# Quantifying pedogenic carbonate accumulations using stable carbon isotopes

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## Abstract

Four pedons from a late Quaternary chronosequence developed in calcareous alluvium in central Texas were investigated to assess the ability of the stable C isotope method to partition and quantify pedogenic carbonate accumulations. To quantify pedogenic carbonate accumulations with this method, $\delta^{13}C$ values of bulk, pedogenic, and parent carbonate must be known. For each pedon, $\delta^{13}C$ values of bulk carbonate were measured on a horizon by horizon basis. The parent carbonate end-member for all pedons was approximated by averaging the bulk $\delta^{13}C$ values for all horizons from the weakly developed floodplain soil. The diffusion model of Cerling (1984) and Quade et al. (1989) was used to estimate the pedogenic carbonate end-member. Quantification of pedogenic carbonate accumulations by the isotopic method was compared to quantitative estimates conducted by field morphology, binocular light microscope point counts, and thin-section point counts. Results suggest that the isotopic method is superior to other methods of quantifying pedogenic carbonate accumulations. Whole-soil pedogenic carbonate accumulations as calculated by the isotopic method for the chronosequence were: (1) 1 to 4 vol.% by 2000 years; (2) 4 to 15 vol.% by 5000 years; and (3) 1 to 12 vol.% after 15,000 years. These results reveal net soil carbonate loss through time for central Texas climates. This corroborates similar conclusions drawn for the same chronosequence using mass balance analysis to calculate the flux of carbonate. Net carbonate loss through time also indicates that these soils do not serve as long-term carbonate C sequesters. © 1998 Elsevier Science B.V.

*Keywords:* stable C isotope; pedogenic carbonate; diffusion model; soil chronosequence

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## 1. Introduction

Pedogenic carbonate is an important constituent of many subhumid to arid soils throughout the world (Birkeland, 1984). It serves as a sink for Mg, Fe, Mn, P, and C, provides calcium for plant growth, and influences porosity and water movement. Furthermore, it is estimated that more than $8 \times 10^{14}$ kg of C are sequestered globally in calcic horizons of aridisols (Schlesinger, 1982). Pedogenic carbonate accumulations are also used to identify calcic and petrocalcic horizons (Soil Survey Staff, 1996), and as a proxy for soil or landscape age (Machette, 1985).

Many soils in Texas have developed from limestones and carbonatic shales, clays, and alluvium. As a result, differentiating pedogenic and lithogenic carbonates in these soils is difficult (Rabenhorst et al., 1984; West et al., 1988; Wilding et al., 1990). Here we present the first systematic application of the stable C isotope diffusion model (Cerling, 1984; Quade et al., 1989) to quantify pedogenic carbonate accumulations in a soil chronosequence developed from calcareous parent materials. Application of the diffusion model was particularly important in this investigation because of the absence of carbonate segregations that could be isolated and analyzed isotopically. Specific objectives were to: (1) review stable C isotope theory as applied to differentiating pedogenic and parent carbonates; (2) quantify pedogenic carbonate accumulations using the diffusion model; and (3) compare quantitative estimates of pedogenic carbonate calculated isotopically with estimates determined by field morphology, thin-section point counts, and binocular light microscope point counts.

## 2. Background

The soil chronosequence in this investigation developed in late Quaternary calcareous alluvium of Cowhouse Creek within the Fort Hood Military Reservation of central Texas (Fig. 1). Mean annual precipitation and temperature are 800 mm and 19°C, respectively (Bomar, 1983). The natural potential vegetation is a Juniper–Oak Savanna (Kuchler, 1964). Four pedons were characterized in the chronosequence, ranging in age from modern to 15,000 years (Nordt, 1992) (Table 1). The detrital carbonate component in the parent alluvium was derived from Lower Cretaceous limestones and clays in the surrounding drainage basin.

Soil descriptions for each pedon were written following standards and procedures of the Soil Survey Division Staff (1993) and Soil Survey Staff (1996). Bulk soil samples were collected from every genetic horizon. Particle size distribution was determined by pipette, $CaCO_3$ equivalent gasometrically, and organic C as the difference in total C determined by dry combustion and carbonate C (Hallmark et al., 1986).

Prior to isotopic analyses, soils were passed through a 2-mm screen to remove coarse roots and organic matter fragments, dried, and pulverized in a

Fig. 1. Location of the four study pedons along Cowhouse Creek within the Fort Hood Military Reservation in central Texas.

centrifugal mill. To determine the isotopic composition of carbonate C, soils were roasted at 380°C for 1 h under vacuum and treated with 100% $H_3PO_4$ in an evacuated reaction vessel. The isotopic composition of the $CO_2$ was determined by mass spectrometry (McCrea, 1950). To determine the isotopic composition of soil organic C, an aliquot of each soil was treated with 1 $N$ HCl to remove carbonate C and combusted at 850°C in sealed quartz tubes (Boutton, 1991a). All isotopic measurements were made on a dual-inlet, triple-collector gas isotope ratio mass spectrometer (VG-903, Middlewich, UK), and expressed as $\delta^{13}C$ (‰) values relative to the international PDB standard (Craig, 1957). Precision was 0.1‰ for both carbonate and organic C measurements.

The relative proportion of pedogenic carbonate in soils developed in calcareous parent materials can be estimated using the isotopic mass balance equation of Salomons and Mook (1976):

$$\% \text{ pedogenic carbonate} = \frac{\left(\delta^{13}C_{bulk} - \delta^{13}C_{parent}\right)}{\left(\delta^{13}C_{pedogenic} - \delta^{13}C_{parent}\right)} \times 100 \qquad (1)$$

Table 1
Soil characterization and stable C isotope data for the four pedons in the chronosequence

