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CARBON DIOXIDE IN THE ATMOSPHERE: EVIDENCE FROM CENOZOIC AND MESOZOIC PALEOSOLS

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ABSTRACT. A diffusion-reaction model for the isotopic composition of soil CO_2 and soil carbonate is evaluated. It shows which variables are important under different conditions and shows that under certain circumstances the carbon isotopic composition of soil carbonate can be used to estimate $P(CO_2)$ of the atmosphere from late Paleozoic to the present. The isotopic composition of soil carbonate produced under uniform conditions is essentially constant below about 20 cm in most soils. Today, the isotopic composition of soil organic matter, which is mostly determined by the fraction of C_4 biomass present, is the most important factor in determining the carbon isotopic composition of soil carbonate. However, prior to the advent of C_4 plants making up a significant fraction of the biomass, probably in the Tertiary, the concentration of CO_2 in the atmosphere can be estimated because of mixing of atmospheric CO_2 with CO_2 produced in the soil. The diffusion-reaction model also suggests that before the advent of higher land plants most soil carbonate should have $\delta^{13}C$ values that are strongly influenced by the atmosphere due to the shallow rooting depth of non-vascular plants.

Preliminary results reported here suggest that $P(CO_2)$ was less than about 700 ppmV during the Eocene and since late Miocene because the limiting carbon isotopic composition of soil carbonate was between -11.5 to -12.5 permil relative to PDB. However, early Cretaceous and early Jurassic paleosols have $\delta^{13}C$ values between -6.5 and -8.5 permil suggesting that $P(CO_2)$ was significantly higher than today, probably on the order of 1500 to 3000 ppmV.

INTRODUCTION

The carbon dioxide content of the atmosphere has an important role in regulating the surface temperature of the planet. While it is possible to measure directly the CO_2 content of the latest Pleistocene and Holocene atmosphere preserved in bubbles in high latitude ice (Barnola and others, 1987), direct measurements of CO_2 of the paleoatmosphere are not possible for the pre-Pleistocene. Other indirect methods to estimate paleo-CO_2 concentrations in the atmosphere have been attempted, including comparisons of the carbon isotopic composition of planktonic and benthic organisms (Shackleton and others, 1983) and forward modeling of the CO_2 global budget (Berner, Lasaga, and Garrels, 1983; Lasaga, Berner, and Garrels, 1985; Berner, 1990).

Paleoclimatic interpretations for most of the Cenozoic and Mesozoic suggest that global temperatures were higher than today. Simulations of Cretaceous climates using General Circulation Models (GCMs) indicate a slight global warming due to repositioning of the continents from today's configuration (Barron and Washington, 1984). However, some specific

predictions made by the GCMs, such as the predicted temperature near the poles and in the interior of large continents, are much lower than geological evidence will permit. However, by increasing $P(CO_2)$ in the atmosphere the GCM calculations predict higher temperatures in these regions (Barron and Washington, 1985).

In this paper I examine paleosols as recorders of paleo-CO_2 levels in the atmosphere. Paleosol carbonates record the isotopic composition of local soil CO_2, which today is determined primarily by the fraction of C_3 and C_4 plants making up the biomass of the local ecosystem and other soil parameters such as soil productivity (Cerling, 1984; Cerling and others, 1989; Quade, Cerling, and Bowman, 1989b). Atmospheric mixing in soils due to diffusion results in a similar isotopic signal to that of C_4 plants. Today, except for ecosystems with very low productivity such as deserts, the atmospheric contribution to the total soil CO_2 in modern soils is very small because of the very low concentration of CO_2 in the modern atmosphere. However, high atmospheric CO_2 would make a significant contribution to total soil CO_2 and, in times when few or no C_4 plants were present, could result in a significant isotopic shift in the $\delta^{13}C$ of soil carbonate precipitated in isotopic equilibrium with soil CO_2. This paper examines the different parameters affecting the carbon isotopic composition of soil CO_2 and soil carbonate formed in soils and the potential use of the isotopic composition of soil carbonate as a paleo-CO_2 indicator.

METHODS AND TERMINOLOGY

The isotopic composition of carbon is given in standard permil notation where:

$$\delta^{13}C = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{PDB}} - 1 \right) \times 1000 \qquad (1)$$

where PDB is the isotopic reference standard PDB. Organic matter was combusted at 800°C with CuO and silver foil in a quartz tube to produce CO_2 which was analyzed on a mass spectrometer. Carbonates were roasted under vacuum and then reacted with 100 percent phosphoric acid at 25°C to produce CO_2 which was analyzed on a mass spectrometer. The isotopic difference between two co-existing phases is:

$$\Delta^{13}C_{A-B} = \delta_A - \delta_B \qquad (2)$$

For the case of isotopic equilibrium of co-existing phases:

$$10^3 \ln \alpha_{A-B} \approx \Delta^{13}C_{A-B} \qquad (3)$$

where:

$$\alpha_{A\text{-}B} = \frac{\left(\frac{^{13}C}{^{12}C}\right)_A}{\left(\frac{^{13}C}{^{12}C}\right)_B} = \frac{1000 + \delta_A}{1000 + \delta_B} \tag{4}$$

It is important to make the distinction between soil CO_2 and soil-respired CO_2. Soil CO_2 refers to the concentration of CO_2 in a particular soil volume and has units of ppmV. Soil-respired CO_2 represents a flux and is the amount of CO_2 passing through a horizontal plane in the soil, such as the soil-air interface, and has units of mmoles/m^2/hr. The isotopic compositions of soil CO_2 and soil-respired CO_2 have very different isotopic compositions, as will be shown below.

MODEL FOR THE ISOTOPIC COMPOSITION OF SOIL CO_2

Soil CO_2 is higher than atmospheric CO_2, because CO_2 is produced by plant respiration and microbial activity in soils. The concentration of soil CO_2 in a soil profile is controlled by the production rate of CO_2 (itself a function of depth in the soil) and diffusion through the soil to its upper boundary, the atmosphere (Kirkham and Powers, 1972; Solomon and Cerling, 1987). The concentration of soil CO_2 can be described by the diffusion-reaction equation:

$$\frac{\partial C_s^*}{\partial t} = D_s^* \frac{\partial^2 C_s^*}{\partial z^2} + \phi_s^*(z) \tag{5}$$

where C_s^* is the concentration of CO_2 in the soil (moles/cm^3), D_s^* is the diffusion coefficient (cm^2/s) for CO_2 in soil, z is depth (cm), and $\phi_s^*(z)$ is the production rate of CO_2 (moles/cm^3/s) in the soil as a function of depth. The subscript "s" refers to "soil," and the superscript "*" refers to bulk CO_2 without isotopic distinction. The diffusion coefficient for CO_2 in soil is related to that in air (D_{air}) by

$$D_s^* = D_{air} \epsilon \rho \tag{6}$$

where ϵ is the free air porosity in the soil, and ρ is a tortuosity factor that is always less than 1.0 (Kirkham and Powers, 1972). D_{air} varies with temperature (T) and pressure (P) and can be corrected to standard conditions T^o,P^o) by (Bird, Stewart, and Lightfoot, 1960):

$$D_{air} = D_{air}^o \left(\frac{P^o T}{P T^o}\right)^{1.823} \tag{7}$$

where D_{air}^o is the diffusion coefficient for CO_2 in air under standard conditions and is taken to be 0.144 cm^2/s.

