Soil CO$_2$ efflux simulations using Monte Carlo method and implications for recording paleo-atmospheric PCO$_2$ in pedogenic gibbsite

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ABSTRACT

Monte Carlo simulation testing of the sensitivity of the Fickian diffusion model used for paleo-PCO$_2$ proxies indicates that assuming annual average soil respiration rate results in over-estimation of PCO$_2$. In all cases, the natural variability of the factors of the model, including soil porosity and inverse tortuosity and the δ^{13}C value of the soil produced CO$_2$ were not able to account for discrepancies between measured δ^{13}C values from a modern soil and modeled results using established assumptions. Assuming that there is negligible carbon isotope fractionation during the occlusion of CO$_2$ in pedogenic gibbsite, the flaw in the model appears to be the assumed value of soil respiration rate. If correct, the implication is that previous paleo-PCO$_2$ estimates from soil hydroxides may be too high by as much as a factor of ten.

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1. Introduction

Increased concern about the link between changing atmospheric greenhouse gas concentrations and climate makes precise knowledge of atmospheric CO$_2$ concentrations throughout Earth's history useful for anticipating future extents and rates of change. The relationship between atmospheric CO$_2$ concentration and climate has been documented for times younger than 740 kya in the Dome C ice core record (Augustin et al., 2004), whose gas bubble CO$_2$ signal and ice O and H isotope pattern serve as credible recorders of coupled climate and atmospheric CO$_2$ change. The stable carbon isotope compositions of pedogenic oxyhydroxides and carbonates is two proxies that have been commonly used as records of atmospheric CO$_2$ on millennia to million year time scales (e.g. Cerling, 1991; Yapp and Poths, 1996; Ekart et al., 1999; Tabor et al., 2004; Royer et al., 2007). Use of these proxies gives insight into the potential range of climate response to changing atmospheric CO$_2$ concentration, because they occurred during periods of earth's history that were either much warmer or much cooler than today (Royer et al., 2007). One of the key assumptions used to assess the changing concentration of CO$_2$ in the atmosphere is the concentration of CO$_2$ in the soil, which is related to the rate of CO$_2$ efflux from the soil reservoir to the atmosphere. CO$_2$ efflux is the net transport of gas out of the earth's surface due to changes in atmospheric pressures and gradients caused by thermal and biological oxidation of carbon. The latter is collectively referred to

as soil respiration which is mediated by the rate of microbial and plant root metabolism.

One potential proxy that has yet to be implemented is the carbon dioxide occluded on or incorporated in pedogenic gibbsite during mineral formation. Using a method similar to that of Yapp and Poths (1992), carbon dioxide was extracted from pedogenic gibbsite by Schroeder and Melear (1999). Because this carbon is thought to be occluded on the surface of the gibbsite in site defects rather than part of a solid solution as is suspected for goethite, it is not possible to use the same model for calculating the pCO$_2$ of the ancient atmosphere that is used for the goethite method (Yapp and Poths, 1990,1996; Schroeder and Melear, 1999). Therefore, a model based on that developed by Cerling et al. (1989), with some important differences, was tested to verify the utility of this mineral as a proxy for paleo-pCO$_2$. Two significant differences stand out: (1) this model does not use the term S(z) to include parameters such as the porosity, inverse tortuosity, and soil respiration rate into an estimation of soil CO$_2$ concentration; and (2) because the soil column in use is an active soil the top 50 cm that is typically not available in paleosols is used. This second difference takes advantage of the shape of the top part of the diffusion curve to more stringently confine the solution. In the study by Schroeder et al. (2006) the measured δ^{13}C values of carbonate evolved during the dehydration–decarbonation of gibbsite were compared to modeled solutions to assess the utility of carbon occluded on gibbsite as a proxy for paleo-pCO$_2$. Finite difference methods were used to allow for the variation of soil properties that are included in the S(z) term with depth. The workers concluded that the soil respiration rate that corresponded to the best fit solution of the stable carbon isotope ratio versus depth in the soil curve was an order of magnitude lower than the measured rate using a static

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chamber method. Possible implications proposed for this difference include the possibility that the stable isotope values of the occluded carbon are representative of a long term average and some period of cool monsoonal climate skewed the results to favor a low soil respiration rate. Or, it is possible that the implicit assumptions of the model are not correct, resulting in a solution that has no utility. This paper will attempt to determine if the assumptions used in the model are correct in order to eliminate this as a source of uncertainty.

