Refining a pedogenic-carbonate CO₂ paleobarometer to quantify a middle Miocene greenhouse spike

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Abstract

Estimates of respired soil CO₂ concentration in paleosols are needed to calculate past atmospheric CO₂ levels from the difference between organic and carbonate carbon isotopic values in paleosols. A new compilation of CO₂ concentrations late in the growing season in modern calcareous soils can be used to estimate respired soil CO₂ by subtracting atmospheric CO₂ concentrations. Furthermore, respired CO₂ shows a significant relationship with depth to calcic horizon, and this relationship can be used to estimate respired CO₂ concentrations in paleosols. These values, as well as estimates of δ¹³C of atmospheric CO₂ from δ¹³C of soil organic matter, and of paleotemperature from Bw horizon chemical composition, refine the Cerling CO₂ paleobarometer. These refinements are applied to quantify the middle Miocene greenhouse, which has been controversial because it was not detected by marine alkenone and boron paleobarometers. New estimates of middle Miocene atmospheric CO₂ from paleosols in Railroad Canyon, Idaho, reveal levels at 16 Ma of 852 ± 86 ppmv. This is similar to predicted values by 2100, and 3 times pre-industrial values (PI=280 ppmv).

1. Introduction

By the year 2100, atmospheric CO₂ concentrations are predicted to triple, from pre-industrial levels of 280 ppmv to some 856 ppmv (+70%/−101 ppmv) based on scenario A2 of a very heterogeneous world with continued population growth (Alley et al., 2007). Such changes are unprecedented in Quaternary records, but their effects can be assessed by proxies for atmospheric CO₂ deeper in geological time (Roey et al., 2001) using mass balance models of sedimentary carbon and sulfur (Bernier, 1997, 2006), algal carbon isotope composition (Pagani et al., 1999; Kaufman and Xiao, 2003; Pagani, 2002), foraminiferal boron isotope composition (Pearson and Palmer, 1999, 2000), stomatal index of fossil plants (McElwain et al., 1999; Retallack, 2002), goethite-occluded carbonate in paleosols (Yapp and Poths, 1992; Tabor and Yapp, 2005), base depletion of paleosols (Sheldon, 2006a, 2006c), strontium isotopic values of marine carbonates (Rothman, 2002), and carbon isotopic values of pedogenic carbonate (Cerling, 1991; Sheldon and Tabor, 2009). This paper refines this last technique, which has been widely applied to paleosols (Ekart et al., 1999; Nordt et al., 2003, Montañez et al., 2007), and which can potentially be employed back at least to 2.6 Ga (Watanabe et al., 2000).

Cerling’s (1991) model for paleosols exploits the marked difference in isotopic compositions of carbon in CO₂ of the atmosphere (about −6.5‰ δ¹³C), and CO₂ produced by soil respiration and oxidation of C3 plants (about −26‰ δ¹³C). As levels of atmospheric CO₂ rise, higher partial pressure of isotopically heavy atmospheric CO₂ offsets isotopically light respired CO₂, and the carbon isotopic value fixed within low magnesium calcite of soil carbonate also rises. Until now only plausible ranges of respired CO₂ and sensitivity analysis could be applied (Mora et al., 1991; Montañez et al., 2007; Breecker et al., 2009). Compilations of global soil data (Brook et al., 1983) reveal that soil CO₂ is strongly related to mean annual precipitation (MAP) and mean annual temperature (MAT). Soil data presented here, now provide transfer functions for estimating respired CO₂ levels from depth to calcareous nodules (8k horizon of Soil Survey Staff 2000). Two additional refinements are (1) calculating atmospheric CO₂ isotopic composition from paleosol organic matter (Arens et al. 2000), as done by Nordt et al. (2003), and (2) calculating paleotemperature from paleosol chemical composition, as done by Sheldon et al. (2002). These refinements are applied to an example calculation of the middle Miocene global greenhouse, which has proven controversial, because stomatal-index data suggest a significantly higher than modern level of middle Miocene CO₂ (Retallack, 2002; Kürschnner et al., 2008), whereas algal alkenone (Pagani, 2002) and foraminiferal boron (Pearson and Palmer, 1999) paleobarometers suggest lower than modern middle Miocene CO₂. Because there is widespread independent evidence of higher than modern middle Miocene temperature and precipitation (Zachos et al., 2001; Bruch et al., 2007; Retallack, 2007), the low alkenone and boron estimates have been taken as evidence of CO₂–climate uncoupling (Cowling, 1999). These discrepancies are thus a challenge to CO₂-greenhouse theory, which guides prediction of future global warming (Alley et al., 2007).
2. Materials and methods