For simple production functions (for example, constant from suface to depth L: $\phi_s^*(z)$ = constant to depth L; linear decrease from surface to depth L where $\phi_s^*(L) = 0$; or exponential decrease with depth $\phi_s^*(z) = \phi_s^*(0)e^{-z/\bar{z}}$ where $\bar{z}$ is the characteristic production depth of CO_2 in the soil) the steady-state solution to this equation is straightforward (Cerling, 1984; Wood and Petraikis, 1984). For the boundary conditions of the CO_2 concentration at the soil-air interface being the same as the atmosphere

$$C_s^* = C_a^* \qquad \text{for } z = 0 \tag{8}$$

where C_a^* is the concentration of CO_2 in the atmosphere, and that the lower boundary is a no-flux boundary at an impermeable barrier (L) (a groundwater table approaches this condition) so that:

$$\frac{\partial C_s^*}{\partial z} = 0 \qquad \text{for } z = L, \text{ or infinity} \tag{9}$$

The general solution to this equation is:

$$C_s^*(z) = \mathbf{S}(z) + C_a^* \tag{10}$$

where $\mathbf{S}(z)$ is the specific solution to eq (5) for a particular production function $\phi_s^*(z)$. For the case where $\phi_s^*(z) = \phi_s^*(0)e^{-(z/\bar{z})}$:

$$\mathbf{S}(z) = \frac{\phi_s^*(0)\bar{z}^2}{D_s^*}\left(1 - e^{-(z/\bar{z})}\right) \tag{11}$$

Similar equations can be derived for $^{12}CO_2$ and $^{13}CO_2$ using the diffusion coefficients D_s^{12} and D_s^{13} rather than the bulk diffusion coefficient for CO_2. Using the standard δ notation, it is possible to derive the equation describing the variation of $\delta^{13}C(CO_2)$ in a soil with depth (see Cerling, 1984 for a specific solution). The general solution is:

$$\delta_s(z) = \left(\frac{1}{R_{PDB}}\left[\frac{\mathbf{S}(z)\dfrac{D_s^*}{D_s^{13}}\widehat{\delta}_\phi + C_a^*\widehat{\delta}_a}{\mathbf{S}(z)\left(1 - \dfrac{D_s^*}{D_s^{13}}\widehat{\delta}_\phi\right) + C_a^*(1 - \widehat{\delta}_a)}\right] - 1\right) \times 1000 \tag{12}$$

where

$$\widehat{\delta}_i = \left[\frac{R_{PDB}\left(\dfrac{\delta_i}{1000} + 1\right)}{1 + R_{PDB}\left(\dfrac{\delta_i}{1000} + 1\right)}\right] \tag{13}$$

where δ_s, δ_a, δ_ϕ are the permil values for soil CO_2, the atmospheric CO_2, or soil-respired CO_2, respectively, and R_{PDB} is the ratio $^{13}C/^{12}C$ in the isotopic reference standard PDB.

Using the modern conditions of STP (25°C and 1 bar pressure) and 300 ppmV CO_2 in the atmosphere with the pre-industrial isotopic composition of −6.5 permil (Friedli and others, 1986), the predicted concentrations and isotopic composition of soil CO_2 display several important features (fig. 1). First, because there is no discontinuity in the concentrations of CO_2, $^{12}CO_2$, and $^{13}CO_2$ at the soil-atmosphere interface and they all increase with depth, the $\delta^{13}C(CO_2)$ values for soil air vary continuously from the atmospheric value at the soil-atmosphere interface to more negative values at depth. Thus, the isotopic composition of soil CO_2 is not constant in a soil (Cerling, 1984; Quade, Cerling, and Bowman, 1989b). Second, the diffusion coefficients of $^{12}CO_2$ and $^{13}CO_2$ differ by (Jost, 1960):

$$\frac{D_s^{12}}{D_s^{13}} = \left[\left(\frac{M(air) + M(^{12}CO_2)}{M(air) \times M(^{12}CO_2)}\right)\left(\frac{M(air) \times M(^{13}CO_2)}{M(air) + M(^{13}CO_2)}\right)\right]^{1/2} = 1.0044 \qquad (14)$$

where $M(^{12}CO_2)$, $M(^{13}pCO_2)$, and M(air) are the atomic masses of $^{12}CO_2$, $^{13}CO_2$, and air, respectively. This results in an enrichment in $^{13}CO_2$ in soil CO_2 compared to soil-respired CO_2: the isotopic composition of soil CO_2

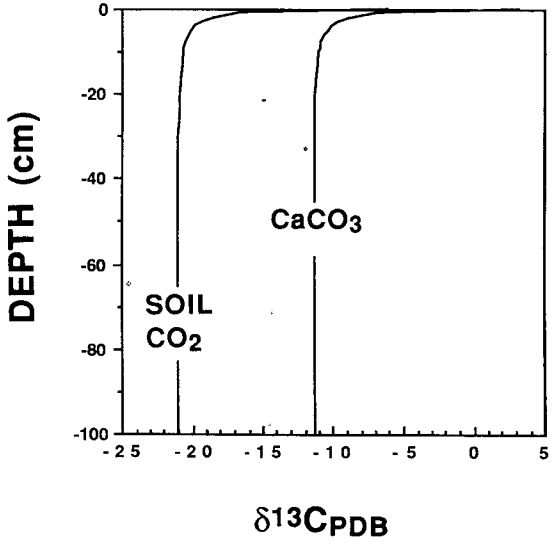

Fig. 1. Carbon isotopic composition of soil CO_2 and soil carbonate in equilibrium with soil CO_2 for soil described in text and in table 1. The $\delta^{13}C$ value for soil carbonate is essentially constant below 30 cm.

is 4.4 permil *or more* enriched in $^{13}CO_2$ relative to soil-respired CO_2 at all levels in the soil (Cerling, 1984; Cerling and others, ms).

SOIL CARBONATE AS AN INDICATOR OF SOIL CO_2

The isotopic composition of soil carbonate is a faithful monitor of the isotopic composition of soil CO_2 (Cerling and others, 1989). Studies of carbonates formed in the Holocene of North America show that the isotopic composition of soil carbonate is constant below about 20 cm (Cerling and others, 1989; Quade, Cerling, and Bowman, 1989b). In desert soils where carbonate is precipitated to the soil-atmosphere interface, the isotopic compositions of soil carbonates formed in the upper 10 cm of the soil vary considerably and are in isotopic equilibrium with the atmospheric value at the soil-atmosphere interface (Quade, Cerling and Bowman, 1989b). The combined effects of diffusion of soil-respired CO_2 and isotopic fractionation between soil CO_2 and carbonate predicts a 14 permil (about 30°) to 17 permil (about 0°C) difference between soil-respired CO_2 and soil carbonate precipitated in isotopic equilibrium for high soil CO_2 respiration rates. Desert soils with low CO_2 respiration rates or carbonates precipitated near the soil-atmosphere interface have even larger Δ values for soil-respired CO_2 and soil carbonate. There is little evidence of isotopic kinetic effects in soil carbonate formation (Quade, Cerling, and Bowman, 1989b). In the following discussion, I will consider that isotopic equilibrium prevails in a soil CO_2 system where mass transfer is dominated by diffusion.