Assuming the theory underlying paleosol oxyhdroxide and carbonate proxies for paleo-PCO₂ is sound, the discrepancy between the modeled soil respiration rate and measured respiration rate lies within the model. Assumptions can be classified as either process assumptions or factor assumptions. Process assumptions involve our understanding of the process by which the isotope composition of the soil CO₂ signal is generated and how that signal is preserved in the mineral record. Factor assumptions involve the accuracy of the equation forms used in the model and the accompanying coefficient values. The purpose of this study is to use Monte Carlo analysis to determine the sensitivity of the model to each factor and to minimize the uncertainty of the outcome. More accurately describing the soil processes and constraining the values will lead to improved assignments of model factors. Additionally, assessing the sensitivity of the model to these factors will reveal whether factor uncertainty or the underlying model process assumptions are incorrect.

Previous work relies on the analytical solution of the one-dimensional Fickian diffusion model of the form:

$$\frac{\partial C}{\partial t} = 0 = D_s^* \frac{\partial^2 C}{\partial z^2} + \varphi^* \tag{1}$$

(Cerling, 1984), where C is the concentration of CO₂ in the soil, D_s^* is the diffusion coefficient of bulk CO₂ through the soil, and φ^* is the bulk production rate of CO₂ in the soil. The difference in $^{12}CO_2$ and $^{13}CO_2$ diffusion rates results in a distinct profile of $\delta^{13}C$ values with depth in the soil. $\delta^{13}C$ is the standard notation established using the Cretaceous Pee Dee Belemnite (PDB) from the Pee Dee Formation in South Carolina. The model used to relate the stable carbon isotope value of pedogenic carbonate includes the diffusion coefficient and the bulk production rate of soil into a concentration term S(z) (Eq. (3))

$$C_s^*(z) = S(z) + C_a^* \tag{2}$$

$$S(z) = \frac{\varphi_s^*(0)\bar{z}^2}{D_s^*}\left(1 - e^{-(z/\bar{z})}\right) \tag{3}$$

(Cerling, 1991), where the variables are as stated and $\bar{z}$ is the characteristic depth of soil CO₂ production. Typically, values used are representative of the mean growing season. These estimates are not well constrained and one of the goals of this research is to attempt to constrain these variables.

The bulk rate of soil efflux and the stable carbon isotope composition of the soil CO₂ is determined by the physical characteristics; air-filled porosity and inverse tortuosity, and the biological characteristics; plant photosynthetic pathway (i.e. Calvin–Benson cycle CO₂ fixing into 3-carbon sugar versus 4-carbon sugar; or C3 versus C4, respectively), the rate of plant and microbial respiration in the soil, as well as the characteristics of the atmosphere, PCO₂ and $\delta^{13}C$ value of the atmosphere.

The analytical model assumes that the rate of CO₂ production and flow through the soil is several orders of magnitude faster than the rate of mineral growth. Under this scenario, carbon occluded onto the gibbsite mineral surfaces is likely to be in equilibrium with the soil carbon isotope composition (Cerling, 1984; Schlesinger, 1977). In attempting to develop this model, the soil respiration rate was assumed to be the annual average rate measured at the field site. Soil

respiration rates however, are known to vary widely depending on the immediate temperature and water content of the soil (Camporese et al., 2008; Irvine et al., 2008). The precipitation of clay sized minerals goethite (FeOOH) and gibbsite (Al(OH)₃) is largely controlled by the saturation of iron and aluminum in the soil solution. It then stands to reason that there is a bias towards the isotope signal that dominates during periods of fast mineral growth rates, which may not necessarily correspond to average annual soil respiration rates.