| Site/horizon | Depth (cm) | Particle size distribution (%) sand (2–0.05 mm) | silt (0.05–0.002 mm) | clay (<0.002 mm) | Organic carbon (%) | Bulk density (1/3 bar) | Measured[a] $\delta^{13}C$ organic matter (‰) | Modeled[b] $\delta^{13}C$ pedogenic carbonate (‰) | Measured $\delta^{13}C$ bulk carbonate (‰) | Measured[c] $\delta^{13}C$ parent carbonate (‰) | Measured CaCO$_3$ equivalent (%) | Calculated[d] pedogenic carbonate wt.% | vol.% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Pedon 1 — < 600 years* | | | | | | | | | | | | | |
| A | 0– 25 | 48.0 | 32.6 | 19.4 | 1.09 | | −19.1 | −3.2 | 0.6 | +1.0 | 43.2 | 9 | 2 |
| Bw | 25– 57 | 64.8 | 20.7 | 14.5 | 0.63 | 1.29 | −20.7 | −3.9 | 0.5 | +1.0 | 49.4 | 10 | 2 |
| Bk | 57– 75 | 60.6 | 23.4 | 16.0 | 0.54 | | −18.1 | −4.0 | 0.4 | +1.0 | 42.4 | 11 | 2 |
| C | 75–100 | 74.6 | 12.6 | 12.8 | 0.34 | | −19.3 | −4.0 | 0.9 | +1.0 | 55.0 | 2 | 1 |
| Akb1 | 100–114 | 50.2 | 30.6 | 19.2 | 0.58 | | −19.7 | −4.0 | 0.9 | +1.0 | 58.7 | 2 | 0 |
| BCb1 | 114–122 | 79.6 | 11.1 | 9.3 | 0.30 | | −19.5 | −4.0 | 1.4 | +1.0 | 76.0 | 0 | 0 |
| Akb2 | 122–143 | 43.2 | 32.2 | 24.6 | 0.64 | | −18.7 | −4.0 | 0.6 | +1.0 | 43.9 | 7 | 2 |
| BCkb2 | 143–171 | 63.3 | 21.1 | 15.6 | 0.32 | | −19.1 | −4.0 | 0.9 | +1.0 | 62.3 | 2 | 1 |
| CBkb2 | 171–220 | 48.1 | 31.0 | 20.9 | 0.66 | 1.16 | −19.3 | −4.0 | 0.8 | +1.0 | 56.3 | 4 | 1 |
| 2C1b2 | 220–237 | 72.7 | 14.0 | 13.3 | 0.40 | | −18.4 | −4.0 | 0.9 | +1.0 | 72.0 | 3 | 1 |
| 2C2b2 | 237–266 | 64.2 | 21.2 | 14.6 | 0.57 | 1.01 | −18.4 | −4.0 | 1.4 | +1.0 | 66.6 | 0 | 0 |
| *Pedon 2 — 2000 years* | | | | | | | | | | | | | |
| A1 | 0– 15 | 49.0 | 31.2 | 19.8 | 1.17 | 1.38 | −19.0 | −2.0 | 0.7 | +1.0 | 46.1 | 9 | 2 |
| A2 | 15– 34 | 46.4 | 34.3 | 19.3 | 1.89 | 1.31 | −19.0 | −3.7 | 0.8 | +1.0 | 46.4 | 5 | 1 |
| Bk1 | 34– 53 | 48.5 | 31.4 | 20.1 | 0.97 | 1.22 | −16.7 | −4.0 | 0.7 | +1.0 | 49.7 | 6 | 1 |
| Bk2 | 53– 85 | 52.7 | 28.6 | 18.7 | 0.94 | 1.21 | −16.7 | −4.0 | 0.6 | +1.0 | 47.5 | 9 | 2 |
| Bk3 | 85–118 | 47.3 | 31.8 | 20.9 | 0.70 | 1.26 | −17.2 | −4.0 | 0.2 | +1.0 | 46.0 | 16 | 3 |
| Bk4 | 118–155 | 45.8 | 31.7 | 22.5 | 0.69 | 1.27 | −16.9 | −4.0 | 0.2 | +1.0 | 42.6 | 16 | 3 |
| Bk5 | 155–166 | 42.3 | 34.6 | 23.1 | 0.72 | 1.29 | −16.9 | −4.0 | 0.0 | +1.0 | 42.1 | 20 | 4 |
| Bk6 | 166–188 | 38.6 | 36.5 | 24.9 | 0.62 | 1.30 | −16.8 | −4.0 | 0.1 | +1.0 | 44.4 | 18 | 4 |
| Bk7 | 188–215 | 37.3 | 37.0 | 25.7 | 0.73 | 1.29 | −16.8 | −4.0 | 0.1 | +1.0 | 49.1 | 18 | 4 |
| Bk8 | 215–267 | 44.8 | 32.8 | 22.4 | 0.58 | 1.28 | −17.5 | −4.0 | 0.2 | +1.0 | 49.5 | 16 | 4 |
| Bk9 | 267–347 | 32.9 | 40.2 | 26.9 | 0.71 | | −17.7 | −4.0 | 0.2 | +1.0 | 43.6 | 15 | 3 |
| BCk | 347–380 | 42.0 | 34.4 | 23.6 | 0.32 | | −17.9 | −4.0 | 0.1 | +1.0 | 50.8 | 17 | 4 |

*Pedon 3 — 5000 years*

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A1 | 0– 16 | 1.87 | 11.1 | 51.8 | 37.1 | 1.23 | −18.2 | −1.6 | −0.9 | +1.0 | 36.5 | 74 | 12 |
| A2 | 16– 32 | 1.37 | 11.3 | 47.7 | 41.0 | 1.25 | −16.7 | −2.7 | −1.7 | +1.0 | 37.1 | 73 | 12 |
| AB | 32– 59 | 1.04 | 11.3 | 45.7 | 43.0 | 1.31 | −14.6 | −2.8 | −1.5 | +1.0 | 38.6 | 64 | 12 |
| Bw | 59– 94 | 0.79 | 14.2 | 43.7 | 42.1 | 1.43 | −14.5 | −2.9 | −1.6 | +1.0 | 39.6 | 66 | 13 |
| Bk1 | 94–122 | 0.58 | 17.2 | 43.5 | 39.3 | 1.39 | −14.0 | −2.9 | −1.9 | +1.0 | 39.4 | 74 | 15 |
| Bk2 | 122–153 | 0.44 | 17.7 | 44.5 | 37.8 | 1.41 | −15.4 | −2.9 | −1.7 | +1.0 | 39.6 | 69 | 14 |
| Bk3 | 153–189 | 0.34 | 18.7 | 44.3 | 37.0 | 1.42 | −15.6 | −2.9 | −1.7 | +1.0 | 37.3 | 69 | 13 |
| Bk4 | 189–252 | 0.37 | 16.8 | 44.8 | 38.4 | 1.35 | −16.7 | 2.9 | 1.7 | +1.0 | 35.5 | 69 | 12 |
| Bk5 | 252–320 | 0.57 | 13.6 | 46.3 | 40.1 | | −18.3 | −2.9 | −1.8 | +1.0 | 34.3 | 71 | 12 |
| Bk6 | 320–370 | 0.67 | 12.1 | 47.9 | 40.0 | | −18.6 | −2.9 | −1.4 | +1.0 | 32.8 | 62 | 10 |
| BCk | 370–400 | 0.49 | 12.0 | 47.1 | 40.9 | | −18.5 | −2.9 | −0.1 | +1.0 | 30.8 | 27 | 4 |

*Pedon 4 — 15,000 years*

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A1 | 0– 8 | 2.25 | 20.7 | 39.6 | 39.7 | 1.12 | −19.1 | +0.5 | −0.9 | +1.0 | 4.2 | 100 | 1 |
| A2 | 8– 14 | 1.73 | 20.6 | 34.5 | 44.9 | 1.25 | −18.4 | −2.0 | −0.3 | +1.0 | 3.0 | 44 | 1 |
| BA | 14– 38 | 1.30 | 21.6 | 31.7 | 46.7 | 1.30 | −14.7 | −2.4 | −2.1 | +1.0 | 4.3 | 91 | 2 |
| Bss1 | 38– 66 | 0.97 | 22.1 | 33.0 | 44.9 | 1.33 | −14.7 | −2.5 | −3.0 | +1.0 | 11.4 | 100 | 6 |
| Bss2 | 66– 98 | 0.72 | 24.6 | 32.2 | 43.2 | 1.40 | −13.4 | −2.5 | −2.1 | +1.0 | 20.0 | 88 | 9 |
| Bk1 | 98–120 | 0.35 | 33.1 | 33.7 | 33.2 | 1.43 | −13.6 | −2.5 | −1.2 | +1.0 | 38.6 | 62 | 12 |
| Bk2 | 120–150 | 0.26 | 46.0 | 30.3 | 23.7 | 1.47 | −14.4 | −2.5 | −0.4 | +1.0 | 48.1 | 40 | 10 |
| Bk3 | 150–190 | 0.42 | 51.0 | 29.7 | 19.3 | 1.47 | −19.4 | −2.5 | −0.2 | +1.0 | 51.1 | 34 | 9 |
| Bk4 | 190–213 | 0.23 | 52.6 | 29.5 | 17.9 | | −19.8 | −2.5 | −0.2 | +1.0 | 52.8 | 35 | 10 |
| Bk5 | 213–250 | 0.01 | 46.0 | 35.0 | 19.0 | | −19.9 | −2.5 | −0.1 | +1.0 | 51.3 | 31 | 8 |
| BC | 250–295 | 0.06 | 44.0 | 36.5 | 19.5 | 1.41 | −20.3 | −2.5 | 0.2 | +1.0 | 49.8 | 23 | 6 |
| CB | 295–350 | 0.07 | 52.5 | 28.8 | 18.7 | 1.55 | −21.1 | −2.5 | 0.4 | +1.0 | 52.3 | 17 | 5 |

[a] Weighted values for the upper 25 cm were used for the respired $CO_2$ input variable in the diffusion model.
[b] Predicted end-member using the diffusion model.
[c] Weighted average of parent material carbonate from all horizons from Pedon 1. and assumed as the parent material value for all pedons.
[d] Wt.% calculated by Eq. (1) in text; vol.% calculated by Eq. (9) in text.