THE ISOTOPIC COMPOSITION OF SOIL CARBONATE: SOURCES OF VARIATION

The isotopic composition of soil carbonate is dependent on many factors, including the isotopic composition of soil-respired CO_2, the depth within a soil, the production rate of soil CO_2, the mean production depth of soil CO_2, soil porosity, soil temperature, absolute pressure, and the concentration and isotopic composition of atmospheric CO_2. Each of these will be considered below by comparing these variables with a model soil (table 1) that is isothermal at 25°C at sealevel (one bar atmospheric pressure) and where atmospheric CO_2 is 300 ppmV with a $\delta^{13}C$ value of

TABLE 1

Parameters for model soil described in text

	Model soil
Temperature	25°C
Pressure	1 bar (sealevel)
Soil CO_2 Production Rate:	8 mmol/m^2/hr @ −26 permil $\phi_s^*(z) = \phi_s^*(0)\ e^{-(z/\bar{z})}$
$\bar{z}$	10 cm
Porosity	0.35
Atmospheric CO_2	300 ppmV @ −6.5 permil

−6.5 permil. A standard soil-respiration rate, typical for temperate and sub-tropical ecosystems during the growing season (Singh and Gupta, 1977; Schlesinger, 1977; Dorr and Munnich, 1987; Gaudry and others, 1990) of 8 mmol/m^2/hr will be used in a soil where the attenuation depth ($\bar{z}$) of 10 cm for CO_2 production is used. A soil-respired $\delta^{13}C(CO_2)$ value of −26 permil is used for the model soil. The prime variable to be considered is that of the concentration of CO_2 in the atmosphere, which is the upper boundary condition for the soil. Eqs (10) and (11) show that the amount of CO_2 contributed by the soil to the total soil CO_2 is mathematically independent of the concentration of CO_2 in the atmosphere. However, greenhouse feedback would result in different soil temperature and moisture conditions which would in turn affect soil CO_2 productivity and mean CO_2 production depth. The net affect on soil respiration due to greenhouse feedback is not considered in this discussion, although soil respiration rates are treated separately in the diffusion-reaction equation. Thus the isotopic composition of soil CO_2 will depend on the concentration of CO_2 in the atmosphere (eq 12): for today's low atmospheric $P(CO_2)$ condition the contribution of atmospheric CO_2 to total CO_2 is very small; for higher $P(CO_2)$ conditions it becomes significant. In the following paragraphs, I will consider the variables affecting the isotopic composition of soil carbonate formed in isotopic equilibrium with CO_2 at 1 m depth in the model soil. Previous studies have shown that the isotopic composition of soil carbonate is essentially constant below about 20 cm (Cerling and others, 1989). This discussion illustrates some of the different factors that should be considered when applying this model to a particular soil or suite of soils.

Isotopic Composition of Soil-respired CO_2

Today, the isotopic composition of soil-respired CO_2, and hence soil carbonate, is dependent primarily on the proportion of C_3 versus C_4 biomass in the local ecosystem (Cerling, 1984; Cerling and others, 1989). C_3 plants have an isotopic composition of about −27 permil and C_4 plants have an isotopic composition of about −13 permil (Deines, 1980). However, modern plants are slightly shifted relative to pre-industrial conditions: the modern atmosphere has a $\delta^{13}C(CO_2)$ value of about −8 permil compared to the pre-industrial value of about −6.5 permil (Friedli and others, 1986). For pre-industrial conditions, then, the isotopic composition of C_3 and C_4 plants should have been about −26 and −12 permil, respectively. Figure 2 shows that the isotopic composition of soil carbonate is very strongly dependent on the isotopic composition of soil-respired CO_2 and therefore in the C_3/C_4 proportions on the local biomass. The proportion of C_3 and C_4 biomass in soils can result in a 14 permil difference in the isotopic composition of soil CO_2. The total biomass of CAM plants, which usually have an isotopic composition intermediate to C_3 and C_4 plants, is insignificant in most ecosystems.

However C_4 plants, while very important in modern grassland ecosystems, have a limited spatial and temporal distribution. C_4 plants

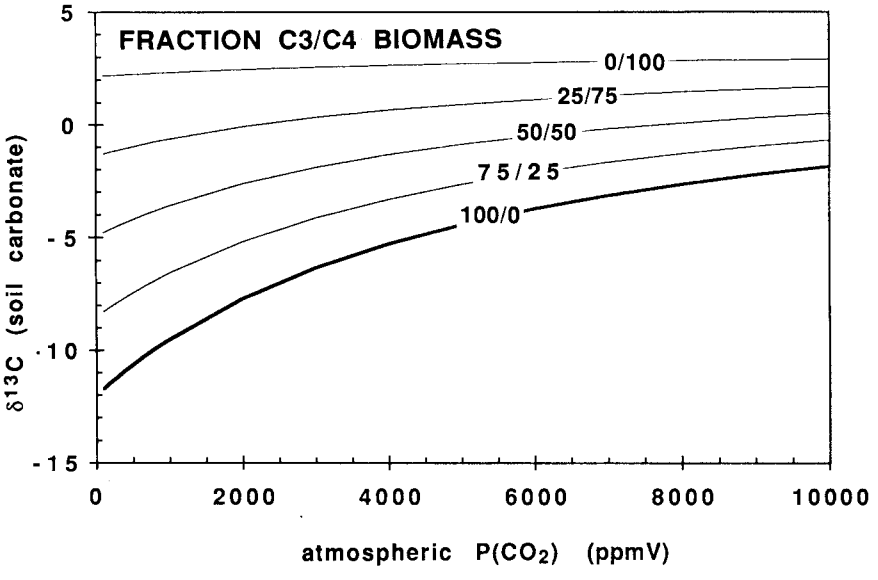

Fig. 2. The isotopic composition of soil carbonate at 1 m depth in the model soil except for varying the isotopic composition of soil-respired CO_2 and the $P(CO_2)$ of the atmosphere. Pure C_3 or pure C_4 biomass is considered to have a $\delta^{13}C$ value of −26 or −12 permil, respectively. Dark curve shows the model soil.

are especially well adapted to moisture stress and heat stress and are well represented in tropical through temperate grasslands and desert ecosystems. The oldest known fossil C_4 plants are late Miocene in age (Nambudiri and others, 1978; Thomasson, Nelson, and Zakrezewski, 1986), and indirect isotopic evidence for C_4 plants in Asia goes back only to about 8 my (Quade, Cerling, and Bowman, 1989a). Therefore, it is likely that pre-Miocene ecosystems had little, if any, C_4 component to them. In any case, the assumption that the local ecosystem was composed of 100 percent C_3 biomass will place an upper limit on atmospheric CO_2.

There is limited variation in the isotopic composition of individual C_3 and C_4 plants. There is only slight variation in C_4 plants, with significantly greater variation in individual C_3 plants. In modern desert ecosystems, C_3 plants are often several permil enriched in ^{13}C (Ehleringer, 1988). The present-day shift is related to moisture stress and high light intensity. However, such desert ecosystems do not have deeply leached zones; such soils are easily recognizable today and should be recognizable in the geologic record by examining the depth to soil carbonate (see discussion below on characteristics of paleosols). Some C_3 plants are also shifted to $\delta^{13}C$ values depleted by several permil in ^{13}C. This is most prevalent in closed canopy forests, where $P(CO_2)$ is significantly higher than the ambient atmosphere, and the isotopic composition of atmo-

spheric CO_2 is several permil depleted in ^{13}C because the degassed soil CO_2 is not easily dissipated under closed canopy conditions. Closed canopy forests are prevalent in rain forest conditions, which generally are completely leached of carbonate in the soil; hence, soil carbonate is not generally preserved in such soils.

Stable isotopic studies of terrestrial organic matter have values of about −26 permil for the Cenozoic and Mesozoic (Popp and others, 1989), except in the past 8 my when C_4 plants are also known to be present (Quade, Cerling, and Bowman, 1989a). Therefore, in this paper I will use the value of −26 permil for the isotopic composition of soil-respired CO_2 for the Mesozoic and early Cenozoic.

Depth in Soil Profile

The isotopic composition of soil carbonate is a function of depth because the isotopic composition of soil CO_2 changes with depth (fig. 1). However, for most soils the $\delta^{13}C$ value of soil carbonate is constant below about 20 cm. In desert soils, the complete isotopic gradient is sometimes preserved (Quade, Cerling, and Bowman, 1989b). However, in well drained soils where annual precipitation is greater than about 30 cm per yr the upper 20 cm of the soil is leached of soil carbonate (Jenny, 1980). For well-preserved paleosols it often is possible to determine if soil carbonate is in the upper 20 cm of the soil profile. In any case, the depth effect is related to atmospheric mixing and therefore, if not taken into account, will provide an overestimate of $P(CO_2)$ and therefore will still provide a maximum estimate of $P(CO_2)$.

