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Factors and processes governing the ^{14}C content of carbonate in desert soils

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Abstract

A model is presented describing the factors and processes which determine the measured ^{14}C ages of soil calcium carbonate. Pedogenic carbonate forms in isotopic equilium with soil CO_2. Carbon dioxide in soils is a mixture of CO_2 derived from two biological sources: respiration by living plant roots and respiration of microorganisms decomposing soil humus. The relative proportion of these two CO_2 sources can greatly affect the initial ^{14}C content of pedogenic carbonate: the greater the contribution of humus-derived CO_2, the greater the initial ^{14}C age of the carbonate mineral. For any given mixture of CO_2 sources, the steady-state $^{14}CO_2$ distribution vs. soil depth can be described by a production/diffusion model. As a soil ages, the ^{14}C age of soil humus increases, as does the steady-state ^{14}C age of soil CO_2 and the initial ^{14}C age of any pedogenic carbonate which forms. The mean ^{14}C age of a complete pedogenic carbonate coating or nodule will underestimate the true age of the soil carbonate. This discrepancy increases the older a soil becomes. Partial removal of outer (and younger) carbonate coatings greatly improves the relationship between measured ^{14}C age and true age. Although the production/diffusion model qualitatively explains the ^{14}C age of pedogenic carbonate vs. soil depth in many soils, other factors, such as climate change, may contribute to the observed trends, particularily in soils older than the Holocene.

1. Introduction

Radiocarbon dating of sedimentary deposits in deserts is hindered by a lack of organic carbon. Paradoxically, most of the deposits in these re-

gions are blanketed with inorganic carbon in the form of pedogenic carbonate. Since the early 1960s, ^{14}C ages have been calculated for these carbonates [1]. Fig. 1 illustrates that an approximate 1:1 relationship exists between ^{14}C ages of soil carbonate and coexisting organic materials and ages determined by other means (see also [2,3]). These relationships are not perfect: some carbonate is younger than independent ages sug-

gest, some is older. This has led to much discussion of the reliability of carbonate ^{14}C ages [2,4,5], with no apparent consensus existing at present.

Until recently, an adequate theoretical model describing the processes that distribute ^{14}C in soil carbonates did not exist. Research and modeling of stable C isotopes in soils [6,7,8] led to principles that can also be applied to [14]C [9,10]. To summarize, the ^{14}C content of soil carbonate is controlled by that of soil CO_2. The ^{14}C content of soil CO_2 is affected by many factors and processes, and can be described by a production/diffusion model that incorporates rates of CO_2 production, rates of [14]CO_2 production, temperature, source of CO_2 production, and the ^{14}C content of decomposing soil organic matter.

In this paper, we review and expand the production/diffusion model [9,10] and evaluate it for different soil conditions, devoting considerable attention to its effects on carbonate ^{14}C ages. [14]C ages of soil carbonate reported in the literature, as well as data generated in this study, are evaluated in the light of the model and their geologic significance is discussed. Recommendations for sampling strategies for soil carbonate

are made that may improve the usefullness of soil carbonate ^{14}C ages as indicators of landform ages.

2. Methods

Pedogenic carbonate was collected from two locations: the Providence Mountain area, Mojave Desert, California and the Wind River Basin, Wyoming.

The Providence Mountain soils formed on alluvium derived from Mesozoic granitic rocks. Carbonate was found at the bottom of gravels as thin, partially continuous coatings. Gravels containing carbonate were collected for isotopic analyses by soil horizon.

The Wind River Basin is a cool, high-elevation desert characterized by cyclic episodes of river incision and the formation of paired terraces. Soil profiles were exposed on major Holocene and Pleistocene terraces of the Wind River. The gravelly layers in the soils contained carbonate coatings on their undersides. Gravels were collected for isotopic analysis in 20 cm depth intervals from the top of the gravelly matrix in the soil (usually
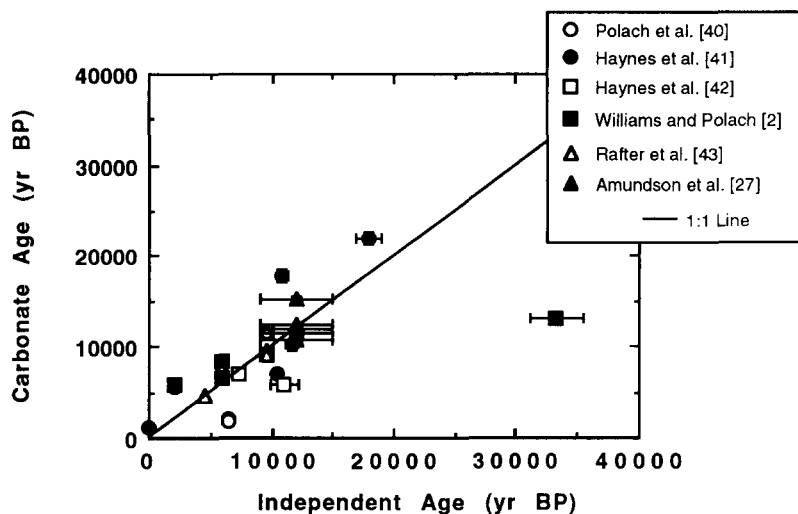

Fig. 1. Radiocarbon ages of pedogenic carbonate and ages of coexisting organic matter (or ages based on geologic evidence) from a variety of published sources. Modeled on previous figures by Williams and Polach [2] and Chen and Polach [3]. The plot shows that there is a correspondence betweem the ^{14}C age of soil carbonate and independent ages, although the relationship is not always 1 : 1.

about 50 cm from the soil surface). In the older terraces, care was taken to collect only those clasts in which the coatings (1) showed no outward evidence of dissolution/reprecipitation, (2) were firmly attached to the gravels (survived blows with a hammer), and (3) were from chemically resistant rocks (quartzite, metaplutonics and volcanics).

Carbonate laminations in the Wind River samples were a minimum of 2 mm thick on the youngest terrace and > 3 cm thick on the early Pleistocene terraces. On clasts from the older soils, outer laminations were removed with a hammer. Then, on clasts from soils of all ages, a drill and sandblaster were used to thin the remaining laminations to a thickness of 0.5 ± (0.2–0.3) mm. Laminations in the Providence Mountain soils were thin and discontinous. The gravels were washed in deionized water and were air dried. Carbonate laminations were then chipped from the clasts with a hammer and chisel, and ground to powder in an agate mortar and pestle.

Subsamples of the carbonate (for stable C isotope analysis) were roasted at 425°C for 4 h under vacuum. The carbon isotopic compositions were determined by reacting weighed samples with 100% H_3PO_4 for 12 h at 25°C. The liberated CO_2 was purified cryogenically and the carbonate content was determined by measuring the CO_2 yield manometrically. The $^{13}C/^{12}C$ ratio was determined by mass spectromety.

Carbonate samples for ^{14}C analysis were reacted with 100% H_3PO_4 under vacuum to release CO_2. The CO_2 was purified cryogenically, then reduced to graphite with H_2 over Co [11]. The graphite was then ionized and its $^{14}C/^{13}C$ ratio measured by accelerator mass spectrometry (AMS) at the Lawrence Livermore National Laboratory Center for AMS.

Representative subsamples of the < 2 mm soil fraction were ground to a fine powder in a mortar and pestle. Samples were acidified with 6N HCl to remove carbonates, rinsed thoroughly with deionized H_2O, and dried. Carbon concentrations and $\delta^{13}C$ values for the organic matter were determined by combusting samples at 875°C in the presence of Cu, CuO and Ag, purifying released CO_2 cryogenically, and determining its

quantity and isotopic composition manometrically and mass spectrometrically [12].

The stable carbon isotope composition of a carbonate or organic matter sample is expressed as the ratio of ^{13}C to ^{12}C in the sample of interest relative to the PDB standard:

$$\delta^{13}C = \left\{ \left[(^{13}C/^{12}C)_{sample} / (^{13}C/^{12}C)_{PDB} \right] - 1 \right\}$$
$$\times 1000\%o$$

The notation used to express the ^{14}C content of a sample is:

$$\delta^{14}C = (R_{sample}/R_{std} - 1) \times 1000$$

where $\delta^{14}C$ is the permil value for ^{14}C content and R_{std} is the absolute $^{14}C/^{12}C$ ratio in the isotopic standard (NBS oxalic acid) corrected to 1950 values and R_{sample} is uncorrected for either time or $\delta^{13}C$ values. The $\delta^{14}C$ notation used here is the same as that used in oceanography. $\delta^{14}C$ values reported in this paper were measured in 1991. The ^{14}C age of a sample is calculated from the measured $^{14}C/^{13}C$ ratios as follows [13]:

radiocarbonage

$$= -8033 \ln\left((^{14}C/^{13}C)_{s[-25]} / (^{14}C/^{13}C)_{1950[-25]} \right)$$

where $(^{14}C/^{13}C)_{s[-25]}$ and $(^{14}C/^{13}C)_{1950[-25]}$ are the $^{14}C/^{13}C$ ratios in a sample and the NBS oxalic acid standard, respectively, which have been corrected to values corresponding to $\delta^{13}C = -25\%o$ using $^{13}C/^{12}C$ ratios measured with a stable isotope ratio mass spectometer.

