A model for soil $^{14}$CO$_2$ and its implications for using $^{14}$C to date pedogenic carbonate

**Yang Wang, 1,* Ronald Amundson, 1 and Susan Trumbore 2**

1Department of Soil Science, University of California, Berkeley, CA 94720, USA
2Department of Geosciences, University of California, Irvine, CA 92717, USA

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Abstract—A diffusion-reaction model for soil $^{14}$CO$_2$ is described that analyzes the $^{14}$CO$_2$ distribution in soils. It shows that the $^{14}$C content of soil CO$_2$ is not the same as that of atmospheric CO$_2$ and varies with depth depending on various factors. The most important factors affecting the $^{14}$C content of soil CO$_2$ include the $^{14}$C content of soil organic matter, the relative contribution of root respired CO$_2$ to total CO$_2$ production, soil respiration rate, atmospheric CO$_2$ concentration and $^{14}$CO$_2$ content, and soil properties such as temperature and moisture content etc. The $^{14}$C content of soil CO$_2$ not only can be a sensitive indicator of the residence time of decomposing organic matter in the soil, but also determines the $^{14}$C content of pedogenic carbonate. Our model suggests that soil CO$_2$ could be enriched or depleted in $^{14}$C relative to atmospheric CO$_2$, depending on the relative contribution of root respiration to total soil respiration and on the turnover rate of the soil organic matter contributing to the soil CO$_2$. Therefore, the initial $^{14}$C dates of soil carbonate could differ from the true ages of pedogenesis. The processes and factors considered by the model are a first step in determining whether the $^{14}$C content of soil carbonate could lead to reliable dates of pedogenesis.

**INTRODUCTION**

Carbon dioxide is produced by decomposition of organic matter and by root respiration in soils. As a result, CO$_2$ concentrations in soils are higher than atmospheric CO$_2$ concentrations. Diffusion is considered the major mechanism by which gases move in soils (Kirkham and Powers, 1972; Jurry et al., 1991). It has been previously shown that the distribution of CO$_2$ and its stable isotopic species (e.g., $^{13}$CO$_2$, $^{12}$CO$_2$ in soils can be described by a diffusion-reaction model (Cerling, 1984, 1991; Solomon and Cerling, 1987; Cerling et al., 1989; Quade et al., 1989). Since the $^{13}$C value of CO$_2$ produced by root respiration is essentially the same as that of CO$_2$ produced by decomposition of soil organic matter, the $^{14}$C value of soil CO$_2$ is determined by soil respiration rate and the $^{13}$C value of soil organic matter, which is more or less constant with depth and time in a stable soil ecosystem (Cerling, 1984, 1991; Cerling et al., 1989, Quade et al., 1989).

However, in the case of the radioactive carbon isotope ($^{14}$C), the model needed to describe the $^{14}$CO$_2$ profile will be more complicated. First of all, the $^{14}$C content of CO$_2$ produced by root respiration is not necessarily the same as that of CO$_2$ derived from organic matter decomposition. While root respiration CO$_2$ can be assumed to be nearly identical with the atmospheric $^{14}$C level (Dorr and Münchich, 1986), the $^{14}$C content of CO$_2$ derived from organic matter decomposition may, depending on the carbon residence time in the soil, be depleted by radioactive decay or even enriched by the contribution of $^{14}$C produced in the late 1950s and early 1960s by atmospheric testing of thermonuclear weapons (bomb $^{14}$C) (Dorr and Münchich, 1986). In other words, the $^{14}$C value of CO$_2$ produced by organic matter decomposition should be determined by the $^{14}$C content of soil organic matter, which is a mixture of compounds with different turnover rates (Trumbore et al., 1990; Trumbore, 1993). Moreover, the $^{14}$C value of organic matter changes with depth and time (Goh et al., 1976; O'Brien and Stout, 1978; Trumbore, 1993), suggesting that the CO$_2$ produced at different depths should have different $^{14}$C contents depending on the $^{14}$C content of soil organic matter at that depth and also on the relative contribution of root respiration to the total CO$_2$ production. Haas et al. (1983) and Thorstenson et al. (1983) observed lower $^{14}$C contents in respired CO$_2$ during winter time due to oxidation of older soil organic matter in the absence of significant root respiration. However, their model failed to describe the $^{14}$CO$_2$-depth profile observed in their study. Dorr and Münchich (1986) also observed an annual $^{14}$C variation of soil-respired CO$_2$, which they suggested is controlled by the seasonally varying contribution of root respiration and CO$_2$ produced by microbial decomposition of organic matter.