The percentage pedogenic carbonate is calculated on a weight basis as the relative amount of the total soil carbonate that is pedogenic. The $\delta^{13}C$ value for the parent carbonate end-member ($\delta^{13}C_{parent}$) is obtained from direct measurement of an assumed parent material. The bulk soil carbonate ($\delta^{13}C_{bulk}$) is measured directly on each horizon throughout the soil, which normally contains a mixture of parent and pedogenic carbonate components. In the absence of pedogenic carbonate segregations that can be directly measured isotopically, the pedogenic end-member ($\delta^{13}C_{pedogenic}$) must be estimated. The following sections show how both the parent carbonate end-member and the non-measurable pedogenic carbonate end-member for Eq. (1) were estimated for soils in the chronosequence. Use of the term 'end-member' in this paper is constrained by the isotopic values of the pedogenic and lithogenic components of each pedon, and has no reference to the full range of pedogenic and lithogenic carbonate values known to occur in nature.

## 3. Parent material carbonate end-member

Ideally, the parent material carbonate end-member should be determined on the unweathered C horizon of each pedon under investigation. However, morphological evidence indicated that appreciable pedogenic carbonate was precipitating deep in Pedons 2, 3, and 4 (3 to 4 m deep), thus obscuring the original $\delta^{13}C$ values of the parent alluvium. As a result, the $\delta^{13}C$ parent value for all pedons in Eq. (1) was taken to be the weighted average of $\delta^{13}C$ values from all horizons in Pedon 1, the weakly developed modern floodplain soil. These values averaged to + 1.0‰ (Table 1), which is reasonable for all four pedons because: (1) it is within the range of limestone values obtained from the surrounding Cretaceous uplands (West et al., 1988) and from carbonate clasts contained within local alluvial deposits (Nordt and Hallmark, 1990); and (2) there is no geomorphic or isotopic evidence suggesting significant past shifts in sediment source or isotopic values in the alluvial sequence.

Undoubtedly some pedogenic carbonate was included in the parent carbonate end-member calculated from Pedon 1. Consequently, estimations of pedogenic carbonate accumulations may slightly exceed the actual amount present.

## 4. Modeling the pedogenic carbonate end-member

The soil environment operates as an open system because the flux of biologically produced $CO_2$ is orders of magnitude greater than the rate of pedogenic carbonate precipitation (Cerling, 1984; Rabenhorst et al., 1984; Quade et al., 1989; Cerling and Quade, 1993; Nordt et al., 1996). Consequently, isotopic equilibrium is maintained between gaseous soil $CO_2$ and $HCO_3^-$ in solution just prior to, and during, pedogenic carbonate precipitation. The $\delta^{13}C$ of pedogenic carbonate will, therefore, vary systematically from soil organic

matter. Two fractionation steps must be considered to estimate the pedogenic carbonate end-member from soil organic matter, as shown by the relationship:

$$\delta^{13}C_{\text{pedogenic carbonate}} = \delta^{13}C_{\text{SOM}} + \Delta_{CO_2 \text{ diffusion}} + \Delta_{CO_2 - CaCO_3} \qquad (2)$$

where $\delta^{13}C_{\text{SOM}}$ is measured from soil organic matter, $\Delta_{CO_2}$diffusion is the $\delta^{13}C$ difference between $^{12}CO_2$ and $^{13}CO_2$, and $\Delta_{CO_2 - CaCO_3}$ is the $\delta^{13}C$ difference between C in carbonate and $CO_2$ occurring during equilibria reactions.

As a substitute for Eq. (2), we used the diffusional model of Cerling (1984) and Quade et al. (1989) to estimate the $\delta^{13}C$ value for the pedogenic carbonate end-member of the soils in the chronosequence because: (1) there were no carbonate segregations in the form of nodules or soft masses that could be isolated for isotopic measurement; and (2) it is difficult to estimate the amount of atmospheric $CO_2$ mixing that may occur in the upper soil profile. The modeled pedogenic end-member values were then placed in Eq. (1) to calculate pedogenic carbonate accumulations for the four pedons. Estimations for the input and fixed variables in the diffusional model are discussed in the following sections in the order in which they occur in Eq. (2). Model variables are also shown in Table 2.

## 4.1. $\delta^{13}C_{SOM}$

The isotopic composition of soil organic matter (Eq. (2)) is controlled by the relative biomass contributions from $C_3$, $C_4$, and CAM plants to the soil organic matter pool (Boutton, 1991b). $C_3$ plants include most woody species and cool

Table 2
Input and fixed variables used to model the $\delta^{13}C$ of pedogenic carbonate by the diffusion model of Cerling (1984) and Quade et al. (1989)

| Model | All pedons | Pedon 1 | Pedon 2 | Pedon 3 | Pedon 4 |
|---|---|---|---|---|---|
| *Input variables* | | | | | |
| $\delta^{13}C$ (‰) respired soil $CO_2$ | | −19.1 | −19.0 | −17.8 | −17.4 |
| Soil $CO_2$ production attenuation depth (cm) | 25 | | | | |
| Soil $CO_2$ production rate (mmol m$^{-2}$ h$^{-1}$) | 6.3 | | | | |
| Atmospheric $CO_2$ concentration (ppmV) | | 293 | 279 | 279 | 279 |
| Atmospheric $CO_2$ $\delta^{13}C$ (‰) | | −6.61 | −6.50 | −6.50 | −6.50 |
| Atmospheric pressure (atm) | 1 | | | | |
| Soil porosity | | 0.56 | 0.52 | 0.48 | 0.47 |
| Soil temperature (°C) | 20 | | | | |
| Total $CO_2$ production depth (cm) | | 266 | 380 | 400 | 350 |
| $\alpha CO_2 - CaCO_3$ (20°C) | 1.01028 | | | | |
| *Fixed variables* | | | | | |
| Diffusional coefficient of $^{12}CO_2 / ^{13}CO_2$ in air | 1.0044 | | | | |
| Diffusional coefficient of $CO_2$ in soil (cm$^2$ s$^{-1}$) | 0.05 | | | | |
| Soil pore tortuosity | 0.6 | | | | |

season grasses, whereas $C_4$ plants consist mainly of warm season grasses. Under equilibrium conditions, contributions from pure $C_3$ and $C_4$ plant communities produce soil organic matter $\delta^{13}C$ values of approximately $-27$ and $-13\permil$, respectively. CAM plants consist mainly of desert succulents and typically yield $\delta^{13}C$ values ranging between, and including, those of $C_3$ and $C_4$ plants.