3. Principles of radiocarbon dating

The ^{14}C content of a sample will accurately reflect the age of that sample only if certain conditions are met [14]:

(1) The ^{14}C content of the atmosphere (C source) is either constant or known through time.

(2) The ^{14}C content of the sample is the same as that of the atmosphere (or its relationship to the atmosphere is known) at the time of its formation.

(3) The decay rate of ^{14}C does not vary with time.

(4) The sample is closed, and does not exchange with external carbon following its formation.

It is known that the ^{14}C content of the atmosphere has not been constant with time [15,16] and that radiocarbon ages may, due to variations in the atmospheric production or transport of ^{14}C, be as much as 3500 yr too young for samples formed 20,000 yr BP. In the case of condition (2) we will show that the initial ^{14}C content of soil carbonate may vary greatly from the atmosphere with time of the year and with soil depth. The model describing this problem is developed in detail in the next section. The decay of radioactive elements, including ^{14}C, is governed by physical laws (condition 3). Condition (4) will be evaluated in this paper for the soils being considered. As we will suggest, it is likely that some soils will contain carbonates that are essentially closed with time while others may not. In addition, we will show how methods of sampling may affect measured radiocarbon ages.

4. Model description

In this section, we develop a model to describe the factors and processes that affect the initial ^{14}C content of pedogenic carbonate (condition (2) above). For this analysis, we assume a constant ^{14}C content of the atmosphere. Since this assumption does not hold for certain time spans

within the range of radiocarbon dating, the application to actual soils would need to figure in the changing atmospheric ^{14}C content. However, for our purposes, which are to demonstrate pedogenic processes that affect carbonate ^{14}C content, atmospheric variations are disregarded to reveal the full extent of the effect of soil processes.

4.1. [14]C content of soil organic matter

The ^{14}C content of soil organic matter can excercise a marked control on the ^{14}C content of pedogenic carbonate because organic matter decomposition is one of two main sources of CO_2 production in soils. There has been a considerable amount of work devoted to modeling the ^{14}C content of soil organic matter [17,18,19] and the discussion in this section builds on these previous papers.

It has been observed that in most environments the ^{14}C content of soil organic matter decreases with soil depth [20] (Fig. 2). Before we begin a discussion of processes responsible for these patterns, it is apparent from Fig. 2 that soil CO_2 derived from the decomposition of this organic matter will possess a wide range of '[14]C ages' that will ultimately affect any carbonate that forms in these soils.

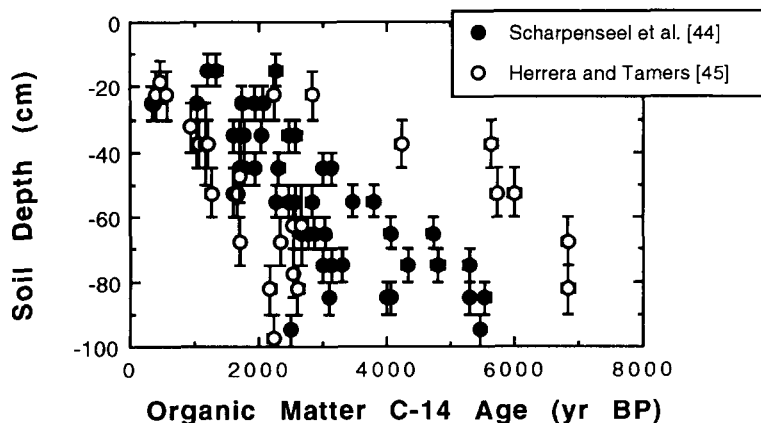Fig. 2. Some published radiocarbon ages of soil organic matter vs. soil depth. The data of Scharpenseel et al. [44] are from German grassland soils while the data of Herrara and Tamers [45] are from alluvial and hillslope soils in Venezuala. While variations in climatic and geologic factors affect the ^{14}C age vs. depth relationship, the trend for most soils is an increase in ^{14}C age with increasing soil depth.

For any soil horizon, the variation in organic carbon with time is:

$$\partial C / \partial t = \text{inputs} - \text{losses} \tag{1}$$

where C = organic C content (g m^{-2} cm^{-1}) and 'inputs' and 'losses' refer to a variety of processes which add or remove C from the soil. Two important C inputs are (1) in-situ production of particulate C by plant roots and (2) downward transport by water or biota [17]. Two important losses are (1) microbial decompostion of organic matter and again (2) downward transport by water or biota. All of these processes may operate in desert soils to varying degrees. In-situ C production by roots is undoubtedly important since field observation commonly indicates that organic matter varies irregularily with depth and is correlated to root densities [21,22]. The importance of downward C transport is less well understood, but the presence of anthropogenic isotopes at depth in soils has been documented in semi-arid regions [23,24]. In terms of C losses, microbial decomposition of humic substances is undoubtedly important [25], and while losses through downward transport probably does occur, it is not well studied.

If we assume that the decomposition of organic matter can be described by a first-order reaction, the following equation can be used to describe soil organic matter processes [17,26]:

$$\frac{\partial C}{\partial t} = D_B \frac{\partial^2 C}{\partial x^2} + I - kC$$

$$= \phi - kC \tag{2}$$

where D = diffusion coefficient (cm^{-2} s^{-1}), I = in-situ production rate of organic C (g m^{-2} cm^{-1} yr^{-1}) and k = decompostion constant of organic C (yr^{-1}). Because the diffusional transport of C in desert soils is not well understood, we adopt a simple strategy to combine the in-situ production and the diffusional transport of C into one net production term ϕ. In this simplification, all C losses are attributed to kC. We also assume that k and ϕ are constant with time for a given soil layer, but that their values vary with soil depth. The variation in k with depth is reasonable in that soil temperature, moisture and aeration (all of which affect the value of k) also vary with

depth. The assumed time-invariance of k and ϕ may not be warranted, but we have no way of evaluating its time dependence.

For the condition that $C = 0$ at $t = 0$, the solution to Eq. (2) is [19]:

$$C = \phi / k \cdot (1 - e^{-kt}) \tag{3}$$

For ^{12}C, a similar relationship can be derived:

$$^{12}C = \phi^{12} / k \cdot (1 - e^{-kt}) \tag{4}$$

where the superscript 12 refers to ^{12}C.

The content of ^{14}C in soil organic carbon is described by the following relationship:

$$\partial^{14}C / \partial t = \phi^{14} - (k + \lambda)^{14}C \tag{5}$$

where the superscript 14 refers to ^{14}C and λ is the decay constant of ^{14}C (0.0001245 yr^{-1}). The solution to Eq. (5) is:

$$^{14}C = \phi^{14} / (k + \lambda) \cdot [1 - e^{-(k+\lambda)t}] \tag{6}$$

where [10]

$$\phi^{14} = \phi^{12} \cdot \left[\left(\delta^{14} C_{\text{input om}} / 1000 + 1 \right) \cdot R_{\text{STD}} \right] \tag{7}$$

$$\phi^{12} = \phi \cdot (1 - \delta^*) \tag{8}$$

and

$$\delta^* = \left(\delta^{13} C_{\text{input om}} / 1000 + 1 \right)$$
$$\times R_{\text{PDB}} / \left[1 + \left(\delta^{13} C_{\text{input om}} / 1000 + 1 \right) \right.$$
$$\left. \times R_{\text{PDB}} \right] \tag{9}$$

If (1) the age of the soil is known (t) or the soil is at steady state with respect to organic, (2) $\delta^{13}C_{\text{input om}}$ and $\delta^{14}C_{\text{input om}}$ values are known, and (3) the total C and $\delta^{14}C_{\text{om}}$ values in the soil profile have been measured, then Eqs. (7), (8) and (9) can be combined with Eq. (6), and Eqs. (4) and (6) can be solved for ϕ and k in the soil depth intervals of interest.

In our calculations, we have assumed that the δ^{14}C value of input organic matter is 0‰ (THE same as the pre-bomb atmosphere). Mechanistically, this implies that most of the C production is from root exudation or decay. If, however, the transport of C by diffusion is important, the true δ^{14}C value of input C would be < 0‰, since soil humus is depleted in ^{14}C. We have no way of accurately estimating either the amount, or ^{14}C

content, of transported C. We therefore emphasize that our calculations may not be entirely quantitative, but they will at least qualitatively capture the dynamics of soil C.