Respiration Rate of Soil CO_2

The respiration rate of soil CO_2 can have an important effect on the isotopic composition of soil CO_2. Eqs (10) and (11) show that soil CO_2 is the sum of atmospheric CO_2 and CO_2 produced in the soil, the latter being directly proportional to soil respiration. Temperate and subtropical ecosystems, including both grassland and woodland, typically have respiration rates between about 4 and 10 mmol/m^2/hr (Dörr and Munnich, 1987; Gaudry and others, 1990) during the growing season. Higher respiration rates are found in cultivated soils (Dörr and others, 1983), while lower rates are found in desert and semi-desert ecosystems. For example, Quade, Cerling, and Bowman (1989b) measured respiration rates between 0.5 and 2 mmol/m^2/hr in the Mojave desert during the growing season. Figure 3 shows that soil respiration rate is important in determining the isotopic composition of modern soil carbonate only for soils with very low CO_2 respiration rates. At respiration rates typical for temperature and subtropical ecosystems, which today form soil carbonate some 10s of cm below the soil surface, a significant isotopic spread is seen for higher atmospheric CO_2 levels (fig. 3). Soil respiration rate is very important in determining the total CO_2 content of the soil and therefore plays a very important role in determining the isotopic composition of soil carbonate for $P(CO_2)$ levels higher than that of today.

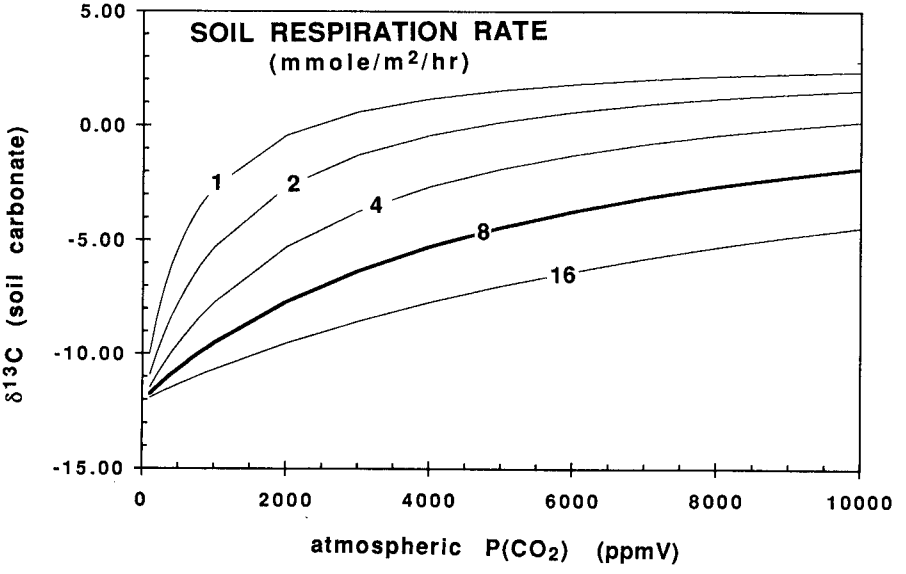

Fig. 3. The isotopic composition of soil carbonate at 1 m depth in the model soil except for varying the soil respiration rate and $P(CO_2)$ of the atmosphere. Dark curve shows the model soil.

Mean CO_2 Production Depth: $\bar{z}$

The isotopic composition of soil CO_2 is weakly related to the mean depth of CO_2 production in the soil. Solomon and Cerling (1987) showed that the concentration of CO_2 at depth in a soil is not sensitive to the function used to describe CO_2 production (for example, constant with depth, linear decrease, exponential decrease) and therefore, from eq (12), the carbon isotopic composition of soil CO_2 is not sensitive to the function used to describe CO_2 production. However, eq (11) shows that CO_2 concentration in soil is sensitive to the mean CO_2 production depth. CO_2 production in soils decreases with depth, generally in exponential fashion (Dörr and Münnich, 1990). Very few studies have determined the attenuation of CO_2 production with depth. However, assuming $\phi_s^*(z) = \phi_s^*(0)\, e^{-(z/\bar{z})}$ where $\bar{z}$ is the attenuation depth, Dörr and Münnich (1990) have found the attenuation depth to be generally about 10 cm for forested soils. Forested soils have their roots concentrated near the surface; grassland soils and desert soils are likely to have $\bar{z}$ for CO_2 production greater than for forested soils as their organic matter content attenuation depth is deeper than for forest soils. Figure 4 shows that the attenuation depth $\bar{z}$ for CO_2 production can affect the isotopic composition of soil carbonate because a greater attenuation depth results in higher $P(CO_2)$ in the soil for any given depth (eq 11).

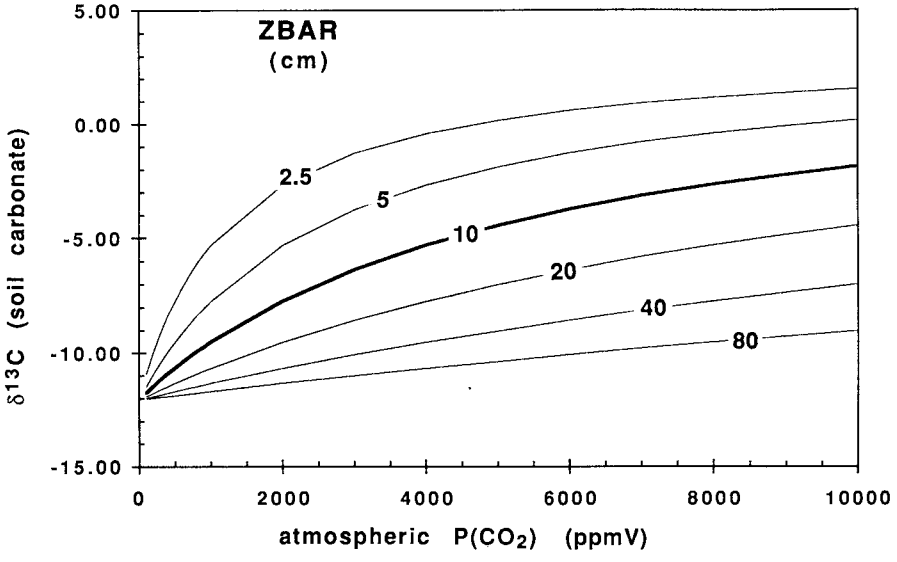

Fig. 4. The isotopic composition of soil carbonate at 1 m depth in the model soil except for varying the attenuation depth for CO_2 production and $P(CO_2)$ of the atmosphere. Dark curve shows the model soil.

For soils that formed before the advent of higher land plants, the attenuation depth must have been less than 1 cm. Carbonates formed in such soils would have had a significant atmospheric contribution for any $P(CO_2)$ level, as can be seen in figure 4. This may be an important factor in interpreting isotopic results of pre-Silurian carbonate bearing paleosols.

Porosity

Free air porosity is defined as the proportion of air-filled pore space in a soil, and it influences the rate of gas diffusion in soils. It varies in real soils from 0 to about 0.5. However, soil carbonates are generally found in well-drained soils and hence in soils where the porosity varies from about 0.3 to 0.4. Higher porosities are found in desert soils, while lower porosities are found in poorly drained soils. Poorly-drained soils, where water fills much of the pore space, generally show gleying (evidence for reduction and re-oxidation of soils). Gleyed conditions are generally easily recognizable in paleosols (Retallack, 1988).

The porosity affects the $P(CO_2)$ concentration in soils because it lowers the diffusion coefficient (eq 6). The tortuosity also lowers the diffusion coefficient in soils (eq 6); for the purposes of comparison the tortuosity will be considered to be constant in the following discussion and is taken to be 0.6. One more effect of porosity is that all the CO_2 is produced in the pore space, and the CO_2 produced must be normalized

to the pore space. The results of these factors are that porosity has a significant effect on $P(CO_2)$ in soils. Figure 5 shows the effect of porosity for the model soil system.

