils (Gile et al. 1966; Machette 1985). However, the RC ages of all pedogenic carbonates (Stages I and II) in the two older piedmont soils overlap and define a finite period of accumulation (13 to 20 ky) despite an order-of-magnitude difference in their exposure times. This period of carbonate accumulation is notably shorter than the exposure time of one of the soils (up to 150 ky for the Jornada II soil), which is estimated from the age of the geomorphic surface. Similarly, the Stage II carbonates in the Lower La Mesa soil define a range of RC ages similar to those in the two older piedmont soils, and thus record only a fraction of the time represented by the soil profile (750 to 900 ky).

This decoupling of carbonate RC ages and estimated soil profile ages, which are based on the age of geomorphic surfaces, suggests that using the sequence of morphologic development of carbonate as a function of time (Leeder 1975; Machette 1985) can be associated with significant uncertainty (i.e., an order-of-magnitude error of thousands of years) (cf. Wright 1990). For example in the two piedmont soils with the same genetic stage of carbonate development (Fig. 2C, D), the presence of a significantly thicker carbonate-bearing horizon in the proximal piedmont Isaacks' Ranch soil (1.2 m thick) versus that developed in the distal piedmont Jornada II soil (2 m thick) would erroneously suggest significantly higher flood-basin accretion rates and lower soil maturity level at the distal alluvial site than at the proximal site. This is in contrast to that indicated by the estimated age of the geomorphic surfaces and the ages of the alluvial deposits. Thus, inferring sediment accretion rates in ancient alluvial sequences from the presence of a particular genetic stage(s) of pedogenic carbonate development (Leeder 1975) can result in erroneous assessments of paleosol maturity and of the distribution of relative time in terrestrial successions (e.g., Marzo et al. 1988; Bown and Kraus 1993; Wright and Marriott 1996).

Moreover, this study indicates that long-term paleoenvironmental trends defined on the basis of carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from a succession of paleosols are likely punctuated by multiple, temporally extensive gaps. Lastly, the assumption of correlation between age and depth of pedogenic carbonates in a paleosol cannot be made with any certainty. Samples distributed laterally within narrow depth intervals in two of the piedmont soils and in the Lower La Mesa soil exhibit significant ranges in RC ages (Figs. 7, 8, 9). Moreover, in the Lower La Mesa soil the range in RC ages of carbonates within a horizon is greater than the range in RC ages distributed vertically.

CONCLUSIONS

This integrated petrographic and stable-isotope and radiogenic-isotope analysis of temporally well-constrained Quaternary Aridisols documents the complex petrographic and isotopic record that can result from carbonate overprinting in slowly buried soils. Carbonates in the studied soils exhibit a significant degree of stable-isotope heterogeneity both within and between profiles, as well as considerable intramorphologic and intranodule variation. The heterogeneity in carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are shown, through the use of RC ages, to record the combined effects of changes in the vegetation type and density, and magnitude of the atmospheric CO_2 contribution to total soil CO_2 of each soil, superimposed on the larger-scale effects of overprinting. For temporally less well-constrained paleosol carbonates, overprinting leads to "time averaging" of evolving soil, climate,

and ecosystem conditions, and potentially changing values of atmospheric $p\text{CO}_2$ and CO_2 $\delta^{13}\text{C}$, throughout the period of accumulation.

The lack of geochronologic constraints in fossil paleosols thus limits the temporal resolution at which paleoecologic, paleoclimatic, and paleo- $p\text{CO}_2$ reconstructions can be derived from overprinted pedogenic carbonates. This study suggests that using paleosol carbonates as quantitative paleoenvironmental proxies is best achieved by characterizing the degree of intrasample and intersample stable-isotope heterogeneity within and between paleosols. Paleoenvironmental reconstructions should be based on the stable-isotope composition of those paleosol carbonates that exhibit the least amount of isotope heterogeneity of all soils studied. In turn, the observed isotopic heterogeneity can be used to constrain the temporal resolution over which climate, ecosystem, and atmospheric $p\text{CO}_2$ and CO_2 $\delta^{13}\text{C}$ reconstructions should be "time averaged," as well as for constraining the level of uncertainty associated with these modeled estimates.