The pedological significance of these relationships is that if the appropriate data are available for all horizons in a soil, the values of the constants can be determined and a series of curves can be calculated showing the distribution of total soil carbon, and its ^{14}C content, vs. soil depth for various times from $t = 0$ to $t = \infty$. We have made these calculations for a grassland soil from Iowa using data found in Trumbore [19] and the parameters given in Table 1. Figs. 3a and b show the results of these calcuations, and the salient points can be summarized as follows:

(1) At all stages of soil development, the organic matter and its ^{14}C content decrease with increasing soil depth.

(2) At early stages of soil development, total soil organic matter is low, and organic matter contribution to soil CO_2 production (ϕ_h) is also probably low ($\phi_h \ll \phi_r$, where ϕ_r = root contribution to total CO_2 production). As organic matter increases with increasing soil age, total organic matter contributions to CO_2 should increase (since $\phi_h = kC$).

(3) At early stages of soil development, the ^{14}C content of soil organic matter is similar to that of the atmosphere but becomes more depleted, relative to the atmosphere, with increasing soil age.

(4) The ^{14}C age of the soil organic C is always less than the true age of the soil due to inputs of fresh organic matter.

(5) Steady state is eventually reached for both total organic C and its ^{14}C content provided that no climatic or biotic perturbations occur.

We emphasize that the calculations illustrated in Figs. 2 and 3 are primarily illustrative due to assumptions in our model and uncertainties about certain processes. However, they do illustrate the likely trend of the total C and ^{14}C evolution between two known points in the soil's evolution ($t = 0$ and $t \approx 20,000$ yr).

4.2. [14]C content of soil CO_2 and carbonate

Elsewhere [9,10] we have reported on a model describing the production and distribution of [14]CO_2 in soils and factors that control its distribution with depth. Here we summarize this model and couple it with the model outlined in the preceding section.

Pedogenic carbonate forms in isotopic equilibrium with the CO_2 present at a given soil depth [6,7,27]. Therefore, if the isotopic composition of soil CO_2 is known, the composition of the carbonates can easily be calculated using equilibrium fractionation factors. The concentration of [14]CO_2 in soil can be described by the following model:

$$\frac{\partial C_s^{14}}{\partial t} = D_s^{14} \frac{\partial^2 C_s^{14}}{\partial z^2} + \Phi_s^{14} - \lambda C_s^{14} \qquad (10)$$

where $C_s^{14} = $ [14]CO_2 concentration in soil air (mole cm^{-3}), $D_s^{14} = $ diffusion coefficient of [14]CO_2 in the soil (cm^2 s^{-1}) and $\Phi_s^{14} = $ production of [14]CO_2 in the soil (mole cm^{-3} s^{-1}). Because the term λC_s^{14} is negligible relative to the other terms on

Table 1
The steady-state organic carbon and organic matter ^{14}C content of a pre-atomic bomb Mollisol from Iowa, with calculated inputs rates and decay constants. Data from [20] and calculated constants from [10,19]

Soil depth (cm)	Org.C (mole cm^{-3} × 10^{-3})	[14]C content (% modern C)	Input rate (I) (mole cm^{-3}yr^{-1} × 10^{-6})	Decay Const. (k) (yr^{-1} × 10^{-3})
0–16	3.708	89.70	4.020354	1.084238
16–28	2.192	83.69	1.400327	0.638835
28–42	1.925	72.53	0.632789	0.328722
42–50	1.050	70.66	0.314827	0.299835
50–64	0.833	62.70	0.174330	0.209280
64–74	0.500	59.21	0.090361	0.180722

the right-hand side of the equation, the equation reduces to:

$$\frac{\partial C_s^{14}}{\partial t} = D_s^{14} \frac{\partial^2 C_s^{14}}{\partial z^2} + \Phi_s^{14} \qquad (11)$$

The total $^{14}CO_2$ produced at any depth is derived from two main sources, decomposing organic matter and living root respiration. These sources have greatly different ^{14}C contents: roots, and bacterial decomposition of root exudates, pro-
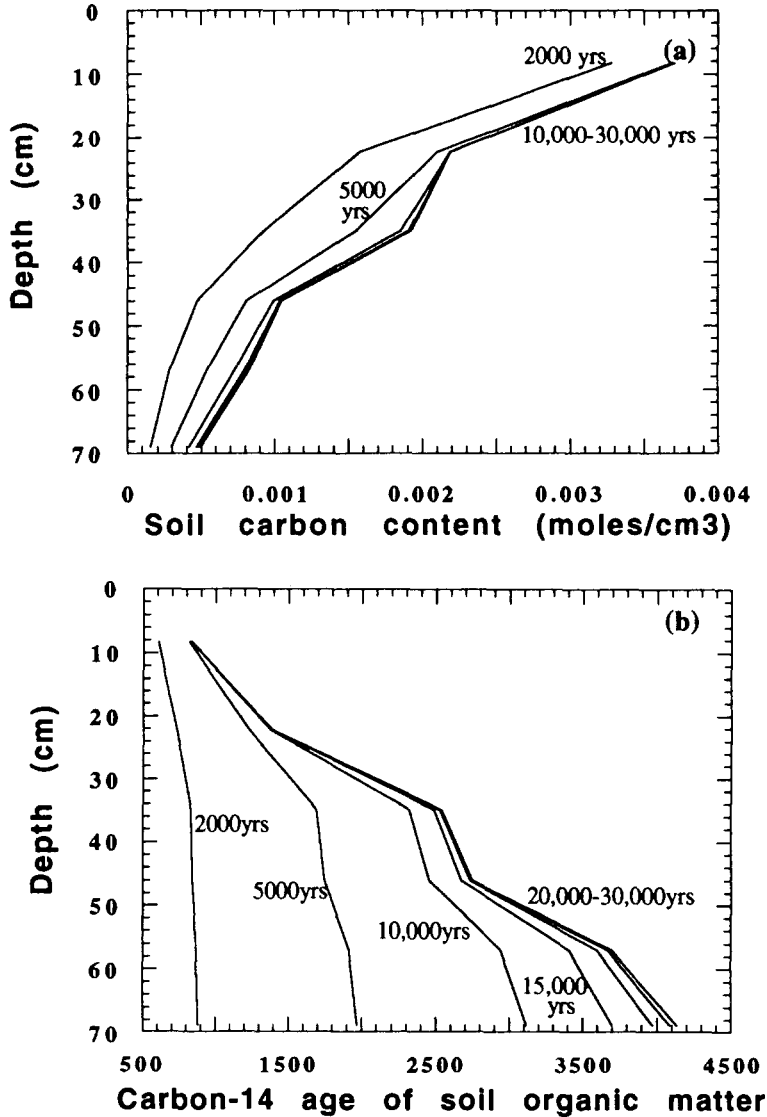

Fig. 3. (a) Model calculations of soil organic carbon content vs. soil depth at various times during soil development and (b) calculated ^{14}C ages of the carbon for the same time intervals. Curves calculated using equations in text and data for an Iowan Mollisol from Trumbore [19]. The parameters for the calculations are found in Table 1. Figure (a) shows that soil carbon content increases with increasing soil depth and that the distribution of carbon reaches steady state (for this particular soil) after ~ 10,000 yr. Figure (b) shows that the ^{14}C age of soil carbon increases with increasing depth and that steady state is reached after ~ 20,000 yr. The ^{14}C ages of soil organic matter are always younger than the true soil age (due to inputs of fresh carbon), and the discrepancy between organic matter ^{14}C age and true soil age increases with increasing soil age.

duce CO_2 that has a ^{14}C content approximately equal to the atmosphere ($\delta^{14}C = 0\%o$ in pre-atomic bomb conditions) [28] and organic matter produces CO_2 that can, depending on soil age and climatic conditions, be significantly depleted in ^{14}C relative to the atmosphere (see Figs. 2 and 3). If F is defined as the relative contribution of CO_2 from organic matter decomposition (and $1 - F$ is the contribution from roots and associated rhizosphere respiration), the ^{14}C content of CO_2 produced at any depth is described by:

$$\Phi^{14}(z) = \Phi^{12}\left[F\left(\frac{\delta^{14}C_{om}}{1000} + 1\right)(R_{STD})\right.$$
$$\left. + (1 - F)\left(\frac{\delta^{14}C_{atm}}{1000} + 1\right)(R_{STD})\right] \quad (12)$$

where $\Phi^{12} = {}^{12}CO_2$ production, $\delta^{14}C_{om}$ and $\delta^{14}C_{atm} = {}^{14}C$ content of decomposing soil organic matter and atmospheric CO_2, respectively, and $R_{STD} =$ the $^{14}C/^{12}C$ ratio in the isotopic standard (NBS oxalic acid). For the condition that the ^{14}C content of decomposing soil organic matter decreases linearly with depth, and that Φ^*