Refinement of the pedogenic CO2 paleobarometer of Cerling (1991) proposed here comes from a literature compilation of growing-season CO2 levels measured within soils. These data are now much more copious than for the earlier compilation of Brook et al. (1983: see also Supplementary data). This study focuses on a subset of these data consisting of all published CO2 measurements from calcic and gypsic soils distributed around the world (Fig. 1). Many of these observations of soil CO2 come from continuously monitored sites revealing seasonal variations (Fig. 2). These data are here used as the basis of transfer functions (Fig. 3) useful for interpreting paleosols.

As a worked example, the refined Cerling (1991) model is applied to middle Miocene paleosols in Railroad Canyon, Idaho. Fieldwork there consisted of measuring the depth to Bk as a proxy for paleoprecipitation, Munsell color, and also thickness of paleosol with calcareous nodules as a proxy for paleoseasonality (Retallack, 2005) within stratigraphic sections measured by the method of eyeheights (Retallack, 2007). These data have been conformed to the same datum as a recent composite section and magnetostratigraphy (modified from Barnosky et al. 2007), and stratigraphic levels of pedogenic carbonate stable isotopic analyses (Kent-Corson et al. 2006).

3. Refining a pedogenic CO2 paleobarometer

3.1. Introduction

The Cerling (1991) pedogenic carbonate CO2 paleobarometer is based on the very different carbon isotopic composition of CO2 in the atmosphere and respired within soils, which can be mixed in various proportions at different times of year and depth within soils. The fundamental equation of the paleobarometer is as follows (Ekart et al., 1999).

\[ P_a = P_r \cdot (\delta^{13}C_a - 1.0044\delta^{13}C_s - 4.4) / (\delta^{13}C_a - \delta^{13}C_s) \]

Variables in this equation are partial pressures of CO2 (P in ppmv), and carbon isotopic values of carbon in CO2 (\(\delta^{13}C\) in ‰). Subscripts are in atmosphere (a), in soil (s), and respired in soil (r). These values in turn are derived from measured carbon isotopic compositions of pedogenic carbonate (\(\delta^{13}C_C\)) and organic matter (\(\delta^{13}C_O\)) in paleosols. For example, \(\delta^{13}C_C\) is approximated by \(\delta^{13}C_C\) (Cerling 1991). The concentration of respired soil CO2 (\(P_r\) in Eq. (1)) is a controlling variable, and until now its value could only be guessed for paleosols based on estimates from comparable modern soils (Montañez et al., 2007; Sheldon and Tabor 2009). A proxy for paleosol respired CO2 is needed.

3.2. A new proxy for CO2 respired by paleosols

Soil CO2 is derived in part from the atmosphere and in part from respiration of roots, animals and microbes, and can reach levels up to 104,000 ppmv in tropical rain forest soils (371 times CO2 concentrations in the pre-industrial atmosphere: Matsumoto et al., 1997). The lowest CO2 concentrations in soils are nearest to the surface, where atmospheric CO2 sets a minimum level (Cerling, 1991). The highest CO2 concentrations are deep within soils, where microbes and roots respire within small pores with tortuous diffusion paths to the atmosphere. The zone of maximal CO2 is within 1–2 m of the surface after growing-season rains, but migrates deeper within the soil in snowy or dry seasons (Fig. 2A: Matsevich, 1957; Buyanovsky, 1972; Buyanovsky et al., 1982). Soil CO2 dissolves in soil water to form
carbonic acid responsible for hydrolytic weathering and carbonate dissolution (Brook et al., 1983), but alkaline earth cations mobilized early in the growing season are precipitated as dolomite or low-magnesian calcite nodules later in the growing season in arid to subhumid soils (McFadden and Tinsley, 1985). At the level of caliche nodules (0.4 m in Fig. 2B) soil CO2 rises following a flush of productivity following growing-season rains, then falls after the growing season (Fig. 2C).