Investigators have shown that the instantaneous production of biological soil $CO_2$, measured as a surface flux to the atmosphere (respired), has virtually the same $\delta^{13}C$ value as the coexisting soil organic matter substrate (Dorr and Munnich, 1980; Cerling et al., 1991; Hesterberg and Siegenthaler, 1991). Consequently, the isotopic signatures of both soil organic matter and the surface flux of $CO_2$ will be the same at $-27$ and $-13\permil$ for pure stands of $C_3$ and $C_4$ plants, respectively. A linear isotopic mixing line can be constructed that connects these plant and soil $CO_2$ end-members.

As an approximation for the soil respired $CO_2$ input variable in the diffusional model (Table 2), the $\delta^{13}C$ of soil organic matter was weighted for all horizons in the upper 25 cm of each pedon using thickness, bulk density, and wt.% of organic C. A 25 cm depth was chosen because: (1) organic matter contents were highest in this zone and decreased appreciably below; (2) this depth coincides with the modeled attenuation depth for $CO_2$ production (see next section); and (3) recent investigations in the area suggest that organic matter below a depth of 25 cm in these soils was inherited from a previous vegetation community, and may be resistant to microbial decay (Nordt et al., 1994). The attenuation depth of 25 cm for $CO_2$ production, which is the approximate depth where $CO_2$ production does not decrease further, is consistent with results for many soils throughout the world (Singh and Gupta, 1977).

## 4.2. $\delta^{13}C$ of soil $CO_2$ ($\Delta_{CO_2\,diffusion}$)

As discussed in the following sections, the $\delta^{13}C$ of soil $CO_2$ ($\Delta_{CO_2\,diffusion}$) in Eq. (2) is dependent on $CO_2$ production rate, diffusional fractionation, and the amount of atmospheric mixing.

### 4.2.1. Production (respiration) rate

Soil $CO_2$ production (respiration) rate is the input variable used to model the concentration of $CO_2$ by assuming steady-state production and a decrease in production rate that is linear, exponential, or uniform with depth (Solomon and Cerling, 1987). As will be shown later, this variable influences the amount of diffusion of atmospheric $CO_2$ into the soil. Cerling et al. (1991) used an exponential depth–decay function in $CO_2$ production based on the equation:

$$\Phi_{(z)} = \Phi_{(z=0)}\exp(-z/z^*) \tag{3}$$

where $\Phi_{(z)}$ is the production rate of $CO_2$ at a given depth in mmol m$^{-2}$ year$^{-1}$, $\Phi_{(z=0)}$ is the $CO_2$ concentration at the soil surface assumed equal to the

atmosphere, $z$ is the depth in the soil in cm, and $z^*$ is the attenuation depth of $CO_2$ production set at 25 cm (Table 2). Cerling (1984) and Quade et al. (1989) demonstrated that this attenuation depth was reasonable for soils with relatively high respiration rates, such as in subhumid grasslands typical for central Texas.

The regression equation of Raich and Schlesinger (1992) was used to estimate the annual soil $CO_2$ production rate for our study area:

$$SR = (9.26 \times MAT) + (0.0127 \times MATxMAP) + 289 \qquad (4)$$

where SR is the soil respiration rate in g C $m^{-2}$ $year^{-1}$, MAT is the mean annual temperature in °C, MAP is the mean annual precipitation in mm, and $R^2$ is 0.5. Based on a MAT of 19°C and MAP of 800 mm (Bomar, 1983), a production rate of 6.3 mmol $CO_2$ $m^{-2}$ $h^{-1}$ was calculated for all four pedons (Table 2). This value matches the measured $CO_2$ production rate of 6.3 mmol $CO_2$ $m^{-2}$ $h^{-1}$ for a tallgrass prairie in Oklahoma (Riser et al., 1981). Although a single value for the respiration rate is an average of potentially widely fluctuating $\delta^{13}C$ values, the diffusion model is not particularly sensitive to this input variable for high respiration rate soils. Consequently, a single input value should have little effect on the predicted pedogenic carbonate end-member.

### 4.2.2. Diffusional fractionation

Assuming steady-state production of biologically produced $CO_2$, in association with the fixed variables in Table 2 and the production function in Eq. (3), the concentration of soil $CO_2$ increases with depth (Wood and Petraikis, 1984; Solomon and Cerling, 1987; Hesterberg and Siegenthaler, 1991). Consequently, a concentration gradient develops such that $CO_2$ diffuses to the soil surface. Along this gradient, the lighter $^{12}CO_2$ molecules diffuse more rapidly to the surface than the heavier $^{13}CO_2$ molecules by an amount equal to the differences in their respective diffusion coefficients. This relationship was first derived by Craig (1954) and simplifies to:

$$\frac{D(^{12}CO_2)}{D(^{13}CO_2)} = 1.0044 \text{ or } 4.4\%o \qquad (5)$$

where $D(^{12}CO_2)$ and $D(^{13}CO_2)$ are the diffusion coefficients of $^{12}CO_2$ and $^{13}CO_2$, respectively. Consequently, according to kinetically based diffusional fractionation, soil $CO_2$ will be 4.4‰ greater in $^{13}C$ content than soil organic matter or $CO_2$ measured as a surface flux. The fractionation factor of 1.0044 is a fixed variable in the diffusional model (Table 2).

Cerling et al. (1991), and Dorr and Munnich (1980), confirmed by field observations that the $\delta^{13}C$ value of soil $CO_2$ is about 4.4‰ greater than the surface flux. Recently, Davidson (1995) discovered that the diffusional coefficient can vary from 4.4‰ depending on the associated vegetation community, but only slightly. Regardless, it is this isotopically enriched subsurface soil $CO_2$ phase that apparently takes part in carbonate equilibria reactions.

### 4.2.3. Atmospheric mixing

$\delta^{13}C$ values for modern and preindustrial atmospheric $CO_2$ are approximately −8 and −6‰, respectively (Boutton, 1991b). This is significantly higher than $\delta^{13}C$ values produced by biological sources. By modeling, Cerling (1984) demonstrated that soils with low $CO_2$ production rates have greater atmospheric mixing in the upper profile than soils with high $CO_2$ production rates. Consequently, $CO_2$ in all soils will be enriched not only by 4.4‰ as predicted by Eq. (5), but by even more depending on the amount of atmospheric mixing.

The concentration of $CO_2$ in the atmosphere has varied through geologic and historic time. Based on atmospheric $CO_2$ trapped in ice cores, the estimated pedogenic end-member of Pedons 2, 3, and 4 of the chronosequence were modeled from average atmospheric concentrations and $\delta^{13}C$ values ($n = 7$) typical of the Holocene (Leuenberger et al., 1992) (Table 2). The pedogenic end-member for Pedon 1, the historic soil, was modeled with atmospheric $CO_2$ concentrations and $\delta^{13}C$ values ($n = 22$) averaged from ice cores for the last two centuries (Friedli et al., 1986) (Table 2). Total pressure (input variable) of one atmosphere was assumed for each pedon for the time of pedogenesis (Table 2).

### 4.3. Other model variables

The model input variable for porosity was determined as a whole-soil weighted average for each pedon based on measured moist bulk densities (Tables 1 and 2). The soil temperature input variable was determined as a mean annual value by adding 1°C to the mean annual atmospheric temperature of 19°C (Brady, 1990). The input variable for total $CO_2$ production depth was taken as the solum thickness for each pedon.