Temperature

The effect of temperature on the isotopic composition of soil carbonate in the model soil is primarily due to the fractionation factor $\alpha_{CO_2\text{-calcite}}$ (eq 4) which is taken from Deines, Langmuir, and Harmon (1974). A secondary effect is that temperature slightly affects the diffusion coefficient (eq 7). Temperature will have an indirect effect in that changing ambient temperature will change the soil productivity and hence soil CO_2 respiration rate. However, soil respiration is discussed separately. Figure 6 shows the temperature effect on the isotopic composition of soil carbonate for the model soil where others factors are kept constant.

Pressure

The absolute pressure is relatively unimportant in describing paleosols, although for a particular application to modern soil it could be an important consideration. For the model soil and for paleosols it is important for its minor effect on the diffusion coefficient. Pressure is important, however, in modeling the behavior of CO_2 at high altitudes (for example, see Solomon and Cerling, 1987) because of the correction for total pressure in the ideal gas law.

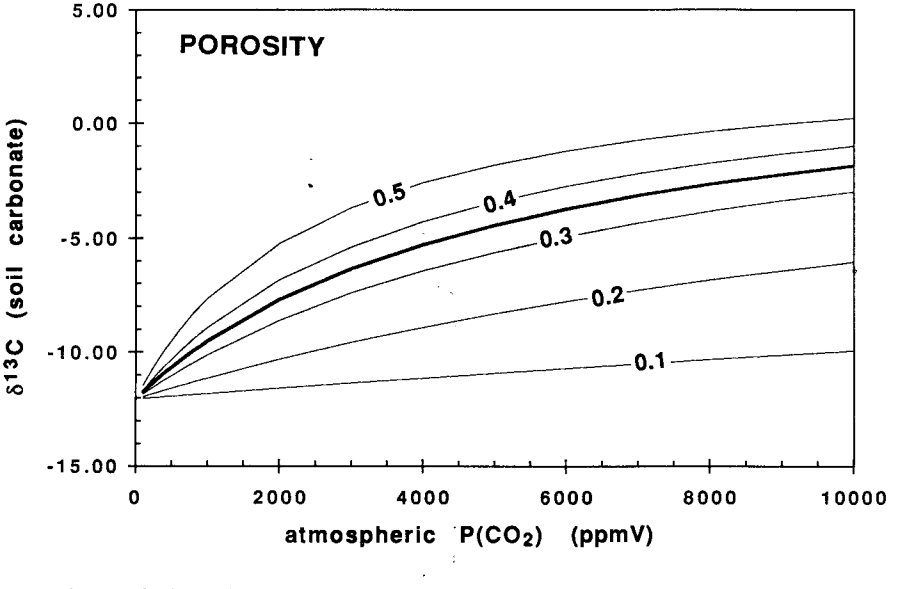

Fig. 5. The isotopic composition of soil carbonate at 1 m depth in the model soil except for varying porosity and $P(CO_2)$ of the atmosphere. Dark curve shows the model soil.

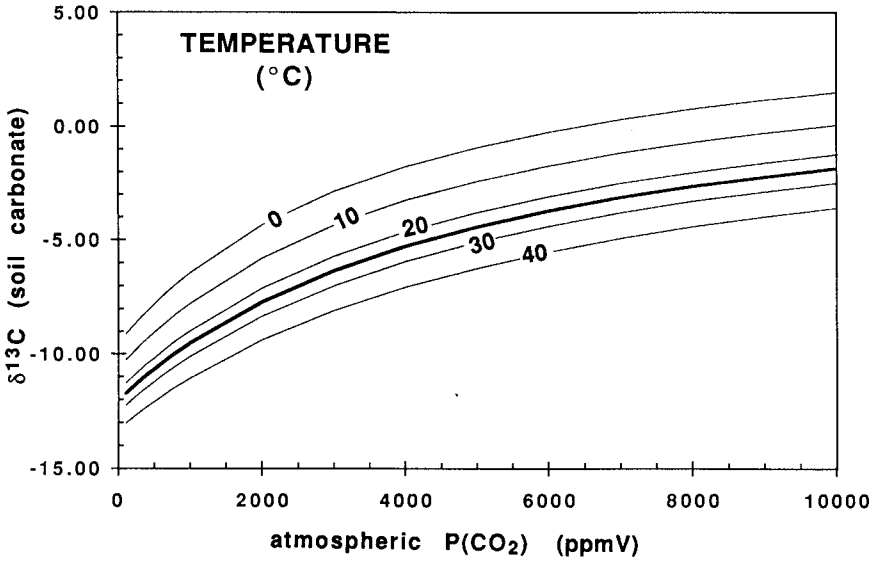

Fig. 6. The isotopic composition of soil carbonate at 1 m depth in the model soil except for varying temperature and $P(CO_2)$ of the atmosphere. Dark curve shows the model soil.

Isotopic Composition of Atmospheric CO_2

For the purposes of the present discussion I will consider the isotopic composition of the atmosphere to be constant at −6.5 permil. There is presently a 19.5 permil difference between the isotopic composition of atmospheric CO_2 and average C_3 terrestrial organic matter. Fossil organic matter from most Mesozoic terrestrial plants has a $\delta^{13}C$ value of about −26 permil. If any changes in fractionation occurred in the past due to changing $P(CO_2)$, $P(O_2)$, or some other factor, it would be highly fortuitous that the net result would combine to result in a $\delta^{13}C$ value for terrestrial organic matter to be −26 permil (Popp and others, 1989). Therefore, changing the isotopic composition of atmospheric CO_2 would result in a systematic offset of the isotopic composition of soil carbonate from the model soil described above.

However, if the isotopic composition of the atmosphere is independently known it should be possible to correct for the systematic shift in $\delta^{13}C$ of the entire system. It is known that the $\delta^{13}C$ of marine $CaCO_3$ varies by about 2 permil during the last 200 Ma (Lindh, ms). This may be a measure of the change in the isotopic composition of the atmosphere, although some caution should be used before assuming that a shift in the isotopic composition of bulk marine sediments necessarily means an identical shift in the isotopic composition of the atmosphere. The modern surface ocean is not in local isotopic composition with the atmosphere (Broecker and Peng, 1982), benthic foraminifera are systematically de-

pleted in ^{13}C relative to planktonic foraminifera, many organisms do not precipitate calcite in isotopic equilibrium with the atmosphere ("vital effects"), and the fractionation factor between dissolved inorganic carbonate and CO_2 is temperature dependent (Mook, Bommerson, and Staverman, 1974). Because of these problems, using the record of the isotopic composition of marine carbonates as a direct measure of the change in the isotopic composition of atmospheric CO_2 must be exercised with some caution.

Other Factors

I have alluded to the possibility of the fractionation factor changing as a function of $P(CO_2)$ of the atmosphere. This seems to be fairly unlikely on the geologic scale since the isotopic composition of C_3 plants seems to be constant during the Mesozoic and Cenozoic (Popp and others, 1989). If the fractionation factor changed as a function of $P(CO_2)$ then the isotopic composition of the atmosphere would have to change just enough to accommodate the change in the fractionation factor, which seems highly unlikely. However, this hypothesis will have to be examined further in the future.

MODEL SOIL FOR COMPARISON OF ATMOSPHERIC $P(CO_2)$

I have shown that there are many factors that individually affect the isotopic composition of soil carbonate. These can be broken down into four categories: those that affect the mixing ratio between atmospheric and soil derived CO_2, those that affect the isotopic fractionation factor; those that transpose the entire isotopic scale; and diagenetic effects. Of particular importance to the interpretation of the isotopic record of atmospheric CO_2 as recorded in paleosols is the isotope mixing ratio, especially the soil derived CO_2. It is apparent that the term $\mathbf{S}(z)$ in eqs (10) to (12) must have units of ppmV and that all the variables that result in soil derived CO_2 must be in that term. Therefore, porosity, soil respiration rate, and the CO_2 production depth dependence can be treated together. In the following discussion I will consider the concentration of soil CO_2 at depth (about 1 m where the concentration gradient is flat and where soil carbonate is commonly encountered) in the soil.