Among the various levels of soil respiration observed during a year, late-growing-season values match best model assumptions of the pedogenic carbonate CO2 paleobarometer (Cerling, 1991). In temperate aridland soils, the first flush of early-growing-season soil respiration and rain promotes dissolution over precipitation of carbonate and little or no intrusion of atmospheric CO2, but during the dry–cold season there is little dissolution or precipitation and atmospheric CO2 penetrates more deeply into hibernating soil (Quade et al., 1989). During the late growing season in contrast, there is a shoulder of soil respiration when soils show modest atmospheric CO2 penetrations (Brook et al., 1983, but were not improved by my compilation of much additional soil CO2 data (see Supplementary data). Nor were these relationships improved that the P5–By relationship may provide a useful check on respired CO2 levels of comparable paleosols. Soil respiration levels of gypsic soils are also of interest for reconstructing productivity of Cambrian and Precambrian paleosols (Retallack, 2008).

The two new transfer functions between respired soil CO2 (P5 in ppmv) and depth to carbonate (D5 in cm) and to gypsum (G5 in cm) are significant (R2 = 0.80, S.E. ± 893 ppmv for Eq. (2), and R2 = 0.79, S.E. ± 431 ppmv for Eq. (3)), and given below.

\[
P5 = 66.7D5 + 588 \\
P5 = 42.3G5 + 73.3
\]

Scatter in these relationships may be due to local variation in Bk depth, which reflects long-term (106–109 years) soil formation, rather than rainfall and respiration pulses over weeks and years of monitored observations (Fig. 2). Similar temporal scaling problems limit significance of larger databases for the relationship between depth to Bk and mean annual precipitation in soils (Retallack, 2005).

These calcic and gypsic proxies for paleosol CO2 are of broad application to paleosols, because the database is global and includes both moderate and low latitudes, as well as ustic (winter dry) and xeric (summer dry) moisture regimes (Fig. 1). The database includes sandy and gravelly soils from Arizona, New Mexico and Nevada, and loess soils from Canada, Israel and central Asia. All the soils in the calibrating climosequence had carbonate in powdery, clast-pendant gypsic relationship is ±431 ppmv.

The greatest limitation for application of these proxies to paleosols is compaction of soils during burial, so that depth to Bk in paleosols (D5 in cm) is less than depth in the original soil (D3 in cm). Original depth can be calculated directly by pygmatic folding of formerly planar features in paleosols, but also can be calculated from estimated thickness of overburden (K in km) using a standard compaction formula for Aridisols (Sheldon and Retallack 2001), as follows.

\[
D3 = D5 / \left[ -0.62 / \left( \sqrt{0.38 / (0.38 + K)} - 1 \right) \right]
\]

Another limitation for application of these proxies to paleosols is erosion before burial, which can be assessed in several ways. Fossil roots converging to trunks in the surface of a paleosol are especially convincing evidence against erosion, and paleosols with near-planar tops in aggrading loess sequences also are unlikely to be eroded (Retallack 1997). Silty paleosols truncated by sandstone paleochannels are suspect (Retallack 1997), as are paleosols with tabular Bk horizons formed over soil durations of more than 10,000 years (Retallack 2005). Soils and paleosols with carbonate deeper than 110 cm and gypsic horizons deeper than 60 cm exceed limits of the climosequence. Use of this proxy for soil CO2 in frigid, tropical and monsoonal climates is also an extrapolation from available data (Fig. 1), but calcic-gypsic soil-CO2 is well within the array of CO2
concentrations in non-calcareous and non-gypsic soils from these climatic extremes (Brook et al., 1983; see Supplementary data). Paleosols developed on bedrock or very clayey substrates should be excluded because unrepresented in the clinosequence.