(total CO_2 production) and F are constant with depth, the steady-state solution to Eq. (11) is [10]:

$$C_s^{14} = \frac{1}{D_s^{14}}\left[-(\Phi^{12})(R_{STD})\right.$$
$$\times F \cdot \left(\frac{A + 1000}{2000} \cdot z^2 + \frac{B}{6000} \cdot z^3\right)$$
$$\left. - \frac{E \cdot z^2}{2} + G \cdot z\right] + C_a^{14} \quad (13)$$

where:

$$E = (\Phi^{12})(R_{STD})(1 - F)\left[(\delta^{14}C_{atm}/1000 + 1)\right]$$

and

$$G = (\Phi^{12})(R_{STD})(F)[(A + 1000/1000)(L)$$
$$+ (B/2000)(L^2)] + E \cdot L$$

Using similar solutions for total CO_2 and $^{12}CO_2$ provided by Cerling [6], the steady-state $\delta^{14}C$ values (or, in this paper, ^{14}C ages) for soil CO_2 (and the carbonate that forms in equilibrium with it) can be calculated for various values of input parameters. Once the $\delta^{14}C$ values of CO_2 have
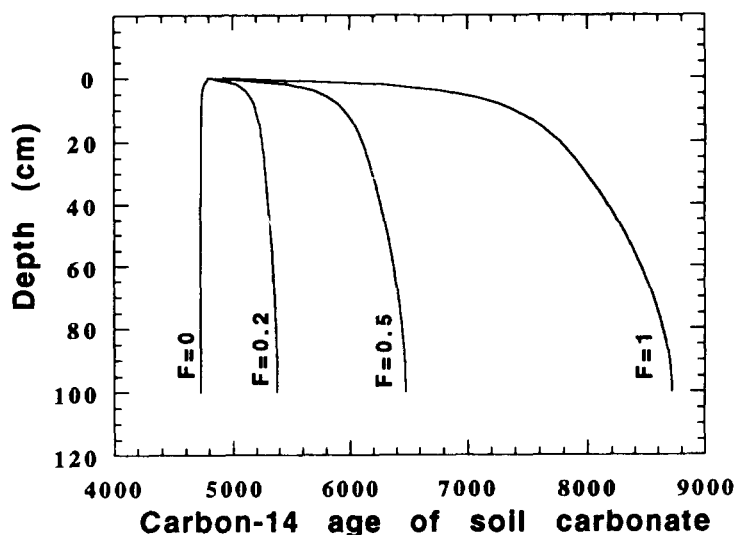
Fig. 4. Initial ^{14}C age of pedogenic carbonate vs. soil depth for different values of F (fraction of total CO_2 production from decomposing soil humus) for the Iowan Mollisol. This calculation is made for a lamination that formed 5000 yr BP in a soil that was 30,000 yr old (in order to maximize the possible effects of different values of F). Data used for calculations are in Tables 1 and 2. The calculations show that as F increases (at any given CO_2 production rate), the inital ^{14}C age of soil carbonate at any soil depth also increases.

been calculated, the corresponding $\delta^{14}C$ values (and ^{14}C ages) for pedogenic carbonate can be determined.

The assumption of constant Φ^* and F with depth in Eq. (13), which greatly simplifies the model calculations, is for illustrative purposes only. In real soils, Φ^* is a function of depth and F may also vary with depth. However, even with our assumptions, the calculations reveal important features of the ^{14}C ages of soil carbonates for several possible soil environements.

Fig. 4 shows the variation in the ^{14}C age of soil carbonate vs. depth for various values of F (organic matter contribution to $\phi^{14}(z)$ for a model soil whose properties are given in Table 2). For F values of 0, the soil carbonate is more enriched in ^{14}C than atmospheric values due to diffusion differences in the different CO_2 isotopic species. As F increases, the ^{14}C ages increase at any depth, reflecting a greater proportion of CO_2 from ^{14}C depleted organic matter. Finally, for any value of $F > 0$, the ^{14}C ages increase with increasing soil depth.

The significance of the conditions imposed on the model soil illustrated in Fig. 4 deserves emphasis. The model soil is intended to approximate the pre-atomic bomb soil environment. In the present ^{14}C-enriched atmosphere, input ^{14}C to soils is greater than 100% modern C and soil organic matter and CO_2, in some environments, may be greatly enriched in ^{14}C due to the bomb 'spikes'. However, since most soil carbonate has formed prior to the advent of nuclear weapon use

and testing, our model should at least qualitatively illustrate the processes which controlled natural conditions.

In the next sections, we will examine how the ^{14}C age of soil carbonate varies with soil age and depth. First, however, we wish to examine the process by which soil carbonate forms, and use this as the basis for further development of our model.

5. Pedogenic carbonate formation

The process of carbonate accumulation in desert soils has been studied extensively [29,30] and follows predictable pathways, or stages, depending on the nature of the parent material (gravelly vs. fine-grained). Here we consider gravelly soils because of their widespread occurrence in deserts and because we believe the application of ^{14}C dating to these soils is less ambiguous than for fine-grained deposits.

Gravelly deposits commonly contain a substantial amount of pore space around the gravels. As pedogenesis proceeds, dissolved carbonate (derived from weathering of calcareous dust, limestone alluvium, and/or weathering of Ca-bearing silicates) in the soil solution is deposited on the gravels as the water is depleted via evapotranspiration. Deposition commonly occurs on gravel bottoms [29], although in hot deserts dominated by late summer rains the deposition may occur on gravel tops [Amundson et al., unpublished]. Up to six stages of coatings and pore infillings have been described [30], the terminal stages involving thick laminations on clasts, pore infilling, and volumetric expansion of the soil.

In the early stages of development (stages I and II), which are the stages of interest in ^{14}C dating, the carbonate laminations can accumulate in unrestricted pore space, developing distinct, nearly horizontal laminae (Fig. 5A). The innermost laminations are dense, nearly pure pedogenic carbonate with minor inclusions of detrital silicates and possibly (where present) limestone. In contrast, the outermost layers (not illustrated in Fig. 5A), where deposition is occurring, can consist of a heterogeneous mixture of pedogenic

Table 2
Parameters used for model calculations involving the Iowa Mollisol

Property	Value
Soil respiration rate	3 mmole m^{-2}/h^{-1}
Soil porosity	0.4
Atmospheric pressure	1 atm
Temperature	20°C
Atmosphere	280 ppmv * CO_2
	$\delta^{13}C = -6‰$
Soil organic matter	$\delta^{13}C = -24‰$
F	0.5
Year of ^{14}C measurement[14]	1993
C content of input organic matter	100% modern C