### 4.4. Carbonate equilibria ($\Delta_{CO_2 - CaCO_3}$)

A final consideration in determining the $\delta^{13}C$ value for the pedogenic carbonate end-member in Eq. (2) is the isotopic fractionation of C in the phase transformation from $CO_2$ to $CaCO_3$ at equilibrium:

$$Ca^{2+} + 2HCO_3^- \leftrightarrow \text{pedogenic } CaCO_3 + CO_2 + H_2O \qquad (6)$$
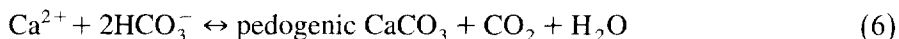
Pedogenic carbonate typically precipitates in response to a decrease in water content or $CO_2$ partial pressure, to an increase in calcium or bicarbonate ion concentration, or to a combination of the above. As C is transferred from the diffusionally fractionated gaseous soil $CO_2$ phase to the pedogenic phase during carbonate precipitation, equilibrium-based isotopic fractionation occurs. Because of physical differences, the heavier $^{13}C$ isotope is preferentially retained in the solid phase during carbonate precipitation. Deines et al. (1974) fitted a linear regression to fractionation factors determined both empirically and by partition

functions by various investigators for the $CO_2$–$CaCO_3$ system. This equation is:

$$1000 \ln \alpha_{CO_2 - CaCO_3} = -3.63 \frac{(1.194 \times 10^6)}{T^2} \tag{7}$$

where $\alpha$ is the fractionation factor (equilibrium constant) in the $CO_2$–$CaCO_3$ system expressed as a natural logarithm, and $T$ is temperature in degrees K. The amount of fractionation is slightly temperature-dependent in the temperature range of soils. For this input variable at 20°C for the chronosequence, the fractionation factor is 1.01028 or ~ 10.3‰ (Table 2).

### 4.5. Summary

At depths below the influence of atmospheric mixing, and assuming a soil temperature of 20°C, the theoretical $\delta^{13}C$ offset between soil organic matter and the pedogenic carbonate end-member should approximate 15‰ for the four soils of the chronosequence. This value is the sum of 4.4‰ and 10.3‰ for molecular diffusion of $CO_2$ and carbonate equilibria reactions, respectively, and by mass balance can be expressed as:

$$\delta^{13}C_{\text{pedogenic carbonate}} = \alpha_{CaCO_3 - CO_2}(\delta^{13}C_{SOM} + 1004.4) - 1000 \tag{8}$$

where $\alpha_{CaCO_3 - CO_2}$ is the fractionation factor between pedogenic carbonate and soil $CO_2$.

The 15‰ offset is consistent with results from other localities where pedogenic carbonate segregations in the subsoil were isolated and analyzed (Cerling et al., 1989; Kelly et al., 1991; Wang et al., 1993; Cole and Monger, 1994). Where atmospheric mixing occurs in upper soil horizons of the chronosequence, the theoretical offset between soil organic matter and pedogenic carbonate will slightly exceed 15‰ by an amount proportional to the quantity of atmospheric mixing. Computer modeling is necessary to make this determination.

## 5. The soil chronosequence

### 5.1. Pedon 1

Pedon 1 was excavated in the floodplain of Cowhouse Creek. The floodplain consists of loamy carbonatic alluvium that has been rapidly aggrading for the last 600 years. Pedon 1 consists of a sequence of stacked and weakly developed soils, with the surface soil classifying as an Entisol. The percentage of organic C, total carbonate, and particle size distribution vary irregularly with depth (Table 1). Between 42.4 and 76.0% of the fine-earth fraction consists of calcium carbonate (Table 1). Numerous observable microfossils in thin-section and little evidence of pedogenic carbonate in either the field or thin-section, suggest that most of the carbonate in Pedon 1 is inherited from the parent material.

The weighted $\delta^{13}C$ average for organic matter in the upper 25 cm of Pedon 1 is −19.1‰ (Table 2). This yields a modeled pedogenic carbonate end-member

of $-4.0\%o$ below a depth of 57 cm (Table 1; Fig. 2a). Because of minor mixing of atmospheric $CO_2$ with soil $CO_2$, the pedogenic end-member is $0.8\%o$ higher in the surface layer (Table 1; Fig. 2a). The $\delta^{13}C$ value for the parent carbonate end-member for Pedon 1 ($+1.0\%o$) was a weighted average of bulk values also from Pedon 1. As a result, the only pedogenic carbonate calculated for Pedon 1 occurred when bulk $\delta^{13}C$ values were less than the mean bulk value used for the parent end-member (Table 1; Fig. 2a).

## 5.2. Pedon 2

Pedon 2 has been developing in loamy carbonatic alluvium of a low terrace of Cowhouse Creek for 2000 years. Depth distributions of sand, silt, and clay reveal faint stratification in the original soil parent material (Table 1). Between 42.1 and 50.8% of the mineral component is comprised of calcium carbonate (Table 1). Pedon 2 has an A–Bk–BCk–C horizon sequence and classifies as a
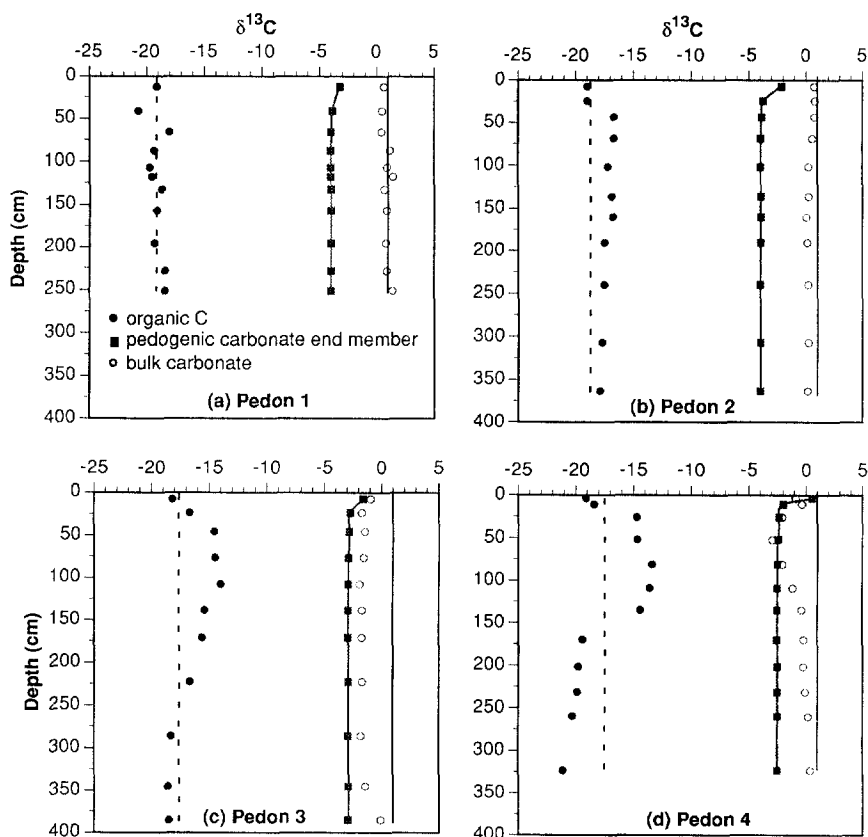


Fig. 2. (a–d) Stable C isotopes of organic matter and pedogenic, bulk, and parent carbonate for Pedons 1–4. The dashed line is the weighted $\delta^{13}C$ average of organic matter for the upper 25 cm. The solid line (far right) is the average $\delta^{13}C$ of bulk carbonate from Pedon 1, taken as the parent material end-member for all pedons. The pedogenic carbonate end-members were modeled.

Mollisol. By field morphology and thin-section, occasional filaments and threads of carbonate are evidence of pedogenic accumulations in the Bk horizons.