3.3. Published proxies for atmospheric $\delta^{13}C$

Another complication for the Cerling (1991) paleobarometer is temporal variation in carbon isotopic values of atmospheric CO$_2$. A useful proxy for atmospheric $\delta^{13}C$ ($\delta^{13}C_{\infty}$ in $\%$) is isotopic composition of organic matter ($\delta^{13}C_{\text{om}}$ in $\%$), according to the following equation ($R^2 = 0.34, \text{S.E.} = \pm 0.4\%$: from Arens et al., 2000).

$$\delta^{13}C_{\text{om}} = \delta^{13}C_{\infty} + 18.67 \frac{1.1}{T}$$

(5)

Fossil plants from coal or leaf beds interbedded with paleosols have been used for this purpose (Montañez et al., 2007), but can be misleading because coal and plant preservation is favored by wet, warm, and high-CO$_2$ times of climatic cycles (Retallack, 2007). Fossil humus in well drained calcareous paleosols may be strongly fractionated by aerobic decay, so that analysis of depth functions of organic carbon isotopic values may be needed to extrapolate original organic carbon isotopic values (Wynn, 2007). Alternatively, organic carbon occluded in bio-mineralized woody seeds from paleosols may be used (Backlund et al., 1991), but this is seldom sufficiently abundant in every paleosol to construct geological time series. An alternative approach is to model variation in $\delta^{13}C$ of atmospheric CO$_2$ through geological time from high resolution marine isotopic records, adjusted to local circumstances by empirical fractional factors (Passey et al., 2002; Nordt et al., 2003).

3.4. Published proxies for soil paleotemperature

Carbon isotopic composition of soil CO$_2$ ($\delta^{13}C_{\infty}$ in $\%$) and soil carbonate ($\delta^{13}C_{\text{carbonate}}$ in $\%$) is also dependent on temperature ($T$ in °C) of crystallization (Romanek et al., 1992), according to the following relationship ($R^2 = 0.93, \text{S.E.} = 0.28\%$).

$$\delta^{13}C_{\text{carbonate}} = \delta^{13}C_{\infty} + 1000 \frac{1.38 - 0.27}{T - 1000}$$

(6)

Deriving paleotemperature from isotopic composition of oxygen ($\delta^{18}O$) in soil carbonate (Dworkin et al., 2005) or clays (Tabor, 2007) may be difficult because of metamorphic alteration of paleosols (Mora et al., 1998), or because of orographic rain-shadow effects (Kent-Corson et al., 2006). Modern surface domains of $\delta^{18}O$ and $\delta^{13}C$ in clays can be used to constrain rain-shadow effects in intermontane paleosols (Tabor and Montañez, 2005). The clumped-isotope carbonate paleothermometer (Ghosh et al., 2007) is very promising, but requires calibration for paleosols. Paleosol mean annual paleotemperature can be derived from a clayeyeness chemical ratio for Inceptisols (Sheldon, 2006b). The most suitable paleotemperature proxy for Aridisols is an alkali ratio ($A = (Na_2O + K_2O)/Al_2O_3$, as a molar ratio), which is related to mean annual temperature ($T$ in °C), by the following equation ($R^2 = 0.37; \text{S.E.} = \pm 4.4°$ C; Sheldon et al., 2002).

$$T = -18.5A + 17.3$$

(7)

4. Middle Miocene CO$_2$ example

4.1. Calcareous paleosols in Railroad Canyon, Idaho

Calcareous paleosols of the kind needed for application of the Cerling (1991) CO$_2$ paleobarometer are widespread in Railroad Canyon, Idaho (Figs. 4–5), an area of Barstovian fossil mammal localities (Barnosky et al., 2007). These paleosols have been the focus of stable isotopic (Kent-Corson et al., 2006), paleopedological, and major element geochemical studies (Retallack, 2007).

The most prominent lithological change in the section is from pale olive-gray Renova Formation below to brown Sixmile Creek Formation above (Figs. 4–5). This contact has been regarded as a regional “unconformity” (Barnosky et al., 2007), and is certainly a shift in palaeoclimatically sensitive features of paleosols such as depth to Bk contact (Fig. 6). However, the age of the regional unconformity has been revised from 16 Ma (early Barstovian) to 20 Ma (early Hemingfordian: Henneman and Wideman, 2006). There is no detectable angular discordance or paleovalley development at this stratigraphic level in Railroad Canyon, which was presumably a local depocenter little affected by basin margin discordance. Late Hemingfordian fossil mammals, not much older than Barstovian, were not found in Railroad Canyon, but are known from the Renova Formation in Maiden Creek, 11 km to the north (Retallack, 2007), and Mollie Gulch 12 km to the southwest (Barnosky et al., 2007). The Renova–Sixmile contact is thus stratigraphically higher than the regional early Hemingfordian hiatus (Henneman and Wideman, 2006), but was nevertheless avoided in the following reconsideration of local magnetostatigraphic dating.