Presently, there is no adequate model describing the $^{14}$CO$_2$ distribution in soils. Previous studies on soil CO$_2$, and $^{13}$C values of soil CO$_2$, and pedogenic carbonates indicate that the CO$_2$ and carbonate in a soil system are in isotopic equilibrium. This implies that any detrital carbonate dissolved in the soil is overwhelmed by soil CO$_2$ and the isotopic composition of pedogenic carbonate is determined by the isotopic composition of soil CO$_2$ (Cerling, 1984, 1991; Cerling et al., 1989; Quade et al., 1989; Amundson et al., 1989, Cerling and Quade, 1992). If this is the case, the $^{14}$C content of pedogenic carbonate should also be determined by $^{14}$C content of soil CO$_2$ and inherited dead carbon should not affect the age of soil pedogenic carbonate. Therefore, a better understanding of $^{14}$CO$_2$ distribution in soils would have very important implications not only in the study of organic carbon cycling in soils, but also in the application of $^{14}$C to date soil carbonate. Furthermore, the $^{14}$C content of soil CO$_2$ is an important parameter in modeling variations of atmo-
The use of soil pedogenic carbonate to 14C date soils or landforms.

A DIFFUSION-REACTION MODEL FOR 14CO2

Carbon dioxide is produced in soils by biological processes and is transported to the atmosphere by diffusion (KIRKHAM and POWERS, 1972; JURY et al., 1991). The diffusion mechanism applies to its isotopic species 13CO2, 12CO2, and 14CO2 as well (HAAS et al., 1983; THORSTENSON et al., 1983; CERLING, 1984, 1991; CERLING et al., 1989; QUADE et al., 1989). Different isotopic species of CO2 react and diffuse independently of each other according to their own concentration gradient and their own sources and sinks (HAAS et al., 1983; THORSTENSON et al., 1983). Since the concentration of 14CO2 in a soil profile is controlled by the production and decay of 14CO2, and by diffusion through the soil to the atmosphere, the concentration of 14CO2 can be described by a diffusion-reaction equation:

\[ \frac{\partial C_{14}^{z}}{\partial t} = D_{14} \frac{\partial^2 C_{14}^{z}}{\partial z^2} + \Phi_{14}^{z} - \lambda C_{14}^{z}, \]  

where \( C_{14}^{z} \) represents the 14CO2 concentration in the soil air (moles/cm3), \( D_{14} \) is the diffusion coefficient of 14CO2 in the soil (cm2/sec), \( \Phi_{14}^{z} \) is the production of 14CO2 in the soil by organic matter decomposition and root respiration (moles/cm2/sec), and \( \lambda \) the decay constant of 14C (3.84 × 10^{-12}/sec). Since the term \( \lambda C_{14}^{z} \) is much smaller compared to the other terms on the right side of the equation, the above equation can be reduced to

\[ \frac{\partial C_{14}^{z}}{\partial t} = D_{14} \frac{\partial^2 C_{14}^{z}}{\partial z^2} + \Phi_{14}^{z}. \] 

To model 14CO2, information is needed regarding the production of 14CO2 (\( \Phi_{14}^{z} \)) in a soil. With the simplified assumption that soil CO2 is primarily produced (a) by root respiration with practically no difference in 14C from atmospheric CO2, and (b) by decomposition of soil organic matter with the same 14C content as decomposing organic matter, the relative contribution of these two reservoirs to the soil 14CO2 production can be calculated with a two-component mixing model following the equation: \( \Phi_{14}^{z} = F \Phi_{14}^{z} \), where \( \Phi_{14}^{z} \) is the 14C content of biologically produced CO2 in the soil at depth \( z \); \( F \) is the relative contribution of CO2 from organic matter decomposition, the fraction of CO2 derived from root respiration is \( 1 - F \); and \( \Phi_{14}^{z} \) and \( \Phi_{14}^{z} \) are 14C content of decomposing organic matter and the atmosphere, respectively. The production of 14CO2 can then be described by:

\[ \Phi_{14}^{z} = \Phi_{14}^{z} \left( \frac{\delta C_{14}^{z} + \delta C_{12}^{z}}{1000} \right) \lambda, \] 

where \( \Phi_{14}^{z} \) and \( \Phi_{14}^{z} \) are the total CO2 and 12CO2 production rates, respectively; \( \delta C_{14}^{z} \) is the 14C value for respired CO2, and \( \delta C_{14}^{z} \) is the 14C value for soil organic matter. The 14C notation here is the same as that used in oceanography and is not corrected for delta C. Substituting the notation into Eqn. 4, we get:

\[ \Phi_{14}^{z} = \Phi_{14}^{z} \left( \frac{\delta C_{14}^{z} + \delta C_{12}^{z}}{1000} \right) \lambda. \] 

Assuming that the soil can be approximated as a one-dimensional box with a non-flux boundary at depth \( L \), the following boundary conditions exist:

\[ C_{14}^{z} = C_{14}^{s} \text{ at } z = 0 \] 

and

\[ \frac{\partial C_{14}^{z}}{\partial z} = 0 \text{ at } z = L. \] 

For the condition that the 14C content of decomposing organic matter diminishes with depth in a linear fashion, i.e., \( C_{14}^{z, \text{soil}} = A + Bz \), which is the case in most soils (O'BRIEN and STOUT, 1977; TRUMBORE et al., 1990; SCHARPENSEEL et al., 1989), and that \( \Phi_{14}^{z} \) and \( F \) is constant with depth, the steady-state solution to Eqn. 2 is

\[ C_{14}^{z} = C_{14}^{s} \left( 1 - \frac{1}{D_{14}} \left( -F \frac{\delta C_{14}^{z} + \delta C_{12}^{z}}{1000} \right) \lambda \right) = C_{14}^{s} \left( 1 - \frac{A + 1000 B}{6000} \right) \frac{F \cdot z^2}{2} + G \cdot z, \] 

where \( C_{14}^{s} \) is the 14C content of decomposing organic matter and the atmosphere,
where

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

and

\[ G = \Phi^{12}(R_{atm}) \cdot F \cdot \left( A + \frac{1000}{1000} \cdot L + \frac{B}{2000} \cdot L^2 \right) + E \cdot L. \]

According to CERLING (1984), the steady-state solutions for diffusion-reaction equations for CO\(_2\) and \( ^{13}C\)O\(_2\), with boundary conditions of \( C^*_i = C^*_a \) and \( C'^{13}_i = C'^{13}_a \) at \( z = 0 \), and \( \frac{\partial C^*_i}{\partial z} = 0 \) and \( \frac{\partial C'^{13}_i}{\partial z} = 0 \) at \( z = L \), are as follows:

\[ C^*_i = \frac{\Phi^{12}D^*_i}{D^*_a} \left( Lz - \frac{z^2}{2} \right) + C^*_a \]  \hspace{1cm} (7)

\[ C'^{13}_i = \frac{\Phi^{13}D'^{13}_i}{D'^{13}_a} \left( Lz - \frac{z^2}{2} \right) + C'^{13}_a, \]  \hspace{1cm} (8)

where \( C^*_i \) and \( C'^{13}_i \) are CO\(_2\) and \( ^{13}C\)O\(_2\) concentrations in the atmosphere; \( C^*_a \) and \( C'^{13}_a \) are corresponding concentrations in the soil air; and \( D^*_i \) and \( D'^{13}_i \) are diffusion coefficients for CO\(_2\) and \( ^{13}C\)O\(_2\), respectively.

The diffusion coefficient for CO\(_2\) in soil is related to that in air (\( D_{air} \)) by

\[ D^*_i = D_{air} \rho \rho, \]

where \( \epsilon \) is the free air porosity in the soil, and \( \rho \) is a tortuosity factor (KIRKHAM and POWERS, 1972; JURY et al., 1991). \( D_{air} \) varies with temperature and pressure (BIRD et al., 1960):

\[ D_{air} = D_{air}^0 \rho^\frac{P_{air} - 1}{P_{air}}, \]

where \( D_{air}^0 \) is the diffusion coefficient for CO\(_2\) in air under standard conditions (\( T = 25^\circ C \) and \( P = 1 \) bar pressure) and is taken to be 0.144 cm\(^2\)/s.