ACKNOWLEDGMENTS

We are indebted to Greg Mack for providing an introduction to the study area, to Tamara Spar and Andy Jonas for assistance in the field, and to Harry Warneke and John Garner for technical assistance. We gratefully acknowledge the help of John Southon and the radiocarbon sample preparation staff of the Lawrence Livermore National Laboratory in making possible the radiocarbon dates. Jack Worrall, (USC), Krassimir Bizholo (UCR), and Tony Sinclair (Hull) provided invaluable assistance on the use of their respective SEMs. The manuscript benefited from the reviews of Oliver Chadwick, Lee Nordt, Steve Driese, and Jay Quade. This project was partially funded by Grants-in-aid from the Geological Society of America, Sigma Xi, and a National Science Foundation grant to I.P. Montañez. The stable isotopic data described in this paper and shown in Figures 6 through 9 have been archived, and are available in digital form, at the World Data Center-A for Marine Geology and Geophysics, NOAA/NGDC, 325 Broadway, Boulder, CO 80303; (phone: 303-497-6339; fax: 303-497-6513; E-mail: wdcamgg@ngdc.noaa.gov; URL: <http://www.ngdc.noaa.gov/mgg/sepm/archive/index.html>).

REFERENCES

- AMUNDSON, R., STERN, L., BAISDEN, T., AND WANG, Y., 1998, The isotopic composition of soil sand soil-respired CO_2 : *Geoderma*, v. 82, p. 83–114.
- AMUNDSON, R.G., CHADWICK, O.A., SOWERS, J.M., AND DONER, H.E., 1988, Relationship between climate vegetation and the stable carbon isotope chemistry of soils in the eastern Mojave desert, Nevada: *Quaternary Research*, v. 29, p. 245–254.
- AMUNDSON, R.G., CHADWICK, O.A., KENDALL, C., WANG, Y., AND DENIRO, M., 1996, Isotopic evidence for shifts in atmospheric circulation patterns during the late Quaternary in mid-North America: *Geology*, v. 24, p. 23–26.
- AMUNDSON, R.G., WANG, Y., CHADWICK, O.A., TRUMBORE, S., MCFADDEN, L., McDONALD, E., WELLS, S., AND DENIRO, M., 1994, Factors and processes governing the ^{14}C content of carbonate in desert soils: *Earth and Planetary Science Letters*, v. 125, p. 385–405.
- BARNOLA, J.M., RAYNAUD, D., KOROTKEVICH, Y.S., AND LORIUS, C., 1987, Vostok ice core provides 160,000-year record of atmospheric CO_2 : *Nature*, v. 329, p. 408–414.
- BOWN, T.M., AND KRAUS, M.J., 1993, Time-stratigraphic reconstruction and integration of paleopedologic, sedimentologic, and biotic events (Willwood Formation, Lower Eocene, north-west Wyoming, U.S.A.): *Palaos*, v. 8, p. 68–90.
- CALVET, F., AND JULIA, R., 1983, Pisoids in the caliche profiles of Tarragona (N.E. Spain), in Peryt, T.M., ed., *Coated Grains*: Berlin, Germany, Springer-Verlag, p. 456–473.
- CAUDILL, M.R., DRIESE, S.G., AND MORA, C.I., 1996, Preservation of a paleo-Vertisol and an estimate of Late Mississippian paleoprecipitation: *Journal of Sedimentary Research*, v. 66, p. 58–70.
- CERLING, T.E., 1984, The stable isotopic composition of modern soil carbonate and its relationship to climate: *Earth and Planetary Science Letters*, v. 71, p. 229–240.
- CERLING, T.E., 1991, Carbon dioxide in the atmosphere: evidence from Cenozoic and Mesozoic paleosols: *American Journal of Science*, v. 291, p. 377–400.
- CERLING, T.E., 1992, Use of carbon isotopes in paleosols as an indicator of the $p(\text{CO}_2)$ of the paleoatmosphere: *Global Geochemical Cycles*, v. 6, p. 307–314.
- CERLING, T.E., AND QUADE, J., 1993, Stable carbon and oxygen isotopes in soil carbonates, in Swart, P.K., Lohmann, K.C., McKenzie, J., and Savin, S. eds., *Continental Isotopic Indicators of Climate*: American Geophysical Union, Geophysical Monograph 78, p. 217–232.
- CERLING, T.E., WANG, Y., AND QUADE, J., 1993, Expansion of C_4 ecosystems as an indicator of global ecological change in the late Miocene: *Nature*, v. 361, p. 344–345.
- COLE, D.R., AND MONGER, H.C., 1994, Influence of atmospheric CO_2 on the decline of C_4 plants during the last deglaciation: *Nature*, v. 368, p. 533–536.
- CONNIN, S.L., VIRGINIA, R.A., AND CHAMBERLAIN, C.P., 1997, Carbon isotopes reveal soil organic matter dynamics following arid land shrub expansion: *Oecologia*, v. 110, p. 374–386.
- DEUTZ, P., 1997, A high resolution study of overprinting in pedogenic calcite: the implications of the use of stable isotope values from paleosol pedogenic calcite in paleoclimatic reconstructions [unpublished Ph.D. thesis]: Riverside, California, University of California, 241 p.