4.2. New age model for Railroad Canyon magnetostratigraphy

The time scale of Cande and Kent (1995) used by Barnosky et al. (2007) for magnetostatigraphic dating of the Railroad Canyon section can now be updated using recent revisions by Ogg and Smith (2004). Levels from the “basic unrevised” magnetostatigraphic of Barnosky et al. (2007) are here plotted against 16 different sets of revised chron ages: in essence, sliding the standard time scale against the proportional thicknesses of magnetozones in Railroad Canyon to determine the best fit (Fig. 7). All but 3 of the 16 alternatives can be rejected using biostratigraphic data. Diverse and definitive Barstovian faunas between 140 and 230 m in the section are no older than 16 Ma and no younger than 12.5 Ma (Tedford et al., 2004). Fossils are sparse above and below that level, so biostratigraphically unconstrained (Barnosky et al. 2007). The three acceptable models date the base of the normal immediately above the base of the Sixmile Creek Formation at 16.721 and 16.472 Ma and 16.268 Ma respectively. Two of these age models (starting at 16.721 and 16.472 Ma) can be rejected because of tephrostratigraphic correlation of a peralkaline ash at 23 m in Railroad Canyon with a 16.6–15.8 Ma ash from McDermitt, Oregon.
Fig. 5. View up Railroad Canyon from the eastern end of Whiskey Spring section (Fig. 4). Pale olive (5Y6/3) deep-calcic, clayey paleosols of the Renova Formation, contrast with light yellowish brown (2.5Y6/3), silty paleosols of the overlying Sixmile Creek Formation.

Fig. 6. Composite section and magnetostratigraphy of Railroad Canyon modified from Barnosky et al. (2007), with degree of paleosol development, depth to calcareous nodules and thickness of soil with calcareous nodules. Carbon isotope sample numbering follows Kent-Corson et al. (2006).
(Barnosky et al., 2007). These same two models can also be rejected for lower correlation than the age model chosen, which shows least variation in sedimentation rate. The 16.721 Ma option adopted by Barnosky et al. (2007) disregards 4 normals between 184 and 228 m, and casts doubt on the ash correlation. By the new age model (Fig. 7) the reversed interval from 76 to 93 m in Railroad Canyon (Fig. 6) correlates with interval R3 at Hephursn Mesa near Yellowstone National Park, Wyoming, which probably includes a 15.88±0.06 Ma ash low in a section 6 km to the northeast of the paleomagnetically-dated Barstow ash (Sheldon and Retallack, 2001), Idaho is too far north and west for C4 plants today (Sage et al., 1999), and Railroad Canyon paleosols predate by about 10 Ma the advent of C4 vegetation in the Great Plains of North America (Passey et al., 2002). There is no evidence that C4 vegetation was introduced into Idaho during the middle Miocene warm–wet spike.

4.4. New middle Miocene atmospheric CO2 estimates

Of the various carbon isotopic compositions needed for the pedogenic carbonate CO2 paleobarometer (Eq. (1)), isotopic composition of pedogenic carbonate (δ13C) was measured from paleosols in Railroad Canyon by Kent-Corson et al. (2006). Two other quantities (δ18O and δ13C2) can be derived from carbon isotopic composition of organic matter (δ13C2), which should be roughly −22‰ from geographic gradient analysis of middle Miocene hackberry seeds in paleosols of the northern Great Plains (Backlund et al., 1991). This is the same as values for water-stressed C3 vegetation calculated for 0.5 Ma intervals of the Miocene (Table 1) using known fractionations from marine isotopic data by Passey et al. (2002). Paleosol depth to Bk, burial depths, and alkali paleotemperature are as previously published (Retallack, 2007).