![Diagram showing depth vs. delta 14C value for soil CO2](image)

**FIG. 1.** \( \delta^{14}C \) value of soil CO\(_2\) vs. depth for a model soil. It shows that the \( \delta^{14}C \) values of soil CO\(_2\) vary with depth from the (pre-atomic bomb) atmospheric value at the soil-atmosphere interface to more negative or more positive values at depth depending on the value of \( F \).

Table 1 Parameters for the model soil described in the text

| Depth (cm) | 10 | 40 | 60 | 80 | 100 | 120 | 140 | 160 | 180 | 200 |
|-----------|----|----|----|----|-----|-----|-----|-----|-----|-----|
| \( \delta^{14}C_{atm} \) | -10 | -50 | -100 | -150 | -200 | -225 | -250 | -275 | -300 | -325 |

\[ \delta^{14}C_{atm} = 1.1176 - 1.7317 \times 10^{-0.80} \times \text{depth} \]

Temperature=25°C

Pressure=1atm

Respired CO\(_2\): \( ^{13}C\)O\(_2\)=20%

Atmospheric CO\(_2\): 300 ppm, \( ^{13}C\)O\(_2\)=6%

Porosity = 0.5

Tortuosity factor = 0.61

The diffusion coefficients of \( ^{14}C\)O\(_2\) and \( ^{13}C\)O\(_2\) are related by

\[ \frac{D_{12}^{12}}{D_{14}^{14}} = \left[ \frac{M(air) + M(12CO_2)}{M(air) + M(14CO_2)} \left( \frac{M(air) \times M(12CO_2)}{M(air) \times M(14CO_2)} \right) \right]^{1/2} \]

= 1.00868.

Using Eqns. 6, 7, and 8 and using various values of soil respiration, an atmospheric CO\(_2\) concentration of 300 ppm, and atmospheric \( \delta^{13}C \) and \( \delta^{14}C \) values of -6% (pre-industrial value) and 0% (pre-bomb value), respectively, it is possible to calculate \( ^{14}C\)O\(_2\) (\( \delta^{14}C \)) profiles in soils for various conditions.

Figure 1 shows how the \( \delta^{14}C \) value of soil CO\(_2\) varies with depth in a model soil where the \( ^{14}C\)O\(_2\) concentration is diffusion-controlled. The parameters for the model soil are listed in Table 1. This diagram displays several important features:

1) The \( \delta^{14}C \) value of soil CO\(_2\) is not necessarily the same as that of atmospheric CO\(_2\), although it has been assumed so in previous studies using \( ^{14}C \) to date soil carbonate. However, the present-day analytical precision at best is \( \pm 3\% \), and for most accelerator labs the analytical precision is \( \pm 8\% \). Therefore, when \( F \) is small, for example \( F = 0.1 \), the \( \delta^{14}C \) value of soil CO\(_2\) can be considered the same as that of atmospheric CO\(_2\).

2) The \( \delta^{14}C \) values of soil CO\(_2\) are not constant with depth. The \( \delta^{14}C \) values of soil CO\(_2\) depend on the \( \delta^{14}C \) values of soil organic matter, soil respiration, and the relative contribution of CO\(_2\) derived from organic matter decomposition to total CO\(_2\) production (\( F \)).

3) When the fraction of CO\(_2\) derived from organic matter decomposition (\( F \)) is small, the \( \delta^{14}C \) values of soil CO\(_2\) vary continuously from the atmospheric value at the soil-atmosphere interface to more negative values at depth. Increasing the value of \( F \), the \( \delta^{14}C \) values of soil CO\(_2\) at any depth become more negative.

4) When \( F = 0 \), the \( \delta^{14}C \) values of soil CO\(_2\) vary continuously from the atmospheric value at the soil-atmosphere interface to more positive values at depth. This increase in \( \delta^{14}C \) values is a result of diffusion effects on the different isotopic species (CERLING et al., 1991). If the \( ^{14}C \) data are corrected for isotope fractionation using \( ^{13}C \) data (i.e., \( \Delta^{14}C \) in STUIVER and POLACH, 1977), this diffusion component will not be seen.