Observations on modern soils show that desert soils have low $P(CO_2)$ values, usually below about 3000 ppmV; well drained temperate and tropical soils have $P(CO_2)$ values between about 5000 and 10,000 ppmV; gleyed soils have higher $P(CO_2)$ levels, above 25,000 ppmV. Desert soils should be recognizable in the geologic record because of their thin leached horizon. High soil $P(CO_2)$ levels are accompanied by low oxygen levels and are generally recognizable by gley features (Retallack, 1988).

Thus, in the absence of C_4 biomass, our model soil can be expressed in terms of the CO_2 contributed by the soil which essentially combines the factors of porosity and soil productivity to give a few distinct fields. In figure 7, I show the isotopic composition of soil carbonate for different

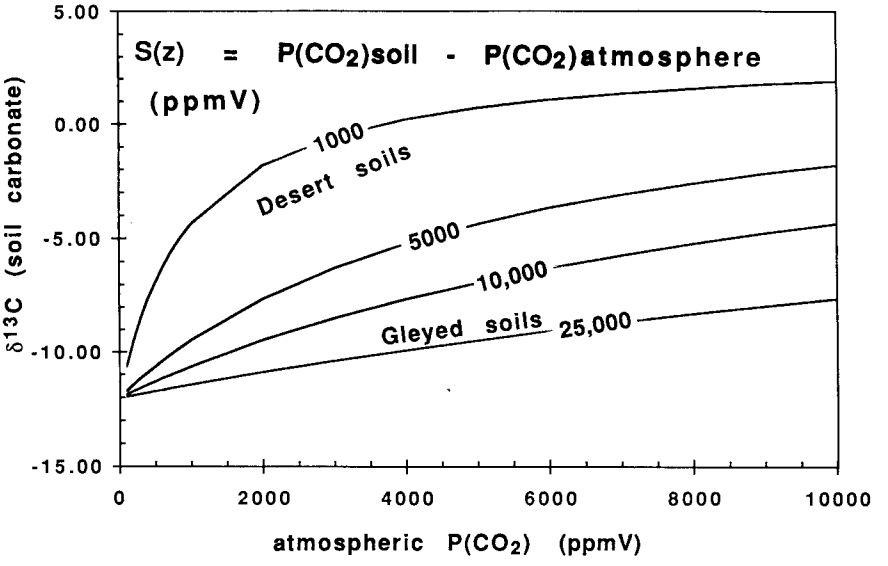

Fig. 7. Isotopic composition of soil carbonate expressed as a function of atmospheric $P(CO_2)$ and soil derived CO_2 (**S**(z)), where $\mathbf{S}(z) = [P(CO_2)_{soil} - P(CO_2)_{air}]$. Well-drained non-desert soils are generally in the range between 5000 and 10,000 for soil derived CO_2 (**S**(z)) at 1 m depth.

levels of total soil derived CO_2 representing desert soils, temperate to tropical soils with soil carbonate, and gleyed soils. In figure 7 the term

$$P(CO_2)_{soil} - P(CO_2)_{air} = \mathbf{S}(z) \qquad (15)$$

has values of 1000, 5000, 10,000, and 25,000 ppmV, where the 5000 to 10,000 ppmV window is considered to be that for temperate to tropical soils containing soil carbonate.

These values, of course, only represent some average conditions. However, by examination of many paleosols from different localities, it will be possible to constrain $P(CO_2)$ of the atmosphere using the carbon isotopic composition of paleosol carbonate. Most of the parameters discussed tend to cause an overestimate of atmospheric $P(CO_2)$ and therefore provide an estimate of the maximum value for $P(CO_2)$ of the atmosphere. Changing the isotopic composition of atmospheric CO_2 (for example, closed canopy conditions or by depleting the ^{13}C concentration in global atmospheric CO_2), increasing the temperature of carbonate precipitation significantly above 25°C, or by having low soil porosity would tend to give an underestimate of $P(CO_2)$. Fortunately, the latter conditions are probably recognizable: dense forest conditions could be recognizable by the absence of soil carbonate, and therefore this condition will be avoided altogether; low porosity could be recognized by finding evidence of gleying; changes in the $\delta^{13}C$ value for atmospheric

CO_2 could be recognized by finding a shift in the isotopic composition of terrestrial organic matter. The carbon isotopic composition of marine carbonate may also be a proxy record of the isotopic composition of the atmosphere, although, as pointed out above, it must be used with some caution.

Ideally, a paleosol with preserved organic matter and pedogenic carbonate would circumvent this problem. Cerling and others (1989) showed that for the modern conditions where $P(CO_2)$ is very small compared to that produced by the soil ($\mathbf{S}(z) \gg C_a^*$) the $\Delta_{CaCO_3\text{-Organic matter}}$ is about 14 permil at 25°C. Unfortunately, preservation of both organic matter and pedogenic carbonate in the same paleosol is rare in Mesozoic and early Tertiary paleosols.

In the following discussion I will consider that soil temperature is 25°C. During Cenozoic or early Tertiary times it is unlikely that soil temperatures were significantly cooler than 15°C. Higher soil temperatures would tend to decrease the isotopic fractionation factor, making the $\delta^{13}C$ values more negative and leading to a lower estimate than the model gives. In any case, temperature could never have been less than 0°C, so that the fairly positive numbers observed in the Mesozoic (discussion below) cannot be due solely to temperature effects.

Figure 7 is used to derive estimates of $P(CO_2)$ in the atmosphere by plotting the isotopic composition of soil carbonate on the diagram. Low temperatures, low respiration rates, and high porosity will tend to make the isotopic composition of soil carbonate higher than the model. Soil carbonates formed under such conditions will tend to give an overestimate of $P(CO_2)$ of the atmosphere. Low porosity, high temperature, and high productivity will give paleosol carbonates that would tend to give an underestimate of the atmospheric $P(CO_2)$ value. Furthermore, diagenetic processes tending to homogenize paleosol carbonate with detrital carbonate will tend to increase the $\delta^{13}C$ value of the carbonate, resulting in an overestimate of atmospheric $P(CO_2)$. Therefore, a conservative estimate of the range of atmospheric CO_2 in paleosols is taken from the average value for a series of soils, skewed toward the more negative values. The soils analyzed in any suite of soils represent soil carbonates precipitated in a range of soil conditions, represented by a range of soil derived CO_2 values ($\mathbf{S}(z)$). The average $\delta^{13}C$ value is taken to give the upper intercept with the 5000 ppmV value for soil derived CO_2, and minus one standard deviation is taken as the intercept with the 10,000 ppmV value. While admittedly arbitrary, this method gives a fairly conservative estimate of the range of atmospheric CO_2 conditions. This $\delta^{13}C$ interval is used below to estimate paleo-$P(CO_2)$ levels for Mesozoic and Tertiary soils thought to have no C_4 biomass present in the local ecosystem.

CHARACTERISTICS OF CARBONATE BEARING PALEOSOLS

There are numerous descriptions of paleosols and features characteristic of paleosols (Weide, 1985; Reinhardt and Sigleo, 1988). Not all

paleosols can be used as $P(CO_2)$ indicators: only those that precipitate $CaCO_3$ are germane to the present argument. Highly leached soils from regions of high rainfall do not have pedogenic carbonate. Even for carbonate-bearing paleosols several important conditions must be met: carbonates must be deposited below about 20 cm in a soil, and the soil must have a relatively high free-air porosity. It is only in desert soils or those formed in groundwater discharge zones that carbonate is precipitated very near the soil-atmosphere interface. The latter have low free-air porosities and therefore may have very high $P(CO_2)$; they often show evidence of gleyed conditions. Therefore, soils that precipitate carbonate to the soil-air interface are to be avoided.