* On a volume basis.
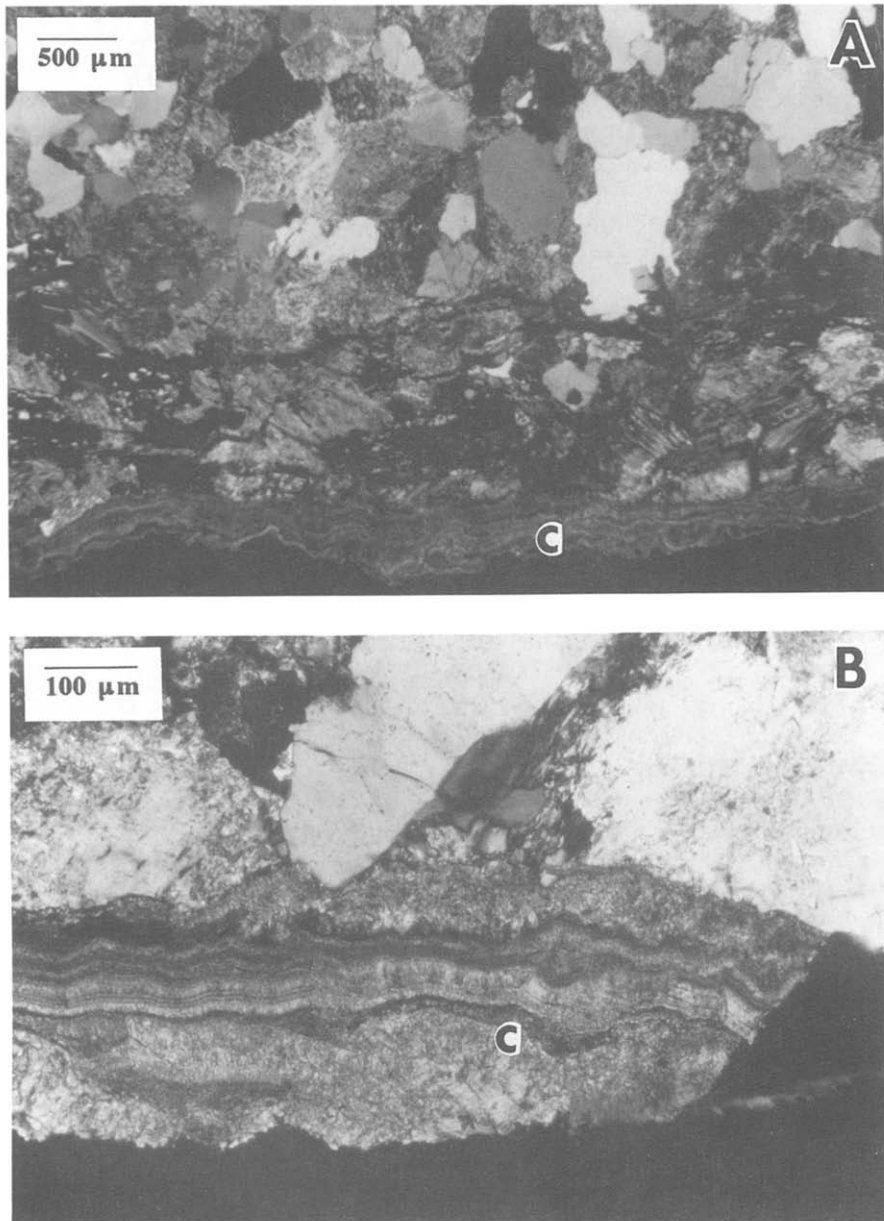
Fig. 5. Thin section photographs (crossed nicols and polarized light) of soil gravels and their carbonate laminations from (A) latest Pleistocene (~ 20 ka), (B) late Pleistocene (~ 103 ka) and (C) mid-Pleistocene soils (~ 1300 ka) from terraces of the Wind River, Wyoming. Outer laminations of each sample have been removed in order to focus on the morphology of the innermost laminations. Age assignments based on dating of volcanic ash in an intermediate terrace and the assumption of linear incision rates for both younger and older terraces [Chadwick and Connel, unpublished]. The photographs illustrate that carbonate (c) forms as roughly parallel laminations on gravel bottoms (although exceptions exist) with relatively little pore space (A). As soil age increases, the thickness of coatings (c) increases (B). The abrupt discontinuity of the carbonate layer on the right of (B) marks a part that was removed for isotopic analysis. In (C) thick sequences of carbonate laminations (c) exist, but are accompanied by pits (p) suggesting dissolution / reprecipitation.

carbonate and detrital grains [27,31]. The deposition of the dense laminations appears to exclude the inclusion of non-pedogenic minerals, particularly silicates. In some cases, non-pedogenic minerals are replaced by carbonate [32].

In summary, the development of pedogenic laminations in gravelly soils involves features that make such laminations potentially suitable for dating: (1) the exclusion of detrital minerals and (2) a sequence of laminations that decreases in age from near the rock toward the soil environment. In contrast to gravelly soils, carbonate in fine-grained deposits forms nodules or concretions within the soil matrix. These concretions can contain a substantial quantity of detrital mineral grains [33] and indistinct evidence of successive stages of growth. While incorporation of detrital silicate grains is of no concern in ^{14}C dating, it does add additional uncertainty as to whether detrital carbonate is present in the sample. In addition, a lack of clear growth stages makes these carbonates less amenable to detailed stratigraphic sectioning.

5.1. Susceptibility of pedogenic carbonate to diagenetic alteration

The reliability of pedogenic carbonate for ^{14}C dating depends on its ability to resist isotopic alteration following its formation. To examine the susceptability of carbonate laminations to such alteration, we measured the ^{14}C content of the innermost 0.5 ± 0.3 mm of carbonate laminations in gravelly soils from the Wind River Basin, Wyoming. The sequence of soils is found on river terraces ranging from latest Pliestocene to early Pliestocene in age. With the exception of soils on terraces younger than 40,000 yr BP, the ^{14}C content of the carbonate should be equal to the laboratory background in our study (0.7% modern C, $\delta^{14}C$ value $= -993‰$).

The extremely low $\delta^{14}C$ values, especially in soils as old as 1300 ka, is encouraging with respect to the long-term stability of the laminations, at least for the Wind River Basin (Fig. 6). However, small amounts of ^{14}C above background levels suggest contamination of the laminations
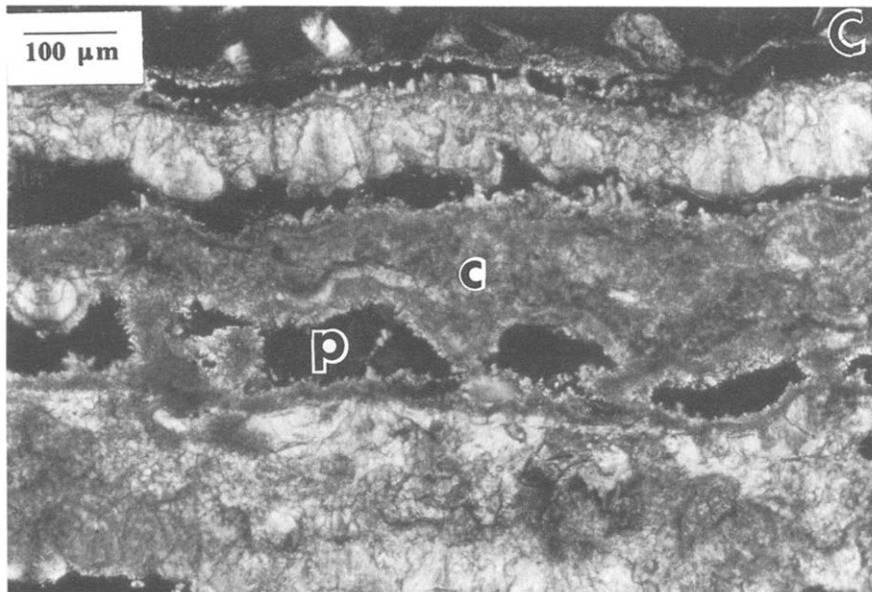

Fig. 5 (continued).

from one (or both) of two sources: (1) grinding and removal of laminations from the clasts in the laboratory, or (2) chemical alteration in situ. Despite efforts to maintain a clean environment during sample removal from the gravels, a considerable amount of carbonate dust was generated, which may be a source of some of the ^{14}C. However, in-situ weathering, and introduction of ^{14}C, is also possible, as suggested by the lamination morphologies. In the youngest soil (WR 2, < 20 ka, Fig. 5A), laminations are thin (< 1 mm), roughly parallel to the clast surface, and contain variable, but small amounts of pore space. As soil age increases (WR 3, ~ 103 ka, Fig. 5B) the thickness and complexity of the laminations increases, although porosity and evidence of chemical alteration is low. However, for mid- to early Pleistocene soils, porosity (a result of apparent solution pitting) increases, commonly preferentially along specific laminar layers (Fig. 5C). In general, the percentage of pitting seems to increase with increasing soil age.

The removal of carbonate by solution, as indicated in thin section, will not alter the ^{14}C content of the samples. The major concern is repre-

cipitation and incorporation of atmospheric ^{14}C. The presence of some crosscutting features in *mid- to early Pleistocene* soils indicates that laminations are not closed for indefinite periods.

Others have reported data to suggest that, at least in late Pleistocene soils, the innermost laminations of carbonate are essentially closed. For example, Damon et al. [34] reported that the ^{14}C age of pedogenic carbonate laminations, on lava fragments in Arizona, increased from the outer layers toward the innermost layers. In addition, the innermost layer analyzed was radiocarbon 'dead', indicating that it was essentially closed with respect to the present environment.