2. Methods

Each parameter in the numerical diffusion model was described as either a physical property of the soil, porosity and inverse tortuosity, or a property of soil respiration, the stable carbon isotope composition of soil respired CO₂. The natural variability as determined from literature values of each factor was assigned a normal probability distribution function which was used during the Monte Carlo simulation to randomly choose realistic inputs for the model and establish the range of variability of calculated $\delta^{13}C$ values of soil CO₂. This range of model results was compared to the measured $\delta^{13}C$ values from the Panola Mountain site by Schroeder and Melear (1999) to assess whether the natural variability of any or all of these parameters accounted for the disparity between the model and measured values. All calculations were made using algorithms written in the C++ programming language; the source code is available for download as a text file or Borland 2006 Studio Project file at http://www.austinj1.myweb.uga.edu/.

Values for porosity of soils typically found in Georgia, USA, were calculated from bulk density data using the equation:

$$\varepsilon = 1 - \frac{\rho_{bulk}}{\rho_{parent}} \tag{4}$$

(Perkins, 1987) where ε is the air-filled porosity, ρ_{bulk} is the bulk density of the soil, and ρ_{parent} is the bulk density of the parent material
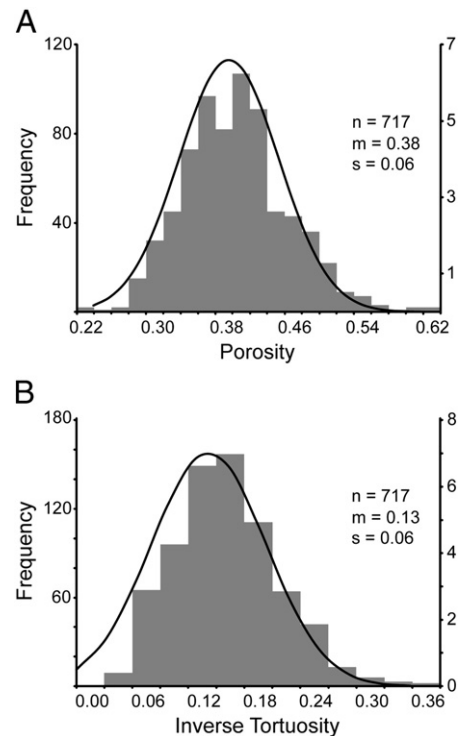

Fig. 1. Histograms and normal probability distribution functions for porosity (A) and inverse tortuosity (B) based on values calculated from bulk density data (Eqs. (2) and (3)) (Perkins, 1987).
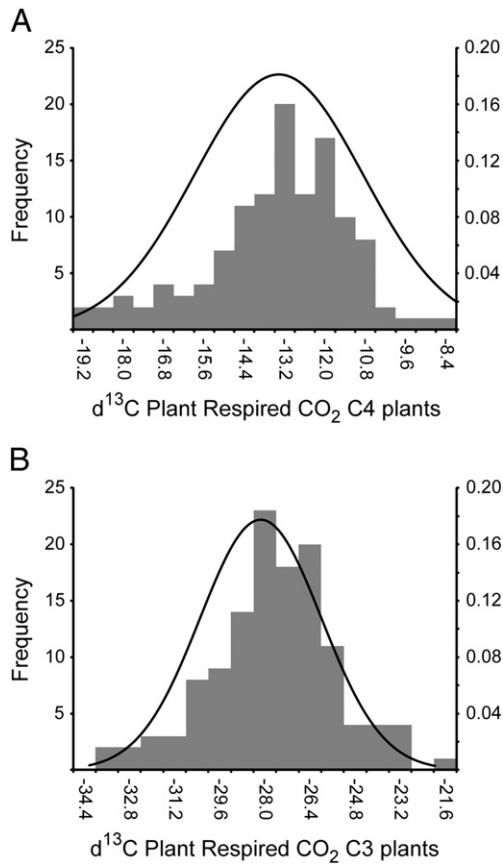
Fig. 2. Histograms and normal probability distribution functions for stable carbon isotope composition of CO_2 produced in soil by C4 (A) and C3 (B) plants (Bender, 1968, 1971; Smith and Epstein, 1971; Hattersley, 1982).