Figure 2 shows how the \( \delta^{14}C \) values of soil CO\(_2\) vary with soil respiration rates. It is evident that at a given value of \( F \), the higher the soil respiration, the more the \( \delta^{14}C \) values of soil CO\(_2\) deviate from that of atmospheric CO\(_2\).
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When all soil CO₂ is derived from root respiration and/or decomposition of short-lived organic matter which has the same δ¹⁴C content as the atmospheric CO₂, the δ¹⁴C values of soil CO₂ are relatively enriched (up to 8.5‰ at 15°C) compared to δ¹⁴C values of atmospheric CO₂ (Fig. 3) due to diffusion effects. The lower the respiration rate or the higher the value of the diffusion coefficient, the less enriched the δ¹⁴C values of soil CO₂ are relative to the δ¹⁴C values of atmospheric CO₂. When soil respiration = 0, the δ¹⁴C values of soil CO₂ are the same as the δ¹⁴C values of atmospheric CO₂. Again, considering the present-day analytical precision of ±8‰ for ¹⁴C analysis, this diffusion effect on ¹⁴C content of soil CO₂ would be beyond detection.

These figures show soil ¹⁴C₀₂ relationships for pre-industrial atmospheric conditions. To use this model to evaluate present-day soil conditions, one must change the atmospheric boundary conditions for CO₂, ¹²C₀₂, and ¹⁴C₀₂. In our test of the model against empirical data given below, various ¹⁴Cₐₐₚ values are used, based on the reported data.

**OBSERVATIONS IN SOILS**

It is important to establish if the above ¹⁴C₀₂ model is valid in soils. Presently, there are few ¹⁴C₀₂ depth profiles available. In Fig. 4, the ¹⁴C data (reported as d ¹⁴C, percent modern carbon (pmc) = (δ¹⁴C/1000 + 1)(1 - 2*δ¹³C(100) + 100) for soil CO₂ and CO₂ concentrations (data obtained in May) from site #6 in HAAS et al. (1983) and THORSTENSON et al. (1983) are plotted (different symbols represent different sampling dates) and compared to our model calculation (solid line). Since there were no ¹⁴Cₐₐₚ data and no CO₂ production information reported in their study, we assumed that the ¹⁴CO₂ production is an exponential function of depth as ϕₜ₄(τ) = ϕₜ₄(0)e⁻ˠτ with \( \frac{∂C_{\text{r}}}{∂z} = 0 \) at \( z = L \) (\( L = 380 \text{ cm} \) was used in the model calculation), where \( ϕₜ₄(0) \) is the production of ¹⁴CO₂ at surface and ρ is a constant (we use \( b = 0.003 \) in the model calculation). We also assume that production of CO₂ is an exponential function of depth in their soil as \( ϕₜ₄(z) = \phiₜ₄(0)e^{-z/\rho} \) with \( \frac{∂C_{\text{r}}}{∂z} = 0 \) at \( z = L' \) (\( L' = 520 \text{ cm} \) was used in the model calculation), where \( ϕₜ₄(0) \) is the production of CO₂ at surface and \( ρ \) is the attenuation depth (we use \( ρ = 300 \text{ cm} \) in the model calculation). The solution to the diffusion Eqn. 2 with the assumed production function and boundary conditions are:

\[
C_{\text{r}} = \frac{\phiₜ₄(0)(L'z)}{(D_{\text{r}}L')^b} \left( 1 - e^{-z/\rho} - \frac{\phiₜ₄(0)(z)}{(D_{\text{r}}L')^b} e^{-z/\rho} + C_{\text{r}} \right)
\]

\[\text{(9)}\]

\[
C_{\text{r}} = \frac{\phiₜ₄(0)(L'z)}{(D_{\text{r}}L')^b} \left( 1 - e^{-z/\rho} \right) + C_{\text{r}} \]

\[\text{(10)}\]

**Fig. 2. Variations of the δ¹⁴C values of soil CO₂ with soil respiration rates at a constant F value. The model shows that the higher the soil respiration rate, the more the δ¹⁴C values of soil CO₂ deviate from that of the atmospheric CO₂.**