- DEUTZ, P., MONTAÑEZ, I.P., MONGER, H.C., AND MORRISON, J., 2001, Derivation of a paleoenvironmental record from pedogenic carbonates in buried and relict Quaternary soils, Rio Grande Rift, New Mexico: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 166, p. 293–317.
- DICK-PEDDIE, W.A., 1975, Vegetation of Southern New Mexico, in Seager, W.R., Clemons, R.E., and Callender, J.F., eds., *Guidebook of the Las Cruces Country*: New Mexico Geological Society, 26th field Conference, 376 p.
- DICKSON, J.A.D., 1965, A modified staining technique for carbonates in thin section: *Nature*, v. 205, p. 587.
- EKART, D.D., CERLING, T.E., MONTAÑEZ, I.P., AND TABOR, N.J., 1999, A 400 million year carbon isotope record of pedogenic carbonate: Implications for paleoatmospheric carbon dioxide: *American Journal of Science*, v. 299, p. 805–827.
- ENCINA-ROJAS, A., 1995, Detailed soil survey of the Jornada LTER (Long Term Ecological Research) transect vicinity, southern New Mexico [unpublished M.S. thesis]: New Mexico State University, Las Cruces, New Mexico, 284 p.
- FRIEDLI, H., LÖTSCHER, H., OESCHGER, H., SIEGENTHALER, U., AND STAUFFER, B., 1986, Ice core record of the $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric CO_2 in the past two centuries: *Nature*, v. 324, p. 237–238.
- GILE, L.H., 1987, A pedogenic chronology for Kilbourne Hole, Southern New Mexico: II. Time of the explosions and soil events before the explosions: *Soil Science Society of America, Journal*, v. 51, p. 752–760.
- GILE, L.H., AND GROSSMAN, R.B., 1979, *The Desert Project Soil Monograph*: U.S. Department of Agriculture, Soil Conservation Service.
- GILE, L.H., PETERSON, F.F., AND GROSSMAN, R.B., 1966, Morphological and genetic sequences of carbonate accumulation in desert soils: *Soil Science*, v. 101, p. 347–360.
- HESELBO, S.P., GROCKE, D.R., JENKINS, H.C., BIJRRUM, C.J., FARRIMOND, P., BELL, H.S.M., AND GREEN, O.R., 2000, Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event: *Nature*, v. 406, p. 392–395.
- HSIEH, J.C.C., KELLY, E.F., SAVIN, S.M., AND CHADWICK, O.A., 1998, Measurement of soil-water $\delta^{18}\text{O}$ values by direct equilibration with CO_2 : *Geoderma*, v. 82, p. 255–268.
- JAHREN, A.H., ARENS, N.C., SARMIENTO, G., GUERRERO, J., AND AMUNDSON, R., 2001, Terrestrial record of methane hydrate dissociation in the Early Cretaceous: *Geology*, v. 29, p. 159–162.
- KING, W.E., AND HAWLEY, J.W., 1975, Geology and ground-water resources of the Las Cruces area, in Seager, W.R., Clemons, R.E., and Callender, J.F., eds., *Guidebook of the Las Cruces Country*: New Mexico Geological Society, 26th field Conference, 376 p.
- KNOX, G.J., 1977, Caliche profile formation, Saldanha Bay (South Africa): *Sedimentology*, v. 24, p. 657–674.
- KOCH, P.L., ZACHOS, J.C., AND DETTMAN, D.L., 1995, Stable isotope stratigraphy and paleoclimatology of the Paleogene Bighorn Basin (Wyoming, U.S.A.): *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 115, p. 61–89.
- KOTLOWSKI, F.E., 1965, Sedimentary basins of south-central and southwestern New Mexico: *American Association of Petroleum Geologists, Bulletin*, v. 49, p. 2120–2139.
- KUPEZ, J.A., MONTAÑEZ, I.P., AND GAO, G., 1993, Recrystallization of dolomite with time, in Rezak, R., and Lavoie, D., eds., *Carbonate Microfabrics*: New York, Springer-Verlag, *Frontiers in Sedimentary Geology*, p. 187–194.
- LATORRE, C., QUADE, J., AND MCINTOSH, W.C., 1997, The expansion of C_4 grasses and global change in the late Miocene: stable isotope evidence from the Americas: *Earth and Planetary Science Letters*, v. 146, p. 83–96.