The weighted $\delta^{13}C$ average of soil organic matter for the upper 25 cm of Pedon 2 is $-19.0‰$; a value very similar to that of Pedon 1 (Table 2). The diffusion model predicts a $\delta^{13}C$ pedogenic carbonate end-member of $-4.0‰$ below a depth of 34 cm (Table 1; Fig. 2b). The isotopic gradient for the pedogenic end-member is steeper in the upper profile of Pedon 2 than Pedon 1. This is because the surface layer of Pedon 2 was sampled at a shallower depth and therefore had more C from atmospheric $CO_2$ mixed with the pedogenic carbonate component.

In Pedon 2, the bulk carbonate values have shifted slightly away from the parent material end-member and slightly toward the pedogenic end-member in the Bk horizons (Fig. 2b). Based on this shift, Eq. (1) estimates that of the total carbonate content, 15 to 20% by weight is pedogenic in the Bk horizons below a depth of 85 cm (Table 1). The isotopic shift towards the pedogenic end-member persists to the bottom of the profile, indicating that pedogenic carbonate is precipitating deep in the profile. In corroboration, the absence of depositional isotopic stratification and the presence of occasional carbonate filaments and threads in the parent material, suggest that the disseminated carbonate in the lower solum was not inherited from alluvial deposition.

$\delta^{13}C$ values for the bulk carbonate in the upper 34 cm of Pedon 2 shift slightly back towards the parent end-member because: (1) atmospheric mixing in these horizons also shifts the pedogenic end-member slightly towards positive values; and (2) there is less pedogenic carbonate in the upper profile where maximum leaching occurs. Total pedogenic carbonate in the upper 85 cm thus reduces to between 5 and 9% by weight (Table 1; Fig. 2b).

## 5.3. Pedon 3

Pedon 3 has been developing for 5000 years in loamy carbonatic alluvium of a low terrace of Cowhouse Creek. This pedon consists of an A–ABBw–Bk–BCk horizon sequence and classifies as a Mollisol. The clay content of the parent alluvium and soil is higher in Pedon 3 than in Pedons 1 and 2, whereas the total carbonate content is slightly lower (Table 1). The particle size distribution reveals minimal stratification with depth. Minor carbonate loss from the surface horizons is evident based on the total carbonate content. Pedogenic accumulation in the form of filaments and threads is evident by field morphology and thin-section in the Bk horizons.

For Pedon 3, the weighted $\delta^{13}C$ average for the soil organic matter in the upper 25 cm increases to $-17.8‰$ because of greater contributions from $C_4$ plants to the biomass at this locality (Table 2). This results in an estimated pedogenic end-member of $-2.9‰$ below a depth of 59 cm (Table 1; Fig. 2c). The bulk carbonate isotopic values are shifted considerably closer to the

pedogenic end-member in this pedon. By Eq. (1), between 62 and 74% of the total carbonate is pedogenic in the upper 370 cm (Table 1). As with Pedon 2, the visible form of this pedogenic component occurs as filaments and threads, both on ped surfaces and within peds. As with Pedons 1 and 2, mixing of atmospheric $CO_2$ with biological $CO_2$ increases the $\delta^{13}C$ value for the estimated pedogenic carbonate end-member in the upper profile. Accordingly, a slight increase in bulk carbonate $\delta^{13}C$ values in the surface horizon appears to reflect precipitation in partial equilibrium with atmospheric $CO_2$. As with Pedon 2, pedogenic carbonate is precipitating deep in the profile. In contrast, Pedon 3 has a significant non-detectable and disseminated carbonate fraction in the surface horizons.

Cerling et al. (1989) proposed that the pedogenic carbonate end-member could be estimated from the $\delta^{13}C$ value of organic matter on a horizon by horizon basis. Interestingly, if the approximated 15‰ enrichment factor is added to the $\delta^{13}C$ values of organic C on a horizon by horizon basis between depths of 32 and 153 cm in Pedon 3, the $\delta^{13}C$ value of the estimated pedogenic end-member exceeds that of the bulk carbonate. In fact, the bulk values fall on the parent carbonate end-member line. This cannot be the case considering that the bulk carbonate contains a $^{13}C$-enriched detrital limestone component mixed with a $^{13}C$-depleted pedogenic component. It is possible that the organic C at this depth is complexed with clays and resistant to microbial decay, thus contributing little $CO_2$ to total soil $CO_2$ production. Furthermore, Nadelhoffer and Fry (1988) confirmed that the $\delta^{13}C$ of organic matter increases with depth, and thus time, because it is here that more resistant and $^{13}C$-enriched organic components persist.

## 5.4. Pedon 4

Pedon 4 has been developing in loamy carbonatic alluvium of a high terrace of Cowhouse Creek for approximately 15,000 years. However, textures in the upper 98 cm are clayey (Table 1) as a result of significant carbonate loss and the subsequent release of occluded smectitic clays (Nordt and Hallmark, 1990). As a consequence, this pedon has an A–Bss–Bk–BC horizon sequence and classifies as a Vertisol. As in Pedons 2 and 3, pedogenic carbonate occurs in the form of filaments and threads as revealed by field observations and thin-sections.

Because of greater $C_4$ plant contributions to the soil organic matter pool in the upper profile of Pedon 4, the weighted $\delta^{13}C$ of organic matter increased to $-17.4‰$ (Table 2). This results in an estimated pedogenic carbonate $\delta^{13}C$ end-member of $-2.5‰$ below a depth of 38 cm (Table 1; Fig. 2d). In the upper 8 cm, mixing of atmospheric $CO_2$ has increased the pedogenic end-member value to $+0.5‰$. This value demonstrates the sensitivity of the estimated pedogenic carbonate end-member to the steep atmospheric $CO_2$ gradient in the upper profile. Because the bulk carbonate values also increase along this

gradient, the pedogenic component present in the upper profile probably precipitated in partial equilibrium with atmospheric $CO_2$. However, atmospheric mixing has apparently not been as great as the diffusion model predicts because the estimated pedogenic end-member exceeds the bulk carbonate value in the surface horizon (Fig. 2).

The bulk carbonate $\delta^{13}C$ values show that most, if not all, of the total carbonate in the upper 98 cm in Pedon 4 is pedogenic (Table 1; Fig. 2d). However, total carbonate content within this depth ranges from only 3 to 20% because of significant carbonate loss during 15,000 years of pedogenesis. Because few filaments and threads were observed in the upper 98 cm by thin-section or field morphology, most of the pedogenic carbonate occurs in a disseminated fraction not identifiable, except isotopically.

The presence of 17% pedogenic carbonate by weight in the deepest horizon sampled, again indicates that a significant disseminated pedogenic fraction is precipitated at great depths (Table 1; Fig. 2d). As with Pedon 3, the estimated pedogenic carbonate end-member in the subsoil would greatly exceed the bulk carbonate value if using the $\delta^{13}C$ of soil organic matter from that same depth. Consequently, soil organic matter below a depth of 14 cm in Pedon 4 appears to be recalcitrant and to contribute little $CO_2$ to the total soil $CO_2$ pool.

## 5.5. Volumetric quantification of isotopically determined pedogenic carbonate

To make comparisons on a horizon by horizon and whole-soil basis to other techniques of estimating pedogenic carbonate, the weight percentages as calculated isotopically by Eq. (1), were converted to volume percentages (cm$^3$ 100 cm$^{-3}$) for each pedon by the equation:

$$\text{pedogenic carbonate(vol.\%)} = \frac{(\text{wt.\% pedogenic carbonate} \times \rho_w \times \text{total carbonate})}{\rho_d \text{ of calcite}} \quad (9)$$

where bulk density ($\rho_w$) is in g cm$^{-3}$, the particle density ($\rho_d$) of calcite is 2.72 in g cm$^{-3}$, and total carbonate is expressed as a decimal (Table 1).