**Fig. 3. δ¹⁴C value of soil CO₂ vs. depth for soils where all CO₂ is derived from root respiration and/or decomposition of short-lived organic matter. It can be seen that the δ¹⁴C values of soil CO₂ are relatively enriched compared to δ¹⁴C values of atmospheric CO₂ due to diffusion effects. Figure 3 (a) shows that the lower the respiration rate, the less enriched the δ¹⁴C values of soil CO₂ are relative to the δ¹⁴C values of atmospheric CO₂. Figure 3 (b) shows the effect of varying diffusion coefficient on the δ¹⁴C content of soil air.**
where $C_{\text{14C}}$ and $C_{*}$ are $^{14}$CO$_2$ and CO$_2$ concentrations in the soil; $C_{\text{14C}}$ and $C_{*}$ are corresponding concentrations in the atmosphere; and $L$ and $L'$ are the depth of the non-flux boundaries for $^{14}$CO$_2$ and CO$_2$, respectively (the non-flux boundary is a boundary where CO$_2$ or $^{14}$CO$_2$ concentration gradient equals to zero). Other assumed parameters used in our model calculation are listed in Table 2. In their study, THORSTENSON et al. (1983) concluded that the measured $^{14}$CO$_2$ profiles cannot be readily explained with a diffusion model due to some as yet unexplained mechanisms. However, Fig. 4 suggests that our curve fits their data reasonably well, except for one datum point at the 15.9 meter depth. This point represents a groundwater CO$_2$ sample and, therefore, may be contaminated by carbon from other sources. The goodness of the fit is adequate to strongly suggest that vertical diffusion is indeed the dominant mechanism affecting $^{14}$CO$_2$ and CO$_2$ distribution in this soil. It should be noted that $^{14}$C value of atmospheric CO$_2$ (the upper boundary condition) is greater than 0% (the boundary condition used in Figs. 1-3). This is because present atmospheric $^{14}$C content is elevated above natural levels by nuclear weapons testing and use.

Figure 5 compares the $^{14}$CO$_2$ and CO$_2$ data from two Oxisol profiles (a forest soil and a 17-year-old pasture soil which is a degraded forest soil) from Paragominas in Brazil (NEPSTAD et al., unpubl. data) and our model calculations. The CO$_2$ samples were collected in May, 1992 by Trumbore, Davidson, et al.
and Nepstad. The measured CO$_2$ respiration rates for May are 25 mmoles/m$^2$/h for the forest soil and 10 mmoles/m$^2$/h for the pasture soil. For each soil, the $^{14}$CO$_2$ and CO$_2$ data are fitted using the same set of parameters (i.e., respiration rate, diffusion coefficient, porosity, temperature, and pressure) (Table 2). The measured CO$_2$ respiration rate for the forest soil seems too high because it requires an unreasonably high diffusion coefficient and/or porosity to produce the observed soil $^{14}$CO$_2$ and CO$_2$ profiles. The high respiration rate reflects the decomposition of abundant litter on the forest floor which could have contributed significant amounts of CO$_2$ to the total CO$_2$ flux measured at the soil surface and higher production of CO$_2$ in the upper 2 meters of the soil. In our model calculation we used a value of 13 mmoles/m$^2$/h for respiration rate which gives a reasonable fit to both the $^{14}$CO$_2$ and CO$_2$ data. Again, vertical diffusion appears to be the dominant mass-transport mechanism affecting $^{14}$CO$_2$ and CO$_2$ distribution in these soils. However, unlike the data of Haas et al. (1983), the $^{14}$C content of soil CO$_2$ is greater than present atmospheric values. Since soil CO$_2$ is produced by root respiration and decomposition of soil organic matter which is a heterogeneous mixture of compounds turning over at different rates, the observed $^{14}$C profiles here suggest that the fractions of soil organic matter whose turnover contribute the most to the soil CO$_2$ contains a considerable quantity of bomb-produced $^{14}$C.