As an example calculation, consider the paleosol at the middle Miocene CO2 maximum (Table 1). This paleosol is at 58 m in the section, and thus 15.61 Ma in the age model of Fig. 7. Its Bk horizon is below 115 cm of near-mollic, pale olive (5Y6/3) claystone, in turn overlain by laminated white (5Y8/1) volcanic ash (Retallack, 2007). The depth to Bk would have been 125 cm before burial compaction under 0.86 km of local overburden (Retallack, 2007), following Eq. (4) (from Sheldon and Retallack, 2001). The equation for Ardisols was used despite the depth to Bk greater than 1 m, because the profile has a Bk horizon more strongly developed than Inceptisols, and does not have the organic or structural character of a deep Mollisol (tall grass prairie soil), which evolved later in geological time (Retallack, 2007).

This original depth is also an extrapolation from the training set for Eq. (2) (up to 110 cm only), but was used to calculate a late

Table 1

<table>
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<tr>
<th>Level (m)</th>
<th>Age (Ma)</th>
<th>δ13C (‰)</th>
<th>δ18O (‰)</th>
<th>δ13C2 (‰)</th>
<th>δ13Co (‰)</th>
<th>Paleotemperature (°C)</th>
<th>Depth Bk (cm)</th>
<th>Burial depth (km)</th>
<th>Paleosol respired CO2 (ppmv)</th>
<th>Atmospheric CO2 (ppmv)</th>
<th>Atmospheric CO2 (PIL)</th>
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</table>

Notes: Age model is modified from Barnosky et al. (2007). Isotopic values δ13C and δ18O were measured from paleosol carbonate by Kent-Corson et al. (2006), but δ13C was calculated from model of Passey et al. (2002) calibrated to Miocene hackberries (Backlund et al., 1991), and δ13C2 was calculated from δ13C using temperature fractionation of Romanek et al. (1992). Paleosol paleotemperature, depth to Bk and depth of burial are from Retallack (2007). PIL means multiple of pre-industrial level (280 ppmv after Alley et al., 2007).
The carbonate of the Bk horizon was measured as δ¹³C = -5.9‰ and δ¹⁸O = -15.3‰ (both vs. PDB: Kent-Corson et al., 2006), and its Bw horizon has modest alkali and alumina content (10.20 wt.% Al₂O₃, 2.14 wt.% K₂O, 0.62 wt.% Na₂O; Retallack, 2007), as in modern soils formed in mean annual temperature of 11.6 °C, using Eq. (7) (after Sheldon et al., 2002). This temperature can be used to calculate carbon isotopic composition of CO₂ gases from which the carbonate was precipitated (δ¹³C, of Eq. (1)), following Eq. (6) (after Romanek et al., 1992). Two remaining variables needed for Eq. (1) are the isotopic composition of organic matter in the paleosols (δ¹³Cₒ), taken as -2.9‰, using the above organic matter value in Eq. (5) (from Arens et al., 2000). Inserting these values into Eq. (1) gives a middle Miocene spike of 852 ppmv, in contrast with near pre-industrial levels of CO₂ for other parts of the Miocene (Fig. 8).

The standard error of this estimate of atmospheric CO₂ (Sᵦ) has several components from the various transfer functions (Sᵦ = ±893 ppmv, δ¹³C_p = ±0.28‰, S_p = ±4.4 °C) and analytic error limits (S_p = ±0.5‰, S_p = ±0.1‰), which can be summed in quadrature for Gaussian error propagation (Eq. (8)).

\[
S_\delta = \sqrt{\left(\frac{\partial P}{\partial \delta_\delta}\right)^2 S_\delta^2 + \left(\frac{\partial P}{\partial S_\delta}\right)^2 S_\delta^2 + \left(\frac{\partial P}{\partial S_p}\right)^2 S_p^2 + \left(\frac{\partial P}{\partial S_p}\right)^2 S_p^2}
\]

Full equations for each partial derivative come from transpositions of Eqs. (1) and (6) (see Supplementary data). In this particular CO₂ determination of 852 ppmv the ±893 ppmv standard error of the respired CO₂ transfer function (Eq. (2); Fig. 3) gives ±86 ppmv atmospheric CO₂, because of the low ratio of Pₛ/Pᵦ (852/8981 = 0.09). This degree of uncertainty is a considerable improvement over past guestimates of ca. ±2000 ppmv respired soil CO₂ (Nordt et al., 2003; Ekart et al., 1999), which gives ±134 ppmv atmospheric CO₂ in this case. Trivial amounts of uncertainty come from carbonate carbon isotopic analysis (±0.05‰) giving ±0.009 ppmv atmospheric CO₂ and atmospheric CO₂ carbon isotopic composition modelled from organic carbon isotopic determination (±0.4‰) giving ±0.0013 ppmv atmospheric CO₂. Additional uncertainty comes from paleotemperature estimates, with ±0.28‰ for Eq. (6) giving ±0.02 ppmv atmospheric CO₂, and ±4.4 °C for Eq. (7) giving ±9 ppmv atmospheric CO₂.