It is possible that all horizons in Pedon 1 contain a small amount of pedogenic carbonate (Table 1). However, much of this component was probably inherited from the alluvial influx of eroded upland soils. Whereas the surface horizons of Pedon 2 have a small disseminated pedogenic fraction, the Bk horizons between depths of 85 and 380 cm have between 3 and 4 vol.% (Table 1). Pedon 3 has 12 vol.% pedogenic carbonate in the surface horizon that increases to a maximum of 15 vol.% in the upper Bk horizon and then decreases to 4 vol.% in the BC horizon (Table 1). The effects of net carbonate loss through time can be observed in Pedon 4 where in the upper solum the percentage of pedogenic and total carbonate is less than that in Pedon 3 (Table 1).

## 5.6. Methodological comparisons

In addition to isotopic analysis, other techniques were used to volumetrically quantify pedogenic carbonate accumulations in the chronosequence. First, visual estimations were made of pedogenic quantities associated with natural aggregates during field sampling. Second, point counts were conducted with a binocular light microscope for most horizons containing pedogenic carbonate that was visible in the field. For this method, three bulk aggregates were analyzed per horizon. Following statistical methods of Drees and Ransom (1994), it was determined that approximately 250 point counts per horizon were sufficient to estimate the mean pedogenic percentage within a probable mean error of 2% at the 80% confidence level. Third, thin-section point counts were utilized to estimate pedogenic carbonate quantities. By this method, however, so few pedogenic forms were observed (always < 1% by volume) that statistical calculations revealing more than 10,000 point counts were needed per horizon to obtain the probable mean error used above. This suggests that thin-section samples were not representative of bulk soil conditions, or that pedogenic carbonate was in a non-detectable form. As a consequence, it was assumed that all horizons contained less than 1% by volume pedogenic carbonate based on thin-section point counts.

### 5.6.1. Pedon 1
Except for two horizons, no pedogenic carbonate was visible in the field for Pedon 1 (Fig. 3a). Most horizons contained a small disseminated component based on the isotopic method. Of the two horizons with visible pedogenic carbonate, the field and binocular light microscope estimates for the shallower of these horizons were much greater than the estimate by the isotopic method. The binocular light microscope estimate was greater than estimates by both the isotopic and field methods in the lower of these two horizons. The possible reason for this discrepancy is discussed in the next section.

### 5.6.2. Pedon 2
Between a depth of 85 and 347 cm in the Bk horizons of Pedon 2, the field and binocular light microscope estimates were similar, with both considerably overestimating the pedogenic carbonate component relative to the isotopic method (Fig. 3b). The reason for this overestimation appears to be related to the morphology of the filaments and threads of pedogenic carbonate in Pedon 2, and perhaps in Pedon 1, as well. As shown by a scanning electron microscopy (SEM) photograph from the Bk5 horizon of Pedon 2 (Fig. 4A), pedogenic carbonate occurs as acicular needles. In the field and under the light microscope, however, these filaments and threads appear to be continuous, dense masses, thus leading to a biased overestimation of their contribution to the total pedogenic carbonate pool.
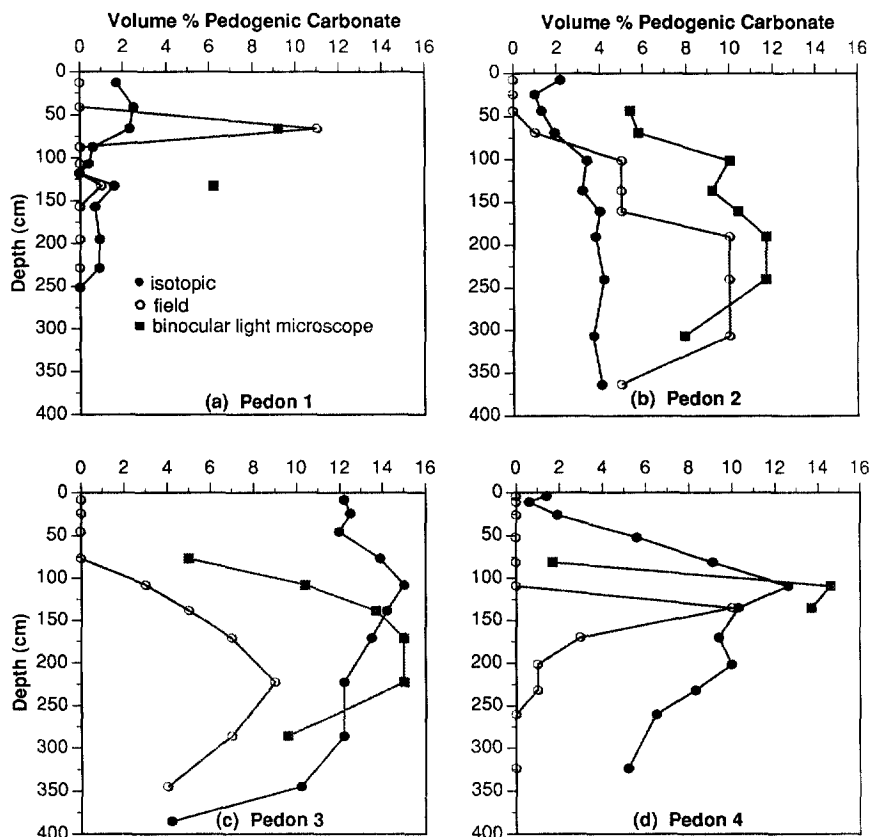
Fig. 3. (a–d) Comparison of three methods of quantifying volumetric pedogenic carbonate accumulations: stable C isotope, field morphology, and binocular light microscope point counts.