**IMPLICATIONS FOR $^{14}$C DATING OF SOIL CARBONATE**

Dates from soil carbonates have been considered unreliable estimates of the age of pedogene because of unknown initial $^{14}$C/$^{12}$C ratios in the carbonate and the possibility of subsequent contamination with environmental $^{14}$C (Callen et al., 1983). Comparison of carbonate $^{14}$C ages with $^{14}$C ages of coexisting organic matter suggests that radiocarbon dates calculated from pedogenic carbonate in arid areas were about 500 to 7000 radiocarbon years too old (Williams and Polach, 1969). On the other hand, radiocarbon dates of pedogenic carbonate from the sub-humid part of southeastern Australia were much younger than either the known age of deposition in which the carbonate is segregated, or the likely age of pedogenesis (Bowler and Polach, 1971). These discrepancies have been attributed to an initial low $^{14}$C content of soil carbonate due to the limestone dilution effect and/or secondary contamination by environmental $^{14}$C. The limestone dilution effect (Bartlett, 1951; Broecker and Walton, 1959) states that soil carbonate derives half of its C from dead calcium carbonate and another half from atmospheric CO$_2$, suggesting that radiocarbon age of such carbonate would be about one half-life of $^{14}$C (about 5570 years) older than the true age. However, studies on soil CO$_2$ and $\delta^{13}$C of soil CO$_2$ and pedogenic carbonates indicate that the CO$_2$ and its isotopic species in a soil system are in isotopic equilibrium. This implies that C derived from dissolution detrital carbonate is ultimately lost through isotopic exchange with soil CO$_2$ and isotopic composition of pedogenic carbonate is determined by the isotopic composition of soil CO$_2$ (Cerling, 1984, 1991; Cerling et al., 1989; Quade et al., 1989; Cerling and Quade, 1992). We have shown that $^{14}$C content of soil CO$_2$ can be depleted or enriched relative to that of atmospheric CO$_2$ depending on various factors. Soil carbonate formed during the early development of a soil, when $^{13}$C content of soil organic matter is about the same as that of the atmospheric CO$_2$, could have $^{14}$C ages younger than the true age of the pedogenesis. On the other hand, carbonate formed later on in a soil, could have $^{14}$C ages older than the true age of the carbonate precipitation. Elsewhere, we (Amundson et al., 1993) explore in detail the effects of our diffusion/reaction model on carbonate $^{14}$C ages.

**CONCLUSIONS**

The distribution of $^{14}$CO$_2$ in soils can be described by a diffusion-reaction model. The $^{14}$C content of soil CO$_2$ varies with depth depending on many factors: the $^{14}$C content of soil organic matter, the relative contribution of root respiration to total CO$_2$ production, soil respiration rate, atmospheric CO$_2$ concentration and $^{14}$C content, soil properties, temperature, etc. Our model suggests that $^{14}$C ages of pedogenic carbonate could be older or younger than the true age of pedogenesis. While there are other factors that can also affect the $^{14}$C age of a carbonate sample (such as sample thickness, i.e., the total time required to form the sample being measured), our basic understanding of the initial $^{14}$C contents of pedogenic carbonates is the first step to critically evaluating their potential as indicators of landform age.

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**REFERENCES**

Amundson R. G., Chadwick O. A., Sowers J. M., and Donner H. E. (1989) The stable isotope chemistry of pedogenic carbonates at Kyle Canyon, Nevada. Soil Sci. Soc. Amer. J. 53, 201-210.

Amundson R. G., Wang Y., Chadwick O. A., Trumbore S., McFadden L., Wells S., and DeNiro M. (1993) Factors and processes governing the carbon-14 content of carbonate in desert soils. (in preparation).

Bartlett H. H. (1951) Radiocarbon datability of peat, marl, caliche, and archaeological materials. Science 114, 55-56.

Bird R. B., Stewart W. E., and Lightfoot E. N. (1960) Transport Phenomena. Wiley.

Bowler J. M. and Polach H. A. (1971) Radiocarbon analyses of soil carbonates: an evaluation from palaeosols in southeastern Australia. In Palaeopedology—Origin, Nature and Dating of Palaeosols (ed. D. Yaalon), pp. 97-108. Intl. Soc. Soil Sci. and Israel Univ. Press.

Broecker W. S. and Walton A. (1959) The geochemistry of C$^{14}$ in fresh water systems. Geochim. Cosmochim. Acta 16, 15-38.