with an assumed value of 2.65 g cm^{-3} (Fig. 1A). Inverse tortuosity (τ^{-1}) values were calculated from the porosity values using the relationship:

$$\tau^{-1} = \frac{(\varepsilon - \theta_w)^{7/3}}{\varepsilon^2} \tag{5}$$

(Millington and Quirk, 1961) where θ_w is the volumetric water content of the soil with an assumed value of 0.2 (Millington and Quirk, 1961; Davidson et al., 2000). The data for typical soils from Georgia was used because of their similarity to the study site and could be applied to paleosols that are identified as ultisols. The porosity and

inverse tortuosity are incorporated into the diffusion coefficient in Eq. (1) by the relationship:

$$D_s^* = D_{air}\epsilon\tau^{-1} \tag{6}$$

The Monte Carlo simulation was set up to calculate the inverse tortuosity related to random porosity value using the relationship in Eq. (5). Similar distributions were established for the stable carbon isotope composition of C3 and C4 plants using data from the literature (Fig. 2) (Bender, 1968; Bender, 1971; Smith and Epstein, 1971; Hattersley, 1982).

The normal probability distributions were used to randomly seed the model, solving the analytical solution in the Monte Carlo simulation with boundary conditions:

$$C(0) = C_{atm} \tag{7}$$

$$\frac{\partial C}{\partial z} = 0 \ at \ z = L \tag{8}$$

where L is the maximum depth represented by an impermeable barrier. The results of ten thousand model runs were plotted and compared to field measured values in order to determine if the natural variability of one or all of these parameters could account for the discrepancy between modeled and measured values. An attempt was made to establish a normal probability distribution for soil respiration rate, however the large variation of this parameter, daily, seasonally, and in response to precipitation, made it impossible to get useful results from the Monte Carlo simulation (Jia and Zhou, 2009). In order to account for respiration rate variability, the model was solved assuming different values for soil respiration rate, a fast measured value (FM), a fast literature value (FL), and slow rates for each of these (SM and SL), equivalent to one-tenth the fast values. The fast measured rate is 900 gC m^{-3} y^{-1} (0.10 gC m^{-3} h^{-1}), the average soil respiration rate measured at Panola Mountain, Georgia from September 1, 1994 to December 1, 1996 (Huntington, 1995). The fast literature rate is 647 gC m^{-3} y^{-1} (0.07 gC m^{-3} h^{-1}), a rate typical for the vegetation type found at the Panola Mountain site, temperate deciduous forest (Raich and Schlesinger, 1992). The corresponding slow rates were 0.010 gC m^{-3} h^{-1} (SM) and 0.007 gC m^{-3} h^{-1} (SL). Solving the model also requires assumptions for the maximum depth, the stable carbon isotope composition of the atmosphere, and the concentration of CO_2 in the atmosphere. Boundary soil depth was assumed to be 150 cm and the pre-industrial values of $-6.5‰$ (PDB) and 250 ppm were chosen for the stable carbon isotope composition of the atmosphere and concentration of CO_2 in the atmosphere respectively (Table 1) (Schroeder and Melear, 1999).

Table 1
Model assumptions and coefficients. ε = air-filled porosity. τ^{-1} = inverse tortuosity.