Diagenesis of carbonates is an important potential problem in these carbonates. Nodules from the Eocene Willwood Formation occasionally are partially recrystallized to sparite whose isotopic composition differs from the original micrite: the $\delta^{13}C$ values are generally about the same, but the $\delta^{18}O$ values are generally depleted in the sparite by up to 10 permil (fig. 8), indicating recrystallization under higher temperature conditions. The paleosol carbonates from the Willwood Formation show that the effects of recrystallization during diagenesis do not significantly

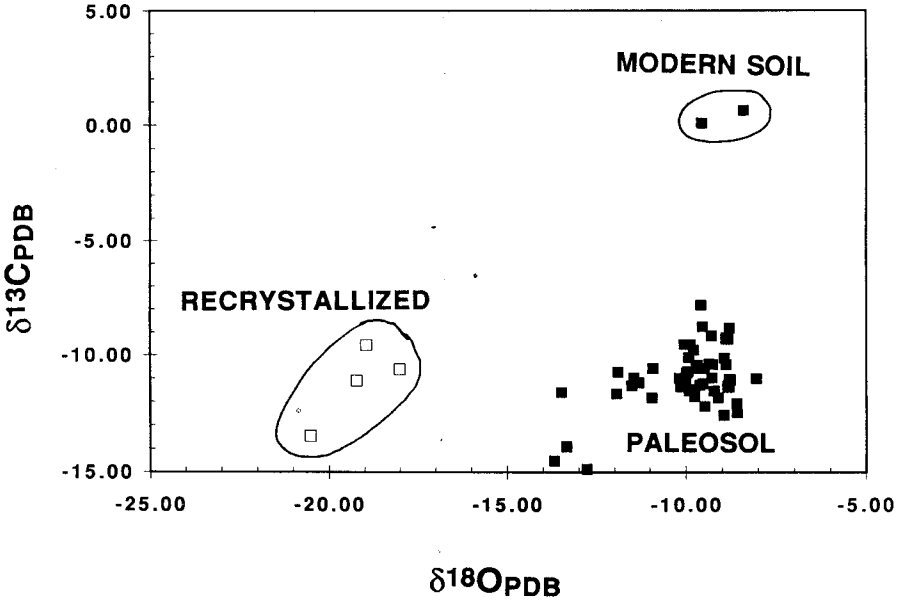

Fig. 8. Isotopic composition of paleosol carbonate from the lower Eocene Willwood Formation in the Bighorn Basin, Wyoming. Modern (Holocene and Pleistocene) soil carbonate from the central Bighorn Basin shown for comparison. Co-existing sparite and micrite from single nodules shows that recrystallization has little effect on the $\delta^{13}C$ value in this formation. Contamination by modern soil carbonate would significantly increase the $\delta^{13}C$ value of paleosol carbonate.

shift the ^{13}C content of nodules, although these nodules become depleted by up to 10 permil in ^{18}O during diagenetic recrystallization.

EVIDENCE FROM CENOZOIC AND MESOZOIC PALEOSOLS

Late Cenozoic: late Miocene through Holocene.—Well-preserved paleosols are abundant in terrestrial sediments from Miocene through Holocene age. Unfortunately, the picture is complicated by the presence of C_4 plants in at least some of the paleosols (Quade, Cerling, and Bowman, 1989a). However, there are a number of soils where both organic matter and pedogenic carbonate are preserved so that the isotopic composition of soil carbonate can be used to estimate $P(CO_2)$ of the atmosphere in spite of evidence for C_4 plants in the biomass in some of the paleosols. Modern soils and paleosols from numerous localities ranging in age from 14 my to the present have $\Delta(CaCO_3$-Organic matter) values between 14 and 16 permil (Cerling and others, 1989; Quade, Cerling and Bowman, 1989a) indicating low levels of atmospheric CO_2.

Early to late Miocene.—The first evidence of C_4 biomass being a significant part of local ecosystems in the Old World is about 7 to 8 my. Carbonates from preserved paleosols in Africa, Asia, and Europe older than 8 my have $\delta^{13}C$ values from about -10 to -12 permil. Figure 7 and table 2 show that these are compatible with a maximum $P(CO_2)$ level of about 700 ppmV.

Thus, $P(CO_2)$ levels during the Miocene have been less than 700 ppmV and are indistinguishable from the present level using this model. Such low levels are in agreement with the modeling results of Berner

TABLE 2

Paleosol carbonate $\delta^{13}C$ values for mid-Miocene, Eocene, lower Cretaceous, and upper Triassic paleosols. These are for periods when C_4 biomass did not contribute significantly to the local ecosystem. $P(CO_2)$ ranges are estimated as in figure 9

Age	$\delta^{13}C$	$P(CO_2)$* (ppmV)
Miocene		
(8-16 my), Pakistan, this study	-10.21 ± 0.91 (n = 48)	<700
(14 my), East Africa, this study	-11.76 ± 1.32 (n = 10)	<400
Eocene		
Willwood Fm., Wyoming, this study	-10.61 ± 1.45 (n = 60)	<600
Lower Cretaceous		
I. Trinity Group, Texas, this study	-7.06 ± 1.05 (n = 5)	2500–3300
II. Cameros Basin, Spain, Platt, 1989	-8.41 ± 0.44 (n = 9)	1600–2600
Upper Triassic/Lower Jurassic		
New Haven Arkose, this study	-7.64 ± 1.04 (n = 7)	2000–3000
New Haven Arkose, Suchecky, Hubert, and Birney de Wit, 1988	-6.86 ± 0.45 (n = 3)	2500–4200
Fundy Rift, Suchecky, Hubert, and Birney de Wit, 1988	-6.37 ± 0.38 (n = 3)	3000–6000

(1990) which suggests that $P(CO_2)$ levels in the late Tertiary were between 1.0 and 1.5 times the present level.

Early Cenozoic.—Paleosols from the lower Eocene Willwood Formation in Wyoming have numerous paleosols (Bown and Kraus, 1981; Kraus and Bown, 1988). The lower part of the Willwood Formation has deeply leached paleosols that are gleyed at depth with abundant iron and manganese nodules. The middle part of the Willwood Formation has numerous leached paleosols with carbonate nodules about 0.5 to 1.5 m below the paleosol upper surface (about 1 to 3 m in the original uncompacted soil). The carbonate nodules are usually 0.5 to 2 cm in diameter and are micrite to sparite. The larger recrystallized carbonate has exchanged oxygen but not carbon isotopes (fig. 8). The limiting $\delta^{13}C$ value for paleosol carbonates from soils in the middle part of the formation is about -10 to -12 permil (fig. 8), indicating that $P(CO_2)$ must have been less than about 700 ppmV (fig. 9 and table 2).

These results suggest that early Tertiary $P(CO_2)$ levels were similar to the present conditions. However, I do not yet have results from Oligocene paleosols. Berner's (1990) modeling results suggest $P(CO_2)$ levels 1.3 and 2.0 times modern CO_2 for the early Eocene, which is in good agreement with this study.