Callen R. A., Wasson R. J., and Gillepsie R. (1983) Reliability of radiocarbon dating of pedogenic carbonate in the Australian arid zone. Sediment Geol. 35, 1-14.

Cerling T. E. (1984) The stable isotopic composition of modern soil carbonate and its relationship to climate. Earth Planet. Sci. Lett. 71, 229-240.

Cerling (1991) Carbon dioxide in the atmosphere: Evidence from Cenozoic and Mesozoic palaeosols. Amer. J. Sci. 291, 377-400.

Cerling T. E. and Quade J. (1997) Carbon isotopes in modern soils. Encly. Earth System Sci. 1, 423-429.

Cerling T. E., Quade J., Wang Y., and Bowman J. R. (1989) Carbon isotopes in soils and palaeosols as ecology and palaeoecology indicators. Nature 341, 138-139.

Dorr H. and Münchn K. O. (1986) Annual variations of the 14C content of soil CO2. Radiocarbon 28, 338-345.

Gorin K. M., Rafter T. A., Stout J. D., and Walker T. W. (1976) The accumulation of soil organic matter and its carbon isotope
content in a chronosequence of soils developed on aeolian sand in New Zealand. *J. Soil Sci.* 27, 89–100.

HAAS H., FISHER D. W., THORSTENSON D. C., and WEEKS E. P. (1983) \(^{14}\)CO\(_2\) and \(^{13}\)CO\(_2\) measurements on soil atmosphere sampled in the sub-surface unsaturated zone in the western great plains of the US. *Radiocarbon* 25, 301–314.

JURY W. A., GARDNER W. R., and GARDNER W. H. (1991) *Soil Physics*, 5th ed. Wiley.

HAAS H., FISHER D. W., THORSTENSON D. C., and WEEKS E. P. (1983) Distribution of gaseous \(^{14}\)CO\(_2\), \(^{13}\)CO\(_2\), and \(^{14}\)C\(_2\) in the sub-soil unsaturated zone of the western US great plains. *Radiocarbon* 25, 315–346.

OLIVER B. J. and STOUT J. D. (1978) Movement and turnover of soil organic matter as indicated by carbon isotope measurements. *Soil Biol. Biochem.* 10, 309–317.

QUADE J., CERLING T. E., and BOWMAN J. R. (1989) Systematic variations in the carbon and oxygen isotopic composition of pedogenic carbonate along elevation transects in the southern Great Basin, United States. *Geol. Soc. Amer. Bull.* 101, 464–475.

SCHARPENSEEL H. W., BECKER-HEIDMANN P., NEUE H. U., and TSUTSUKI K. (1989) Bomb-carbon, \(^{14}\)C dating and \(^{13}\)C measurements as tracers of organic matter dynamics as well as of morphogenetic and turbation processes. *Sci. Total Environ.* 81/82, 99–110.

SOLOMON D. K. and CERLING T. E. (1987) The annual carbon dioxide cycle in a montane soil: Observations, modeling, and implications for weathering. *Water Resources Res.* 12, 257.

STUIVER M. and POLACHE H. (1977) Reporting of \(^{14}\)C data. *Radiocarbon* 19, 355–363.

THORSTENSON D. C., WEEKS E. P., HAAS H., and FISHER D. W. (1983) Distribution of gaseous \(^{13}\)CO\(_2\), \(^{14}\)CO\(_2\), and \(^{14}\)C\(_2\) in the sub-soil unsaturated zone of the western US great plains. *Radiocarbon* 25, 315–346.

TRUMBORE S. E. (1993) Comparison of carbon dynamics in tropical and temperate soils using radiocarbon measurements. *Global Biogeochem. Cycles* 7, 275–290.

TRUMBORE S. E., BONANI G., and WOLFLI W. (1990) The rates of fractionated soil organic matter. In *Soils and the Greenhouse Effect* (ed. A. F. BOUWMAN), pp. 405–414. Wiley.

WILLIAMS G. E. and POLACH H. A. (1969) The evaluation of \(^{14}\)C ages for soil carbonate from the arid zone. *Earth Planet. Sci. Lett.* 7, 240–242.