Run number	Soil respiration rate (gC m^{-3} h^{-1})	ε		τ^{-1}		δ^{13}C C3 (‰)		%	δ^{13}C C4 (‰)		%
		μ**	σ**	μ**	σ**	μ**	σ**		μ**	σ**	
009 (FL)[†]	0.07	0.38	0.06	0.13	0.06	−28.05		100			0
011 (SL)[†]	0.007	0.38	0.06	0.13	0.06	−28.05		100			0
013 (FL)[†]	0.07	0.38	0.06	*		−28.05	2.5	100			0
015 (SL)[†]	0.007	0.38	0.06	*		−28.05	2.5	100			0
037 (FL)[†]	0.07	0.38	0.06	*		−24.90	2.5	100			0
038 (SL)[†]	0.007	0.38	0.06	*		−24.90	2.5	100			0

* Calculated using Eq. (5).
** Where these fields are blank, the parameter was held constant during the Monte Carlo Simulation. Where there is an explicit value, they define the mean (μ) and standard deviation (σ) of the normal probability distribution used.
[†] Designates soil respiration rate used (FL = fast literature, SL = slow literature). See text for more details.
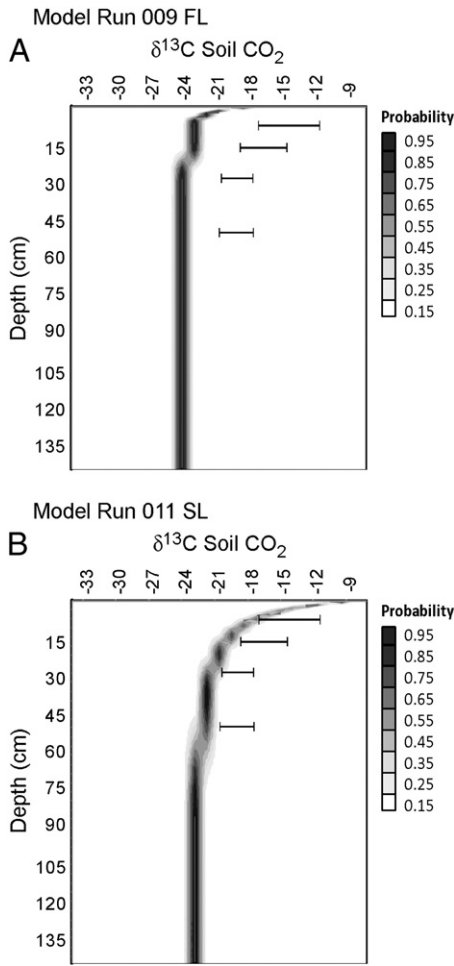
Fig. 3. Results of FL (A) and SL (B) Monte Carlo simulations using parameters listed for run numbers 009 and 011 in Table 1. Data points represent measured $\delta^{13}C$ measurements of the carbonate associated with pedogenic gibbsite (Schroeder et al., 2006).

Fig. 4. Results of FL (A) and SL (B) Monte Carlo simulations using parameters listed for run numbers 013 and 015 in Table 1. Data points represent measured $\delta^{13}C$ measurements of the carbonate associated with pedogenic gibbsite (Schroeder et al., 2006).

3. Results

The calculated $\delta^{13}C$ values of the models run (Table 1) are compared to the measured $\delta^{13}C$ values reported by Schroeder et al. (2006). These data are plotted with error bars representing the maximum amount of variability (± 1.5‰) of multiple measurements. The model solution is considered successful if the data error bars overlap the range of possible solutions. Each simulation was conducted in pairs using the above mentioned FL and SL values for soil respiration rate. The run number corresponding to the run number in Table 1 will be listed in parentheses.