- LEEDER, M.R., 1975, Pedogenic carbonates and flood sediment accretion rates; a quantitative model for alluvial arid-zone lithofacies: *Geological Magazine*, v. 112, p. 257–270.
- LIU, B., PHILLIPS, F.M., HOINES, S., CAMPBELL, A.R., AND SHARMA, P., 1995, Water movement in desert soils traced by stable isotopes, Cl, chlorine-36, southern Arizona: *Journal of Hydrology*, v. 168, p. 91–110.
- MACHETTE, M.N., 1985, Calcic soils of the southwestern United States, in Weide, D.L., ed., *Soils and Quaternary Geology of the Southwestern United States*: Geological Society of America, Special Paper 203, p. 1–21.
- MACK, G.H., SALYARDS, S.L., AND JAMES, W.C., 1993, Magnetostratigraphy of the Plio-Pleistocene Camp Rice and Palomas Formations in the Rio Grande rift of southern New Mexico: *American Journal of Science*, v. 293, p. 49–77.
- MACLEOD, K.G., SMITH, R.M.H., KOCH, P.L., AND WARD, P.D., 2000, Timing of mammal-like reptile extinctions across the Permian-Triassic boundary in South Africa: *Geology*, v. 28, p. 227–230.
- MARZO, M., NIJMAN, W., AND PUIGDEFABREGAS, C., 1988, Architecture of the Castissent fluvial sheet sandstones, Eocene, south Pyrenees, Spain: *Sedimentology*, v. 35, p. 719–738.
- MONGER, H.C., COLE, D.R., GISH, J.W., AND GIORDANO, T.H., 1998, Stable carbon and oxygen isotopes in Quaternary soil carbonates as indicators of ecogeomorphic changes in the northern Chihuahuan Desert, U.S.A.: *Geoderma*, v. 82, p. 137–172.
- MONGER, H.C., DAUGHERTY, L.A., AND GILE, L.H., 1991a, A microscopic examination of pedogenic calcite in an Aridisol of southern New Mexico, in Nettleton, W.D., ed., *Occurrence, Characteristics, and Genesis of Carbonate, Gypsum, and Silica Accumulations in Soils*: Soil Science Society of America, Special Publication 26, p. 37–60.
- MONGER, H.C., DAUGHERTY, L.A., AND LINDEMANN, W.C., 1991b, Microbial precipitation of pedogenic calcite: *Geology*, v. 19, p. 997–1000.
- MONTAÑEZ, I.P., AND READ, J.F., 1992, Fluid-rock interaction history during stabilization of early dolomites, Upper Knox Group (Lower Ordovician), U.S. Appalachians: *Journal of Sedimentary Petrology*, v. 62, p. 753–778.
- MORA, C.I., AND DRIESE, S.G., 1999, Palaeoclimatic significance and stable carbon isotopes of Palaeozoic red bed paleosols, Appalachian Basin, U.S.A. and Canada, in Thiry, M., and Simon-Coignon, R., eds., *Palaeoweathering, Palaeosurfaces and Related Continental Deposits*: International Association of Sedimentologists Special Publication 27, p. 61–84.
- MORA, C.I., DRIESE, S.G., AND COLARUSSO, L.A., 1996, Middle to late Paleozoic atmospheric CO_2 levels from soil carbonate and organic matter: *Science*, v. 271, p. 1105–1107.
- PARKER, L.W., MILLER, J., STEINBERGER, Y., AND WHITFORD, W.G., 1983, Soil respiration in a Chihuahuan Desert rangeland: *Soil Biology and Biochemistry*, v. 15, p. 303–309.
- PENDALL, E., AND AMUNDSON, R., 1990, The stable isotope chemistry of pedogenic carbonate in an alluvial soil from the Punjab, Pakistan: *Soil Science*, v. 194, p. 199–211.
- PENDALL, E., HARDEN, J.W., AND TRUMBORE, S., 1991, Pedogenic isotopic indicators of climate and carbon cycling in Fish Lake Valley, Nevada: U.S. Geological Survey, Open File Report 91-296, 18 p.
- QUADE, J., CATER, J.M.L., OJHA, T.P., ADAM, J., AND HARRISON, T.M., 1995, Late Miocene environmental change in Nepal and the northern Indian subcontinent: Stable isotopic evidence from paleosols: *Geological Society of America, Bulletin*, v. 107, p. 1381–1397.
- QUADE, J., CERLING, T.E., AND BOWMAN, J.R., 1989, Systematic variations in the carbon and oxygen isotopic composition of pedogenic carbonates along elevation transects in the southern Great Basin, United States: *Geological Society of America Bulletin*, v. 101, p. 464–475.