While some soils seem to form pedogenic carbonate that remains closed for some period of time, it is unlikely that all soils behave in such a manner or that any soil will remain closed indefinitely. Changes in climate can shift conditions from a carbonate-forming to a carbonate-dissolving environment. Horizons close to the soil surface may experience conditions that are conducive to carbonate formation in dry years, and then undergo dissolution during years with greater rainfall. Burial of a soil may help reduce alter-

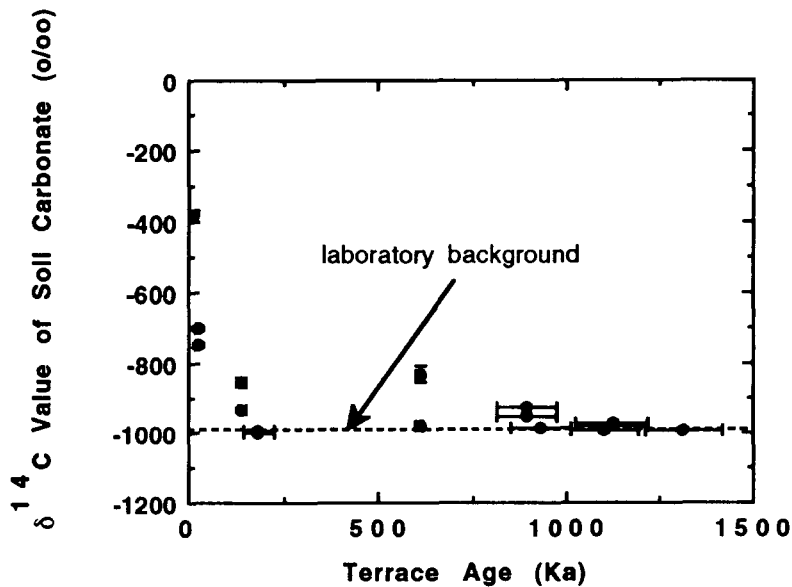Fig. 6. The δ^{14}C value of the inner ~ 0.5 mm of carbonate laminations on soil gravels from the Wind River Basin, Wyoming. The data show that as a soil ages, the ^{14}C content of measured samples falls to levels near laboratory backgrounds. For soils older than 40 ka, δ^{14}C values above the background suggest either laboratory ^{14}C contamination and/or in-situ dissolution/reprecipitation.

ation of carbonates, but this will only occur if the soil is removed from later rainwater infiltration or groundwater alteration. Indeed, many possible environments exist, and the evaluation of the reliability of carbonate as a dating substrate must involve chemical, morphologic and geologic criteria.

6. Application of model to soils

6.1. Evaluation of the model for a hypothetical soil

For this exercise, we will consider the Mollisol that was discussed in the previous section. In Fig. 3b we have calculated the ^{14}C content of soil C at different stages in the soil's development. We assume, for these calculations, that this organic matter will contribute to the ^{14}C content of the soil CO_2 through microbial decomposition. This assumption has limits, since empirical measurements have shown that the $\delta^{14}C$ value of CO_2 respired from soil organic matter is not identical to the $\delta^{14}C$ values of the total soil organic matter fraction [Trumbore, unpublished]. However, because it is not possible a priori to determine what the relationship will be between the ^{14}C value of humus-derived CO_2 and the humus itself, in this exercise we assume they are the same. From another perspective, Fig. 3b may be interpreted as the $\delta^{14}C$ value of the humus fraction that will contribute to CO_2 production. If we assume that 50% of the soil CO_2 production is due to organic matter decomposition and the remainder is due to root respiration [25], we can calculate (using the production/diffusion model described above) the ^{14}C content of the soil CO_2 (and the ^{14}C content of soil carbonate that would form) for the same time intervals of the soil's existence. Using the parameters given in Table 2, and the production/diffusion model developed earlier, the initial ^{14}C age of soil carbonate which forms at different times during a soil's development was calculated. The results of these calculations, illustrated in Fig. 7a, show that as the age of the soil increases, the ^{14}C age of the soil CO_2 increases, leading to soil carbonate that forms with an initial ^{14}C content that is much less than that of the

atmosphere. As the calculations show, the age effect of this ^{14}C depletion is more pronounced at greater soil depths and is minimized near the soil surface. For the soil considered, the maximum initial ^{14}C age of soil carbonate is about 1500 radiocarbon years.

While the calculations in Fig. 7a provide a good illustration of the ^{14}C age of soil carbonate forming at any given time period in a soil's existence, they do not show the ^{14}C age that would result if the entire carbonate lamination were measured. The measured ^{14}C age will reflect the ^{14}C content of the many generations of carbonate laminations and will, to some extent, be an average of these different carbonate layers. For a carbonate lamination of some given thickness, the ^{14}C activity of the total sample ($^{14}A_T$) can be descibed by the following equation:

$$^{14}A_T = \left(n_1\left(^{14}A_{o1}e^{-\lambda t1}\right) + n_2\left(^{14}A_{o2}e^{-\lambda t2}\right) + \ldots \right.$$
$$\left. + n_p\left(^{14}A_{op}e^{-\lambda tp}\right) \right) / \sum_p^{i=1} n_i \qquad (14)$$

where n_i = the thickness of carbonate formed in a given time interval, $^{14}A_{oi}$ = the initial ^{14}C activity of carbonate formed during a given time interval, t_i = the true age of a given layer, and $\sum_p^{i=1} n_i$ = total thickness of the measured carbonate sample.

A form of Eq. (14) was used to evaluate the ^{14}C age of total soil carbonate at different time intervals for the model soil described above. In Fig. 7b, we consider a 30,000 yr old soil, with a carbonate layer consisting of six laminae. For the purposes of modeling, we consider that each layer forms instantaneously at the beginning of a 5000 yr time interval, and possesses an initial ^{14}C age appropriate for that time interval as shown in Fig. 7a. As Fig. 7b shows, the oldest, and innermost, lamination deposited 30,000 yr ago (at $t = 0$ for that soil's development) presently has a ^{14}C age which equals the age of the soil. The next oldest lamination, which formed 25,000 yr BP, reflects that age plus its initial ^{14}C age contributed by CO_2 derived from decomposing organic matter. As the figure illustrates, each successively younger lamination will reflect its age plus its inital ^{14}C

content. The younger the lamination, the greater the difference between its ^{14}C age and its true age.

In practice, entire carbonate laminations are commonly ^{14}C dated. If, for example, the entire carbonate accumulation modeled in Fig. 7b were
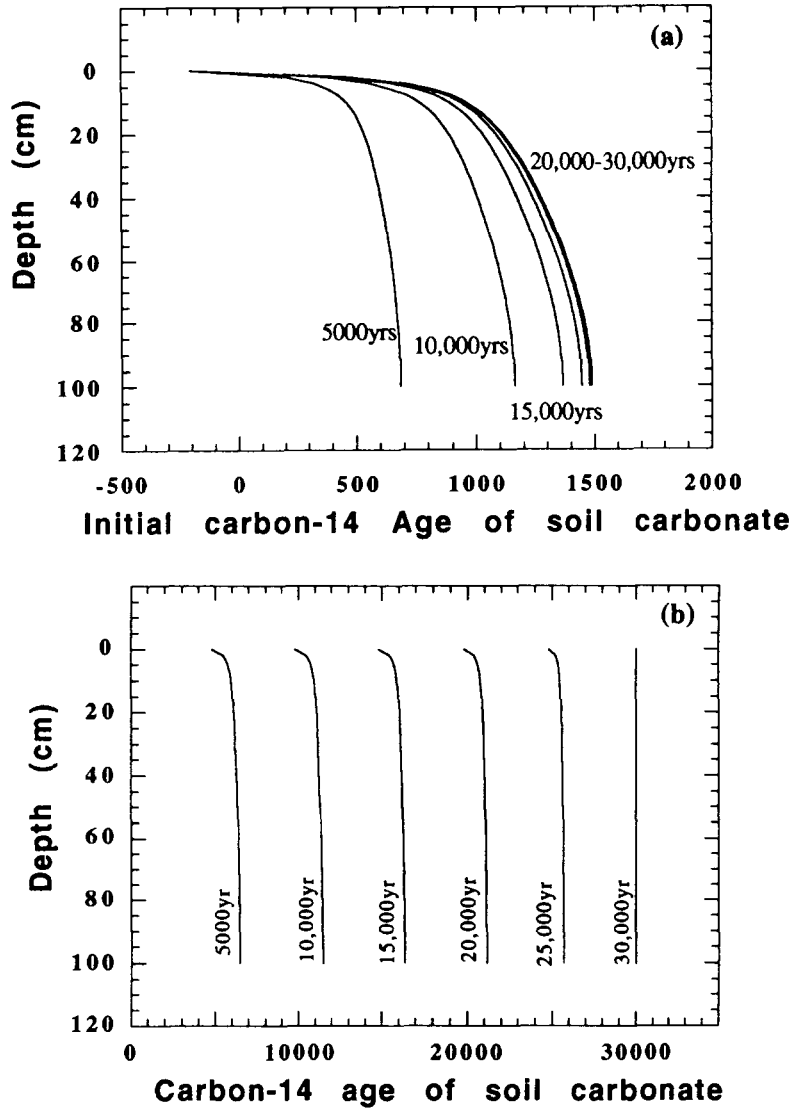
Fig. 7. (a) Calculated variations in the initial ^{14}C age of pedogenic carbonate vs. soil depth at different stages of the development of a Iowan Mollisol. For modeling purposes, the laminations are assumed to form instantaneouly in 5000 yr intervals with an initial ^{14}C content appropriate for the time interval (predicted from Fig. 5A). Values along the curves indicate the true ages of the soils. The calculations show that for a soil that is 20,000 yr old, any carbonate now forming at the 100 cm depth would have an initial age of ~ 1450 radiocarbon years. (b) The calculated ^{14}C ages of individual laminations in the total carbonate accumulation for a 30,000 yr old Mollisol. Values along the curves indicate the true age of the laminations. For example, for a layer formed 30,000 yr ago (prior to the presence of any soil organic matter), the ^{14}C age would now be 30,000 yr BP (i.e., there is no contribution from CO_2 from decomposing soil organic matter). For a carbonate lamination that formed 5000 yr ago, the measured ^{14}C age of the lamination would be the age of the sample (5000 yr) plus the initial ^{14}C age derived from the soil CO_2 (up to 1500 yr).

analyzed, its mean ^{14}C age would be much younger than the soil's true age, even though individual laminations may in fact have ^{14}C ages greater than their true age. In Fig. 8a, we model the mean ^{14}C age of total carbonate for the same Mollisol at different points in the soil's development. This figure illustrates several points:

(1) For any soil age, the mean ^{14}C age of the carbonate increases with increasing soil depth.