The variability of the soil parameters, porosity and the resulting inverse tortuosity calculated using Eq. (5) results in a relatively small amount of variation in possible solutions (Fig. 3). There is not enough variability to cause the data to overlap the solutions at any depth in the profile. Changing the respiration rate from the FM (009) to SM (011) makes the range of possible solutions closer to the measured values but the chosen respiration rate is still too high. Adding the variability of the stable carbon isotope composition of the soil produced CO_2, assuming 100% C3 plants with a $\delta^{13}C$ value of −28.05‰ PDB, the mean of the C3 data (Fig. 2B), results in a much wider range in the possible solutions (Fig. 4). In this case the data points at greater depth in the profile, 28 cm and 51 cm, overlap the range of the solution representing 5% probability for FL (013) soil respiration rate. If the SL (015) soil respiration rate is used, the data overlaps at all depths with at least 20% probability of including all data
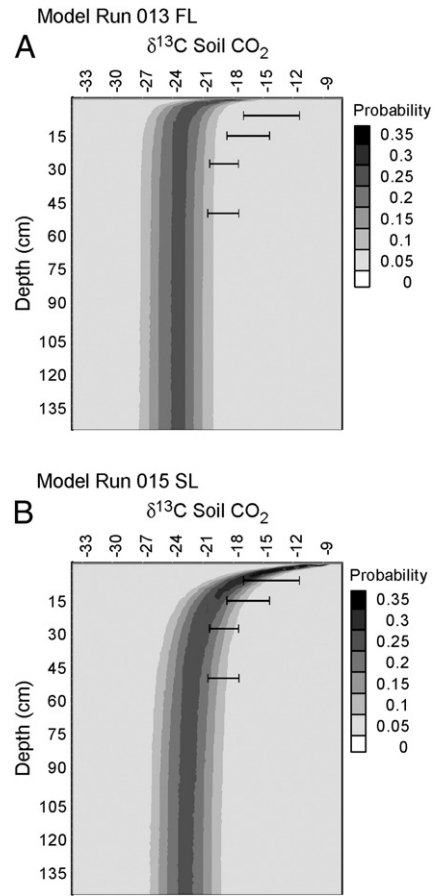
points. The bulk soil carbon $\delta^{13}C$ value of the Panola mountain sample site ranged from −18.9‰ to −24.9‰. This indicates that the most likely scenario is 100% C3 plants with a $\delta^{13}C$ value of −24.9‰ which is the value lowest in the soil profile (Schroeder et al., 2006).

Because there is no evidence of C4 plants at the Panola Mountain site, the model was run using −24.9‰, the $\delta^{13}C$ value of the bulk soil at 140 cm measured by Schroeder and Melear (1999), for model runs 037 (SL) and 038 (FL). In this case, the SL (037) solution appears to be the best fit of all the model runs with all data points falling within at least 25% probability, while the FL (038) model results in at best 5% probability (Fig. 5). In this case the model solution is acceptable with a 100% C3 source with a respiration rate that is 10% the amount typical for the vegetation at the site.

4. Discussion

The utility of this model relies ultimately on predicting the concentration of CO_2 in the atmosphere based on the profile of the $\delta^{13}C$ value of CO_2 occluded in soil minerals. When used for this purpose, conditions under which those minerals formed in the soil need to be assumed. The more sensitive the model is to the physical properties of the soil and the CO_2 in the soil, the more imperative it is that the assumptions be accurate. The results of these Monte Carlo simulations identify two important facts about this model and the utility of pedogenic gibbsite as a proxy for paleo-pCO2.

The results of simulations 009 and 011 (Fig. 3) indicate that the model is not sensitive enough to the natural variability of physical properties of the soil to account for the discrepancy between the measured $\delta^{13}C$ values of the CO_2 associated with pedogenic gibbsite