- RETALLACK, G.J., 1990, *Soils of the Past: An Introduction to Paleopedology*: Boston, Massachusetts, Unwin Hyman Publishers, 520 p.
- RETALLACK, G.J., 1994, The environmental factor approach to the interpretation of paleosols, in Amundson, R., Harden, J., and Singer, M., eds., *Factors of Soil Formation: A Fiftieth Anniversary Retrospective*: Soil Science Society of America, Special Publication 33, p. 31–64.
- REYNOLDS, J.F., VIRGINIA, R.A., KEMP, P.R., DE SOYZA, A.G., AND TREMMEL, D.C., 1999, Impact of drought on desert shrubs: Effects of seasonality and degree of resource island development: *Ecological Monographs*, v. 69, p. 69–106.
- SEHGAL, J.L., AND STOOPS, G., 1972, Pedogenic calcite accumulation in arid and semiarid regions of the Indo-Gangetic alluvial plain of erstwhile Pujab (India): Their morphology and origin: *Geoderma*, v. 8, p. 59–72.
- SOIL SURVEY STAFF, 1992, *Keys to Soil Taxonomy*: U.S. Department of Agriculture, Soil Management Support Services, Technical Monograph No. 19, 5th Edition: Blacksburg, Virginia, Virginia Polytechnic Institute and State University, 541 p.
- SOLOMON, S.T., AND WALKDEN, G.M., 1985, The application of cathodoluminescence to interpreting the diagenesis of an ancient calcrete profile: *Sedimentology*, v. 32, p. 877–896.
- STUIVER, M., AND POLACH, D., 1977, Reporting of ^{14}C data: *Radiocarbon*, v. 19, p. 355–363.
- VERRECCHIA, E.P., AND VERRECCHIA, K.E., 1994, Needle-fiber calcite: a critical review and a proposed classification: *Journal of Sedimentary Research*, v. A64, p. 650–664.
- WANG, Y., AMUNDSON, R., AND TRUMBORE, S., 1993, Processes controlling the ^{14}C content of soil carbon dioxide: Model development: *Chemical Geology*, v. 107, p. 225–226.
- WANG, Y., AMUNDSON, R., AND TRUMBORE, S., 1994, A model for soil $^{14}\text{CO}_2$ and its implications for using ^{14}C to date pedogenic carbonates: *Geochimica et Cosmochimica Acta*, v. 58, p. 393–399.
- WANG, Y., McDONALD, E., AMUNDSON, R., MCFADDEN, L., AND CHADWICK, O., 1996, An isotopic study of soils in chronological sequences of alluvial deposits, Providence Mountains, California: *Geological Society of America, Bulletin*, v. 108, p. 379–391.
- WHITE, T., GONZALEZ, L., LUDVIGSON, G., AND POULSEN, C., 2001, Middle Cretaceous greenhouse hydrologic cycle of North America: *Geology*, v. 29, p. 363–366.
- WIEDER, M., AND YAALON, D.H., 1974, Effect of matrix composition on carbonate nodule crystallization: *Geoderma*, v. 11, p. 95–121.
- WIEDER, M., AND YAALON, D.H., 1982, Micromorphological fabrics and developmental stages of carbonate nodular forms related to soil characteristics: *Geoderma*, v. 28, p. 203–220.
- WIERENGA, P.J., TOORMAN, A.F., HUDSON, D.B., VINSON, J., NASH, M., AND HILLS, R.G., 1989, Soil physical properties at the Las Cruces trench site: Washington D.C., U.S. Nuclear Regulatory Commission, 91 p.
- WRIGHT, V.P., 1990, Estimating rates of calcrete formation and sediment accretion in ancient alluvial deposits: *Geological Magazine*, v. 127, p. 273–276.
- WRIGHT, V.P., AND MARRIOTT, S.B., 1996, A quantitative approach to soil occurrence in alluvial deposits and its application to the Old Red Sandstone of Britain: *Geological Society of London, Journal*, v. 153, p. 907–913.
- WRIGHT, V.P., AND PEETERS, C., 1989, Origins of some early Carboniferous calcrete fabrics revealed by cathodoluminescence: Implications for interpreting the sites of calcrete formation: *Sedimentary Geology*, v. 65, p. 345–353.
- WRIGHT, V.P., AND TUCKER, M.E., 1991, eds., *Calcretes*: International Association of Sedimentologists, Reprint Series, v. 2, 352 p.

Received 18 September 2001; accepted 1 April 2002.