(2) The difference between true soil age and mean carbonate ^{14}C age decreases with increasing depth.

(3) The ^{14}C age vs. depth gradient increases with increasing soil age.

(4) The absolute and relative difference between true soil age and mean carbonate ^{14}C age increases with increasing soil age.

As Fig. 8a shows, the measured ^{14}C age of the total carbonate for a 30,000 yr old soil is about 19,000 yr BP (for the given model conditions). In some cases, it may be possible to selectively remove a certain portion of the youngest laminae of the carbonate accumulation, allowing one to measure only older carbonate layers. Fig. 8b illustrates the effect that this would have on the ^{14}C age of the Mollisol. If only the inner 50% of the lamination were measured, the ^{14}C age would be about 25,000 radiocarbon yr BP; if the inner 33% were measured, the ^{14}C age would be about 28,000 yr BP. Therefore, it appears that great improvements in the approximation of true soil age can be made by partial removal of younger carbonate laminations.

6.2. Relationship of the model to measured carbonate ^{14}C ages

The ^{14}C ages of soil carbonate almost invariably increase with soil depth [35,36,37] (Fig. 9). Four possible explanations can be given for this observation:

(1) ^{14}C ages reflect changes in the depth of carbonate formation caused by shifts from wetter to drier conditions (i.e., the depth at which carbonates form decreases as the climate becomes drier) or by increases in the water holding capacity of the soil.

(2) Soil carbonate near the soil surface is not closed and is contaminated with younger C.

(3) ^{14}C ages reflect conditions predicted by a production/diffusion model.

(4) ^{14}C ages reflect some combination of scenarios (1)–(3).

It is very likely that soils older than the Holocene have been subjected to significant climate change (i.e., that they are polygenetic) and scenario (1) must therefore be considered an explanation for the observed ^{14}C ages. In all but the most arid regions, the soil surface is not conducive to carbonate formation. Therefore, carbonate laminations near the soil surface are of questionable value in carbonate dating due to the likelihood that they have been at least partially dissolved and reprecipitated at least once since their period of formation. However, for Holocene soils that show a distinct ^{14}C vs. depth trend, it is difficult to conclude that they do not reflect diffusional processes as long as dissolution/reprecipitation can be ruled out. We believe that Pleistocene soil carbonates also reflect the results of this diffusion mechanism, but that the measured ^{14}C ages are also affected to some extent by the climate change scenerio described above.

Reported ^{14}C ages for Holocene soil carbonates [38,39] exhibit increasing radiocarbon age vs. soil depth, as predicted by the diffusional model described here. We have also measured the ^{14}C content of several Holocene soils and our results qualitatively agree with the published data and with the production/diffusion model. Below we discuss some of these data, and complications that appear to exist with respect to their origin.

Fig. 10(top) shows the $\delta^{13}C$ values of soil carbonates in two Holocene soils on alluvial deposits along the flanks of the Providence Mountains. Based on stratigraphic and weathering principles, the surface 7 soil is considered to be younger than surface 6. Using a production/diffusion model, with the parameters given in Fig. 10(top), the stable isotopic data for both soils can be shown to fit a CO_2 production rate of 0.35 mmole m^{-2} h^{-1} (the measured $\delta^{13}C$ value of organic matter is $-24\%o$). Using this CO_2 production rate and soil CO_2 data derived from the model Mollisol (see discussion below for assumptions

made), the measured ^{14}C ages of the soil carbonates fall between a series of curves for soils of different ages (Fig. 10, bottom). The curves which fit the data suggest that the measured ^{14}C ages correspond to true soil ages of 5000–~9000 yr

BP. No one curve perfectly fits the data for either soil. For the younger surface 7, model curves for a 5000–7500 yr old soil fit the data, while for the older surface 6 model curves for soils between 6000 and 9000 yr fit the measurements. Fig.
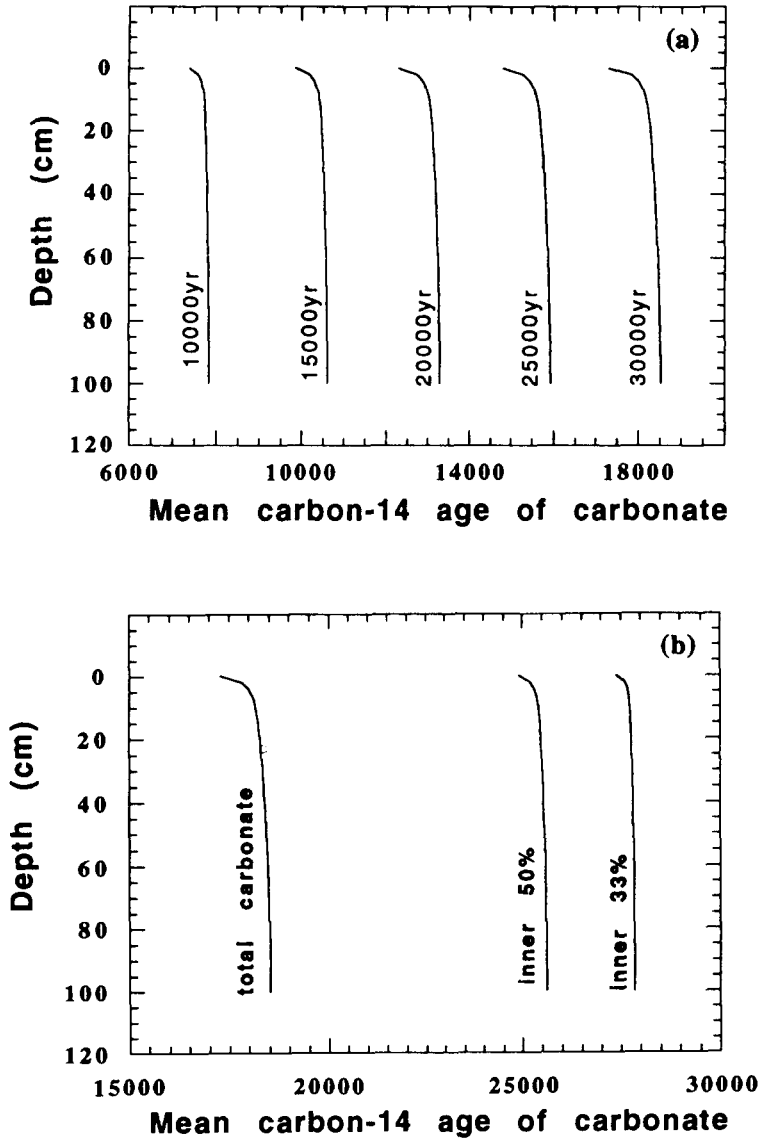
Fig. 8. (a) Calculated mean ^{14}C age vs. soil depth of the total pedogenic carbonate accumulation for the Iowan Mollisol at various stages of its development. Values along the curves indicate the true age of the soil. The calculations show that the mean ^{14}C age of soil carbonate is younger than the true age of the soil and the difference between the measured and true ages increases with increasing soil age. (b) Calculated effect of removing various proportions of the outer (and younger) parts of the total accumulation on the measured ^{14}C age of the sample for the 30,000 yr old soil. The calculations suggest that even a partial removal of outer (and younger) carbonate laminations greatly improves the relationship between the measured ^{14}C age and the true age of the soil.

10(bottom) illustrates that the measured radio-carbon age vs. depth slope is less than the model predictions (i.e., no one curve fits the data for each soil). Below we discuss the likely reasons for this, and the empirical data that will be needed to constrain the model more accurately.

One of our modeling assumptions is that soils at $t = 0$ have no organic carbon, and that the first increment of organic C added to the soil has a radiocarbon age of 0 yr BP. We acknowledge that there is probably a difference between these as-sumptions and the conditions that actually exist in sedimentary deposits in deserts. Most fluvial and aeolian deposits will contain some organic carbon at $t = 0$, and that carbon may have a radiocarbon age much greater than 0 yr BP. While it is well known that recent deposits contain organic carbon, there are no data on its ^{14}C age. Because we have no way of assuming a realistic ^{14}C age for this inital organic carbon, we have made our calculations in Fig. 10(bottom) with the assumption of no C at $t = 0$. We are conducting research to explore this problem and provide more realistic data to constrain the initial bound-ary conditions of our model.