Model Run 038 FL

A

$\delta^{13}C$ Soil CO_2

Model Run 037 SL

B
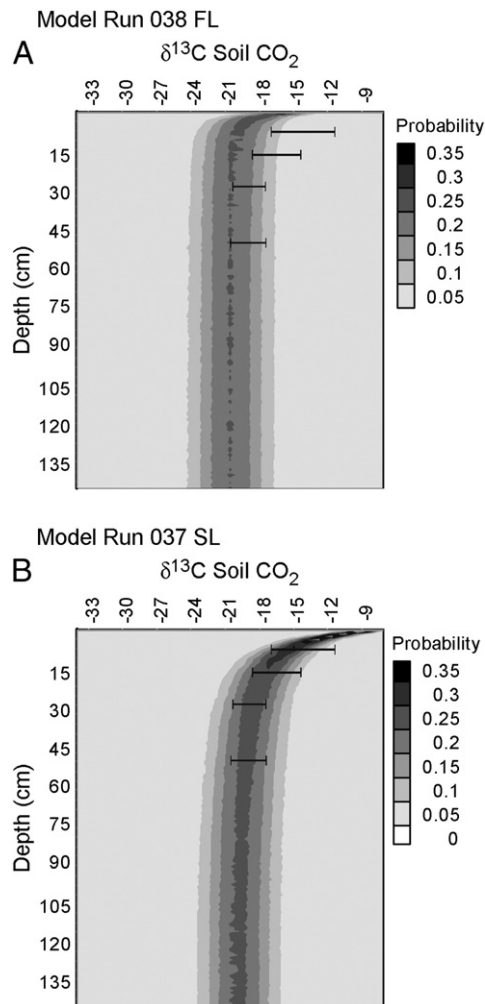
$\delta^{13}C$ Soil CO_2

Fig. 5. Results of FL (A) and SL (B) Monte Carlo simulations using parameters listed for run numbers 037 and 038 in Table 1. Data points represent measured $\delta^{13}C$ measurements of the carbonate associated with pedogenic gibbsite (Schroeder et al., 2006).

and the predicted values of $\delta^{13}C$ for soil respired CO_2. This agrees with the fact that using a finite difference model to more accurately represent changes in soil properties with depth did not improve the fit of the model without simultaneously choosing a lower respiration rate (Schroeder et al., 2006). Likewise, the natural variability of $\delta^{13}C$ values of the soil produced CO_2, assuming the photosynthetic pathway of the dominant biomass is known, is not able to account for the difference. While the possibility of mixing C3 and C4 sources can account for the difference between measured and modeled $\delta^{13}C$ value profiles, C4 plants are generally restricted by climate, preferring dry and warm climates typical of grasslands and deserts and are therefore not a factor in this case(Cerling, 1991).

Therefore, if the $\delta^{13}C$ of soil produced CO_2 can be determined based on the likely climate during formation, age of the sample, or some organic material preserved in the paleosol, it can be stated that the failure of the model to correctly predict the $\delta^{13}C$ value of the CO_2 occluded in pedogenic gibbsite is not caused by the factor assumptions of the model; leaving only the process assumptions. The first of two process assumptions that should be considered involve the way the CO_2 becomes associated with pedogenic gibbsite. This proxy was developed after the methods of Yapp and Poths (1996) which used the carbonate component of goethite as a proxy for paleo-CO_2. Based on the availability of space in the c-axis channel of the goethite structure to accommodate the carbonate molecule and infrared spectral evidence for a carbonate component in solid solution in

goethite, Yapp and Poths (1990) determined that the carbonate was incorporated into the goethite structure. In the gibbsite structure, there is no channel that will accommodate the carbonate molecule; a fact which led Schroeder and Melear (1999) to propose that the carbonate was occluded in site defects during mineral formation. In both cases, it was assumed that there was no fractionation of the carbon isotopes in the process of incorporating the carbonate in or on the mineral structure. Molecular dynamics modeling indicates fractionation factors of between +3.9 and +12.3‰ if the carbonate component is incorporated into the gibbsite structure, depending on where in the structure the CO_2 is located (Rosso and Rustad, 2001). All of the simulations in this study assume that the carbonate is occluded on the mineral surface in edge defects during mineral formation and therefore, it was assumed that there was no fractionation of carbon isotopes. The effect of fractionation would be to over-estimate the pCO_2 of the atmosphere. If you compare the solutions of two models where one uses the $\delta^{13}C$ value of the soil organic material, and one used +4.00‰ enrichment, the solution of the fractionated model would be shifted towards more positive values. If the fractionation was incorrectly assumed to be zero, it would appear that there was a larger contribution from the atmosphere. This can be seen graphically by comparing the solutions to models 015 and 037 (Figs. 4B and 5B).