### 5.6.3. Pedon 3

The isotopic method for Pedon 3 detected a significant disseminated pedogenic fraction for the surface horizons that was not visible in the field (Fig. 3c). Throughout the remaining profile, the percentage of pedogenic carbonate in the field was also underestimated compared to the isotopic method. This suggests the presence of a significant non-detectable and disseminated pedogenic carbonate fraction in the subsoil of Pedon 3. Estimates under the binocular light microscope, however, were similar to estimates by the isotopic method between a depth of 94 and 320 cm. As seen on a scanning electron photomicrograph from the Bk2 horizon (Fig. 4B), carbonatic filaments and threads in Pedon 3 are present as thick and dense calcans. Under these conditions, point counts with the light microscope appear to more accurately reflect the volumetric quantity of pedogenic carbonate as determined isotopically, rather than by the field method.
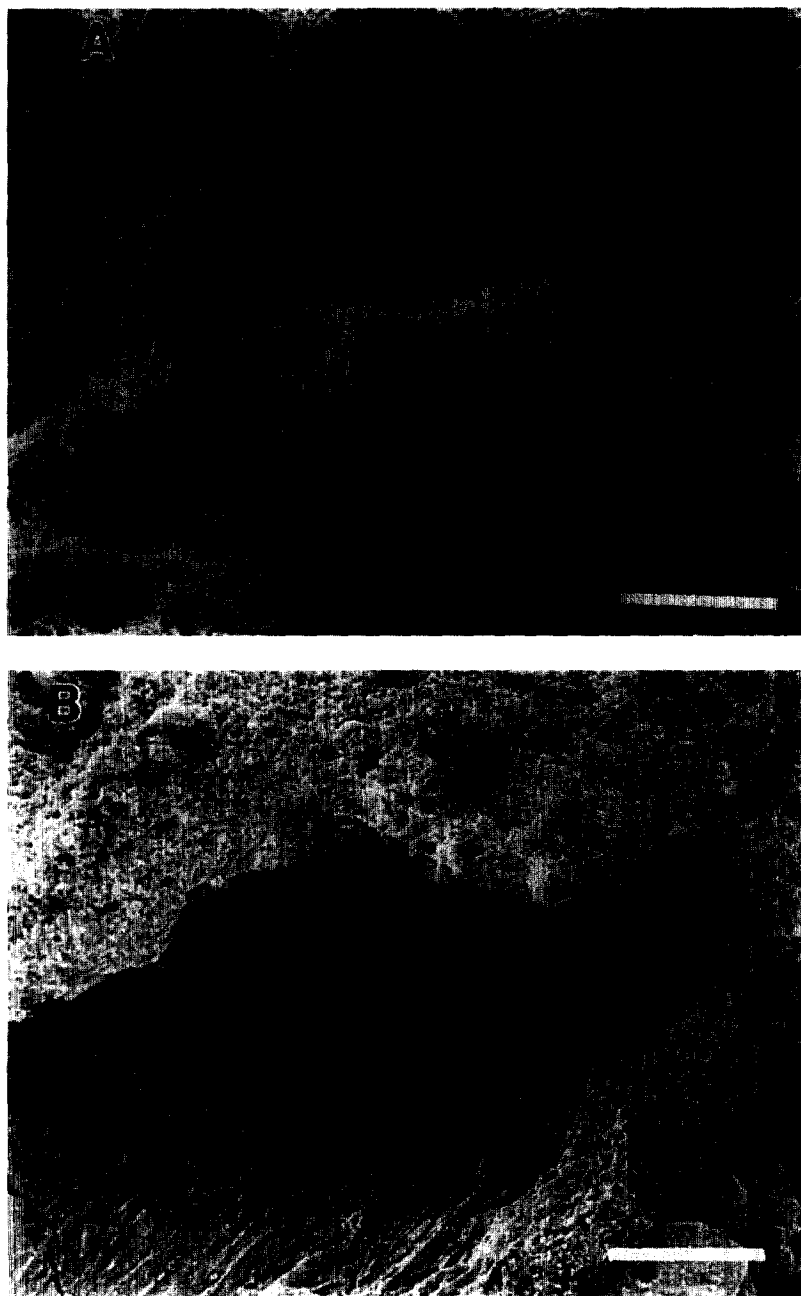
Fig. 4. Scanning electron microscope (SEM) photomicrographs of pedogenic carbonate forms (bar scale equals 100 μm). (A) Acicular needles from the Bk5 horizon of Pedon 2. (B) Dense pore coats (calcans) from the Bk2 horizon of Pedon 3.

*5.6.4. Pedon 4*

Similar to Pedon 3, Pedon 4 has a large disseminated pedogenic fraction throughout most of the profile that was not visible in the field (Fig. 3d). The morphology of the filaments and threads of pedogenic carbonate seem to be similar to those in Pedon 3 based on appearances in the field and in thin-section. Consequently, as with Pedon 3, the binocular light microscope and isotopic estimates approximate each other in the maximum expression of the Bk horizons in Pedon 4.

There is a large discrepancy in quantitative estimates of pedogenic carbonate in Pedon 4 between the field (0%) and binocular light microscope (15%) at a depth of approximately 110 cm. This could have occurred for two reasons. Firstly, the clods for the binocular light microscope estimates were collected at a later time when the soil was dry, whereas the bulk soil samples were collected when the soil was moist. Moisture obscures the visibility of weakly developed filaments and threads. Secondly, weakly developed filaments and threads are more visible under a microscope than in the field.

## 6. Conclusions

To quantify pedogenic carbonate accumulations in soils developed from calcareous parent materials, the $\delta^{13}C$ value of bulk, parent, and pedogenic carbonate must be known. Bulk carbonate values can be measured directly on a horizon-by-horizon basis. Parent carbonate values can be measured on an assumed parent material. In the absence of pedogenic carbonate segregations that can be analyzed isotopically, a $CO_2$ diffusion model should be used to estimate the pedogenic carbonate end-member. The $\delta^{13}C$ value of the modeled pedogenic end-member is most sensitive to the input variables 'soil $CO_2$ production' and '$\delta^{13}C$ of respired $CO_2$'. Unfortunately, these and the other input variables are based on mean annual values. It is not clear how these factors vary over an annual cycle and potentially influence the isotopic composition of soil $CO_2$ and the pedogenic carbonate $\delta^{13}C$ value. However, in soils with high respiration rates the annual $CO_2$ cycle may have little influence on the $\delta^{13}C$ of the pedogenic carbonate end-member. Furthermore, estimating the pedogenic end-member can be strengthened in soils with carbonate segregations that can be analyzed isotopically. Isotopic work is also needed to assess the close-range spatial variability of bulk soil carbonate samples.

The results of this investigation show that for quantifying pedogenic carbonate accumulations, the superiority of detection and quantification appears to be isotopic > binocular light microscope > field ≫ thin-section. However, further work is needed to determine if the isotopic method is more effective in differentiating pedogenic and lithogenic carbonates in other geographical areas. Regardless, it is important to use all quantitative methods available for estimating pedogenic carbonate contents.

Other investigators have identified and quantified similar percentages of disseminated pedogenic carbonate in soils throughout the midwestern U.S.A. using the diffusion model (Kelly et al., 1991). Furthermore, the diffusion model appears to have worked well in this investigation because identification of pedogenic carbonate precipitating at great depths, coupled with a decrease in total carbonate after 15,000 years of pedogenesis (Pedon 4), are consistent with conclusions drawn for the same chronosequence calculating net carbonate losses using mass balance analysis (Nordt and Hallmark, 1990). Consequently, the stable C isotope diffusion model provides a powerful tool for estimating pedogenic carbonate accumulations in soils developed from calcareous parent materials.

In this investigation, problems with the binocular light microscope and field estimations arise from quantitatively estimating the percentage of individual filaments and threads having different densities and thicknesses. All filaments and threads in the field and under the light microscope appear the same and carry the same quantitative weight. However, the isotopic method can more objectively quantify pedogenic amounts in horizons containing acicular needles versus dense calcans. Another problem with field and binocular light microscope estimates is the difficulty of detecting a disseminated pedogenic fraction. This fraction can only be quantified by the isotopic method.

The gross underestimation of pedogenic carbonate using thin-sections is perplexing. Apparently the filaments and threads occur so infrequently in natural aggregates that the chances of randomly cutting a thin-section through a pedogenic form is remote. Furthermore, because of numerous wetting events, ped faces and pores may be so unstable that pedogenic forms never accumulate to a visible size (field observations) before being partly dissolved and reprecipitated to greater depths. This process, along with shrink–swell activity and bioturbation, may contribute to maintaining the pedogenic carbonate in a relatively fine-grained and transient fraction.

Results from this investigation suggest that disseminated pedogenic carbonate may be an important component of many soils. This fine-grained, highly reactive fraction has a strong influence on many physical and chemical soil properties. Its recognition would lead to the increased identification of calcic horizons relative to the current definition of calcics, which exclude non-resolvable forms of pedogenic carbonate (Soil Survey Staff, 1996). Pedogenic carbonate may play a role in the global C cycle; however, observed net carbonate loss through time in our chronosequence suggests that many soils in the Southern Plains of the U.S. may not serve as a long-term sink for C.

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