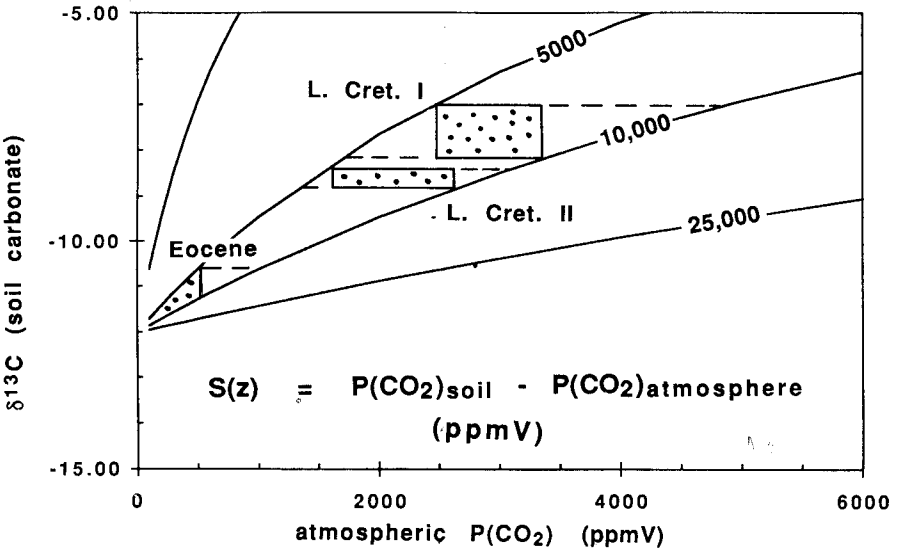

Fig. 9. Estimated range for $P(CO_2)$ from the Eocene and lower Cretaceous (Trinity Group) paleosols based on the $\delta^{13}C$ of soil carbonate using the model described in the text. The enclosed areas for each are bracketed by the average $\delta^{13}C$ value to -1σ, and between 5000 and 10,000 ppmV for **S**(z), with the 1000 and 25,000 values for **S**(z) shown for reference. The more negative $\delta^{13}C$ values for soil carbonate are most likely associated with soils of higher productivity, here taken to be about 10,000 ppm for **S**(z), while the mean value is probably representative of lower **S**(z) values. Therefore, the range of $P(CO_2)$ is taken to be the central box of values shown as the dark stippled area.

Late Mesozoic.—Paleosol carbonates from early Cretaceous paleosols (Barremian to mid-Albian) in the Trinity Group at Proctor Lake, Texas (Winkler, Murrey, and Jacobs, 1989) have $\delta^{13}C$ values from about −6.2 to −8.2 permil (table 2). Most of the parameters discussed above tend to make the isotopic composition of soil carbonate enriched in ^{13}C. Therefore, I will consider the limiting $\delta^{13}C$ value for soil carbonates to be between the average value and –one sigma or between −7.1 and −8.1 permil which from figure 9 indicates that $P(CO_2)$ was between about 2500 and 3300 ppmV. Barremian to mid-Albian marine carbonates are about 1.5 permil enriched in ^{13}C relative to modern marine carbonates (Lindh, ms). If the marine record is an accurate proxy record of the isotopic composition of the atmosphere (see cautionary remarks above), then the isotopic curves of figure 7 should be shifted upward by about 1.5 permil. If this were the case, then the isotopic record of these paleosol carbonates would indicate $P(CO_2)$ values of about 1400 to 2100 ppm, a value still considerably higher than present.

Platt (1989) has made measurements on pedogenic carbonates formed in assocation with lacustrine deposits of Lower Cretaceous age (Berriasian). Because of their intimate association with fine grained lacustrine sediments, these pedogenic carbonates may have a lower free air porosity than described in the model above. Nevertheless, these carbonates have $\delta^{13}C$ values that average −8.4 permil and indicate that $P(CO_2)$ was probably between 1600 and 2600 ppmV. The carbon isotopic composition of marine carbonates from the Berriasian have essentially the same value as modern marine carbonate (Lindh, ms), and so no correction is made for a different $\delta^{13}C$ value for the Berriasian atmosphere. More firm evidence could be obtained from soil carbonates from parts of the basin farther from lacustrine influence.

However, thus far the range in $\delta^{13}C$ values for soil carbonates of lower Cretaceous age indicates that $P(CO_2)$ during the lower Cretaceous was considerably higher than present, probably on the order of between about 1500 and 3000 ppmV. This is based so far on the study of paleosols from only two localities. These preliminary results are in agreement with those of Berner (1990) who estimates that $P(CO_2)$ during the lower Cretaceous was 2 to 9 times higher than the present level.

Early Mesozoic.—Lower Jurassic paleosols from the New Haven arkose and the Upper Triassic Fundy Basin sediments (Hubert, 1978; Hubert and others, 1978) were examined. $\delta^{13}C$ values for paleosol carbonates from these sediments (Suchecky, Hubert, and Birney de Wit, 1988; this study) average between −6.5 and −7.5 permil (table 2), indicating that $P(CO_2)$ of the atmosphere was between about 2000 and 4000 ppmV. Lower Triassic and Upper Jurassic marine carbonates have $\delta^{13}C$ values similar to the modern ocean, (Lindh, ms) so that no correction is made for a changing $\delta^{13}C$ value for the atmosphere. Berner (1990) estimates that $P(CO_2)$ was 3 to 7 times higher during upper Triassic and lower Jurassic time than at present.

Cenozoic and Mesozoic atmosphereic CO_2 levels.—I have reported above preliminary results on stable isotopic evidence for paleo-$P(CO_2)$ levels of Cenozoic and Mesozoic atmospheres. All Miocene and Eocene paleosols indicate $P(CO_2)$ levels that are indistinguishable from modern, whereas all Mesozoic paleosols indicate significantly higher $P(CO_2)$ levels. There is virtually no overlap in the ranges of the two data sets of 118 and 27 analyses, respectively. Because diagenesis of paleosol carbonates results in little carbon isotopic exchange (discussion above) the observed differences between the isotopic composition of Mesozoic and Cenozoic paleosol carbonates probably are primary features and likely indicate significant differences in the $P(CO_2)$ of the paleoatmosphere. These preliminary results agree very well with the modeling results of Berner (1990).

CONCLUSIONS

The stable carbon isotope composition of soil carbonate is an indicator of local conditions. Many variables determine the $\delta^{13}C$ value for soil carbonate, including soil porosity, depth of CO_2 production, soil productivity, depth in the soil profile, fraction of C_4 biomass, and the concentration and isotopic composition of atmospheric CO_2. However, depth in the soil profile, the fraction of C_4 biomass, and $P(CO_2)$ of the atmosphere are the most important variables for most soils. Depth in the soil profile is significant only in the upper 20 cm in most soils; below about 20 cm the carbon isotopic composition of soil carbonate is essentially constant. Under favorable circumstances, the carbon isotopic composition of soil carbonate can be used to determine the proportion of C_4 biomass present in the local ecosystem or the concentration of CO_2 in the atmosphere. There is little evidence for C_4 plants older than late Miocene. In the absence of C_4 plants, the isotopic composition of soil carbonate is a potential indicator of atmospheric $P(CO_2)$ levels. At high atmospheric $P(CO_2)$ levels, the atmospheric contribution to total soil CO_2 is high enough that it can significantly affect the isotopic composition of soil CO_2 and, hence, soil carbonate precipitated in isotopic equilibrium with soil CO_2.

Measurements reported here suggest than $P(CO_2)$ was less than about 700 ppmV for the Eocene and Miocene through the present. Initial results of Mesozoic paleosols indicate that $P(CO_2)$ of the atmosphere during Lower Cretaceous and Upper Triassic times was considerably higher than today, probably between 1500 and 3000 ppmV. These preliminary results are in good agreement with the modeling results of Berner (1990).

The carbon isotopic composition of paleosol carbonate is a potential indicator of ancient atmospheric $P(CO_2)$ levels. However, numerous measurements will be required at many stratigraphic levels and localities before a firm estimate can be made of the limiting $P(CO_2)$ for any time period. As has been shown in the above discussion, there are many factors that can influence the isotopic composition of soil (and paleosol) carbonate, although the most significant are the proportion of C_4 biomass

present and the CO_2 composition of the atmosphere. For any particular soil, extreme values for one of the less significant parameters may result in an anomalous value for $\delta^{13}C$. Therefore, many soils must be studied before the $P(CO_2)$ "limiting" value for $\delta^{13}C$ soil carbonate can be known with confidence for any stratigraphic interval. Diagenesis, of course, must always be accessed for a particular study area.

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