The remaining process assumption that the $\delta^{13}C$ value of the carbonate occluded in soil minerals is representative of a profile resulting from the average annual respiration rate. This assumes that mineral formation is a constant process that is integrating the entire range of soil respiration rates throughout the year. In all of the simulation runs, assuming a respiration rate one-tenth the annual average resulted in a solution closer to the measured $\delta^{13}C$ values. This has been seen to be the case for pedogenic carbonates, where the solubility of calcite resulted in mineral formation only during warm, dry periods. As a result of this the stable carbon isotope composition of the calcite was not representative of the annual average, but was biased towards these conditions (Breecker et al., 2009). This indicates that mineral precipitation is an episodic event which most likely occurs when soil conditions are appropriate; i.e. when the soil is dry and the soil solution becomes saturated. Based on the well-established relationship between soil moisture and soil respiration rate, soil conditions ideal for gibbsite formation correspond with low soil respiration rates (Jia and Zhou, 2009). This is reflected in bias in the $\delta^{13}C$ value of the carbon occluded in pedogenic gibbsite towards periods of low respiration rate. Calculated soil CO_2 concentration corresponding to a respiration rate of 0.07 gC m^{-3} h^{-1} is 4400 ppm at a soil depth of 150 cm. Soil CO_2 concentrations this low are common for desert soils but temperate soils typically have soil CO_2 concentrations ranging between 10,000 and 25,000 ppm. The concentration of CO_2 in the soil however has been shown to be related to soil moisture and soil temperature and during periods of low soil moisture or cold temperatures concentrations as low as 4000 ppm are not uncommon (Albanito et al., 2009; Ota and Yamazawa, 2010; Zhang et al., 2010). Low calculated soil CO_2 concentrations for an acceptable model solution may give some insight into the conditions that exist during gibbsite precipitation and subsequent CO_2 occlusion, specifically, during conditions of low soil moisture content when biological activity is low, resulting in low soil CO_2 concentrations and corresponding low respiration rates.

5. Conclusions

The model used to predict paleo-pCO2, based on the stable carbon isotopes in pedogenic gibbsite, incorrectly assumes the average annual soil respiration rate. A lower rate, corresponding to conditions likely for gibbsite precipitation, is more appropriate. In light of these results, it is important to consider the process by which gibbsite occludes CO_2. The location of the CO_2, incorporated into the structure or surrounded by it, will have implications for both the fractionation

of carbon isotopes and the timing of the inclusion of CO_2 in the mineral. Additionally, it stands to reason that the evaporative environment that favors gibbsite precipitation may have a measurable effect of the oxygen and hydrogen stable isotopes in the gibbsite. Evaporation would serve to concentrate the heavy isotopes in the soil water. Therefore, you would predict that the $\delta^{18}O$ and δD of the gibbsite would be enriched compared to meteoric water. The seasonal variation of th1e $\delta^{13}C$ values of pedogenic carbonates and the model results presented in this paper indicate that the mineral precipitation process is episodic. Therefore, in order for the gibbsite paleo-pCO$_2$ proxy to accurately predict paleo-pCO$_2$, care must be taken when assigning a value for soil respiration rate.

If this method is applied to paleosol gibbsite the assumed soil respiration rate will proportionally affect the predicted pCO$_2$ of the atmosphere. For example, if a model assuming a soil respiration rate of 0.07 gC m^3 h^{-1} predicted a paleo-pCO$_2$ of 4000 ppm the same model assuming a respiration rate of 0.007 gC m^3 h^{-1} would predict a paleo-pCO$_2$ of 400 ppm. Therefore, it is imperative that the soil respiration rate that is assumed be correct.

Acknowledgments

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