Thus middle Miocene atmospheric CO₂ is here estimated at 852 ± 86 ppmv, or ±0.31 PIL (pre-industrial level of 280 ppmv) and 2008 (386 ± 2 ppmv standard deviation of seasonal variation) levels of atmospheric CO₂.

4.5. Comparison with other Miocene CO₂ estimates

New CO₂ estimates from Idaho paleosols presented here (Fig. 8E) support stomatal-index estimates (Fig. 8F) of high middle Miocene atmospheric CO₂ (Retallack, 2002; Kürschner et al., 2008). Error of isotopic analyses is small (~0.05‰), unlike stomatal-index measurements, which have large standard deviations (typically 1% in measures that range from 5 to 12%; Retallack, 2001; Kürschner et al., 2008). Also compatible with estimates presented here are 2–7 PIL CO₂ from thermodynamic modelling of base depletion in middle Miocene intrabasaltic paleosols from Oregon (Sheldón, 2006c).

In contrast, these new results are very different from marine alkenone (Paganì, 2002) and boron (Pearson and Palmer, 1999) paleobarometers (Fig. 8F), and their attendant implications of CO₂-climate uncoupling (Cowling, 1999). The alkenone and boron paleobarometers had sensitivity and other limitations anyway (discussed at length by Retallack, 2002; Royer et al., 2001). The middle Miocene CO₂ greenhouse spike in Idaho–Montana had higher precipitation and temperature as predicted by greenhouse theory (Fig. 8A–D), and these changes were globally widespread because they are reflected in marine stable isotopic records (Fig. 8G–H). The climate and atmosphere of the middle Miocene is thus the most recent analog for the world predicted for 2100 by current models of atmospheric CO₂ pollution (Alley et al., 2007).
5. Conclusions
Past estimation of atmospheric CO₂ from pedogenic carbonate isotope composition of paleosols was compromised by unknown respired CO₂ concentrations of paleosols (Cerling, 1991). Relationships between depth to calcic or gypsic horizon in modern soils and respired soil CO₂ concentration (Fig. 3) can now be used to estimate respired soil CO₂ concentration in paleosols, after correction for compaction during burial (Sheldon and Retallack, 2001b). This and refinements of the pedogenic carbonate CO₂ paleobarometer for temperature and atmospheric isotopic variation are here demonstrated with a worked example of fluctuations in atmospheric CO₂ during the middle Miocene (Fig. 8). This and other refinements of the Cerling (1991) CO₂ paleobarometer give estimates of atmospheric CO₂ from paleosols (maximum at 15.6 Ma of 852 ± 86 ppmv) comparable with estimates from stomatal index of fossil plants (Kürschner et al., 2008), but with less standard error. Calcareous paleosols have additional advantages of much greater temporal resolution (Retallack, 2007) than plants with preserved cuticle (Retallack, 2002). Calcareous paleosols are now known as old as 2.6 Ga (Watanabe et al., 2000), and support mass balance approaches to non-calcareous paleosols for calculating atmospheric CO₂ during the Precambrian (Sheldon, 2006a). Paleosol records can thus be extended further back in time than CO₂ proxies based on foraminifera (Pearson and Palmer, 1999; Pagani, 2002). Calcareous paleosols reveal short-lived spikes in atmospheric CO₂ (Fig. 8), not apparent in geochemical approaches of coarse temporal resolution (Rothman, 2002; Berner, 2006), and are more accurate proxies of CO₂ than marine algal carbon isotopic composition (Kaufman and Xiao, 2003).

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Appendix A. Supplementary data
Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.palaeo.2009.07.011.

References