In our calcuations we have used ^{14}C data from a pre-atomic bomb soil from Iowa, which may not accurately reflect desert soils. An additional limi-tation of our calculations is that we assumed an F value of 0.9. In fact, F must depend on the time of year that the carbonate forms. While we can-not predict with certainty how the proportion of humus to root/atmospheric CO_2 will vary with season, the ratio is certain to change from the summer to the winter months. Therefore, the curves fit to our data, using data from an pre-atomic bomb Iowa soil, should be viewed as illus-trative rather than completely quantitative. How-ever, it is apparent that the production/diffusion model fits the stable isotope data and the general features of the radioactive isotope data.

As noted, the empirical data illustrated in Fig. 10(bottom) for a given soil do not fall on a single curve, and the upper data point lies on a curve for a younger soil than the data point at lower depths. This could be a result of our assumption regarding the initial boundary conditions of the soil. However, a second interpretation focuses on the stability of the uppermost sample, and its resistance to dissolution and reprecipitation. It is

Carbonate Radiocarbon Age (yr BP)

Fig. 9. Published radiocarbon age of soil carbonate vs. depth from for a number of soils in Texas [35,36]. The ^{14}C ages increase with soil depth, as qualitatively predicted by the production/diffusion model described in the text. However, the trend could also result from climate change (and a trend of shallower deposition of carbonate) or from instability of carbonate near the soil surface (and subsequent contamination of carbonates through dissolution and reprecipitation).
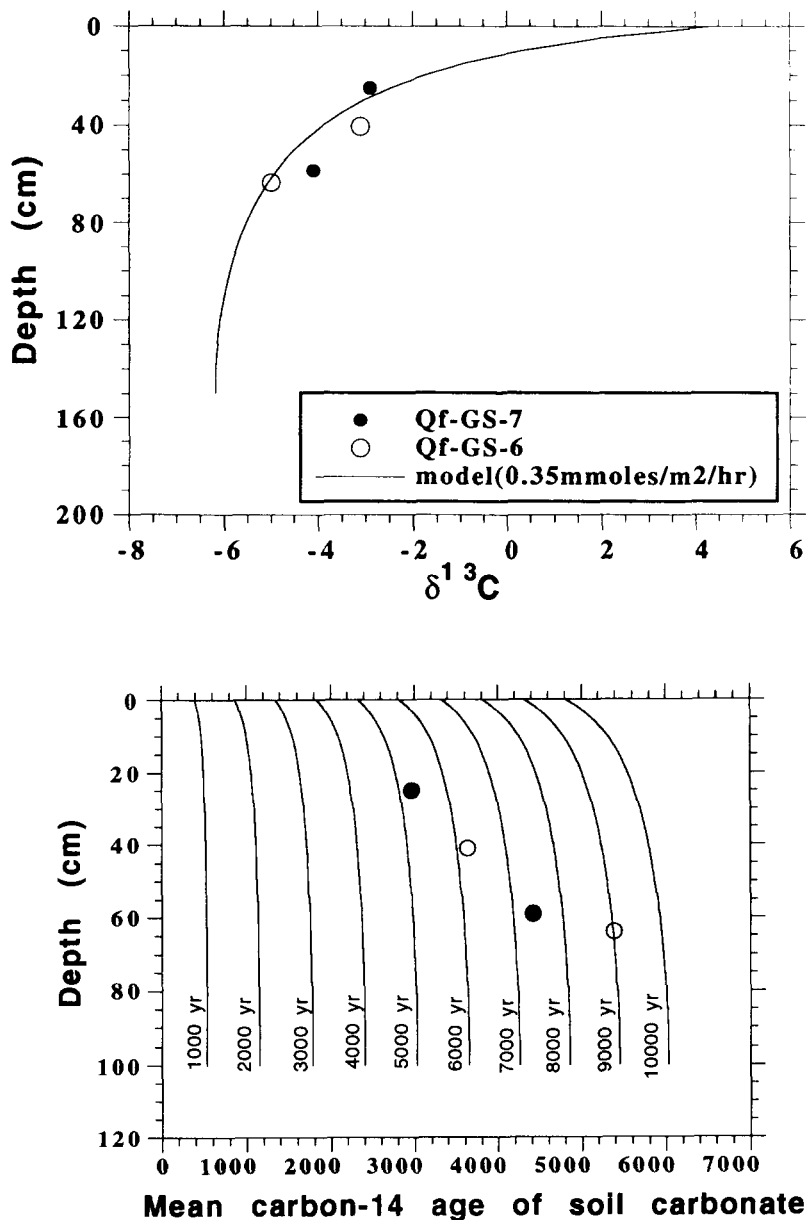
Fig. 10. (top) The $\delta^{13}C$ values of pedogenic carbonate vs. depth for Holocene soils near the Providence Mountains. A production/diffusion model was used to fit a CO_2 production rate to the data (0.35 mmole m^{-2} h^{-1}). (bottom) The measured ^{14}C ages of the carbonates illustrated in the top figure compared to model curves for predicted ^{14}C ages of soil carbonates for various soil ages (respiration rate = 0.35 mmole m^{-2} h^{-1}; $F = 0.9$; other parameters same as in Table 2). Basic assumptions in the model calculations are (1) the soils contain no C at $t = 0$ and (2) the first increment of organic carbon added to the soil has a radiocarbon age of 0 yr BP. The values along the curves in the bottom figure are the true ages for the soil. The figure shows that measured data for the surface 7 soil fall within model curves for soils between 5000 and 7500 yr old (all solid curves calculated with F values of 0.9) while the surface 6 soil carbonate falls within curves for soils between 6000 and 9000 yr old.

entirely probable that these samples, being nearest the soil surface, are poor candidates for accurate ^{14}C dating. Dissolution/reprecipitation will not affect the $\delta^{13}C$ values vs. depth profile (Fig. 10, top) as long as vegetation conditions remain reasonably constant, but such a process would have a profound effect on the ^{14}C age vs. depth relationships. While Holocene soils are the most promising candidates for carbonate radiocarbon dating, it seems that even in these soils the ^{14}C ages of the carbonates cannot be unambiguously interpreted, particularily those nearest the soil surface.

7. Conclusions

Soil CO_2, the master variable in determing the ^{14}C content of pedogenic carbonate, is derived from biologic sources whose ^{14}C content can vary from that of the atmosphere (ca. O radiocarbon years) to that of soil humus (radiocarbon ages of several thousand years BP). Therefore, pedogenic carbonate may have initial ^{14}C ages of several thousand radiocarbon years, thereby overestimating its true age. However, since most soil carbonates that are collected for ^{14}C dating contain several generations of laminae, the mean ^{14}C age will greatly underestimate the true age of the soil. We have shown, via model calculations and empirical measurements, that the measured ^{14}C age of pedogenic carbonate is a function of soil depth. This depth relationship, which is predicted from a production/diffusion model, can be further enhanced, and exaggerated, by factors such as climate change and instability of carbonate near the soil surface.

We have deliberately emphasized the complexity of ^{14}C ages derived from soil carbonates. What, if any, is the future of carbonate ^{14}C dating in geologic studies of arid regions? First, we have shown, for a variety of reasons, that ^{14}C dates for Holocene carbonates are subject to fewer complicating factors than Pleistocene carbonates, making them a more suitable substrate for dating. Second, we have shown that even partial removal of exterior, and younger, layers of carbonate greatly improves the relationship of the resulting

^{14}C age to the true age of the soil. For younger soils, the discepancy between measured ^{14}C ages on partially partitioned samples and the true age of the soil will be about 1 ka, with the discrepancy increasing with the age of the soil. It is apparent that if microscopic sampling techniques improve, so enabling us to ^{14}C date the innermost increment of carbonate that formed in a soil gravel, the measured ages should, in most geologic studies, be more accurate. Finally, it should be possible to determine the age of soils by measuring the ^{14}C age of entire laminations, and then by fitting the measured ages to model predictions of the relationship between measured ages and the true age of the soil (e.g., Fig. 8a).

While our paper presents a vastly different theoretical picture for interpreting the ^{14}C content of soil carbonate, we agree with some previous scientists who have suggested that the ^{14}C age of soil carbonate can provide good minimum ages for a soil or sedimentary deposit and that they can be useful in providing relative age constraints on sedimentary deposits at a given location. The main challenge for the future is in the development of techniques to sample carbonate laminations more precisely. With the small sample sizes required by AMS, the development of these techniques should be a research priority of the near future.

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