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EFFECTS OF DIFFERENT ORGANIC-MATTER SOURCES ON ESTIMATES OF ATMOSPHERIC AND SOIL pCO_2 USING PEDOGENIC CARBONATE

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ABSTRACT: **Carbon isotope analysis of paleosol carbonates is one of the most widely used methods for producing quantitative estimates of CO_2 levels in the ancient atmosphere, and is increasingly used to estimate soil pCO_2 as a proxy for primary productivity. Recent efforts to improve the carbonate CO_2 paleobarometer by refining input parameters (e.g., soil temperature, soil CO_2 production function) have yielded more accurate estimates of ancient atmospheric pCO_2. The carbonate CO_2 paleobarometer is especially sensitive to input values for the carbon-isotope composition of soil organic matter (OM), which should ideally reflect the $\delta^{13}C$ value of OM present when pedogenic carbonates were forming. Published soil pCO_2 estimates derived from pedogenic carbonate in Upper Jurassic paleosols are re-evaluated here using OM occluded within pedogenic carbonates rather than average values of fossilized plant material collected throughout the sampled stratigraphic sections. The new soil pCO_2 estimates calculated using occluded OM range from 4,600 to 20,000 ppmV and are much lower than the previously published estimates, which were often in excess of 60,000 ppmV. In order to determine which OM source provides more accurate results, estimates of atmospheric pCO_2 obtained using plant material and occluded OM from a carbonate-bearing modern soil are compared with measured, pre-industrial atmospheric CO_2 levels. In the modern soil profile, plant OM $\delta^{13}C$ is highly variable and slightly more negative than the $\delta^{13}C$ of occluded OM. The observed $\sim$ 1‰ offset between the average $\delta^{13}C$ values of plant material and occluded OM is much less than the overall range of $\sim$ 6‰ in plant OM. Estimates of atmospheric pCO_2 from the modern soil that are calculated using occluded OM differ by less than 100 ppmV, on average, from estimates based on plant OM. These results suggest that occluded OM produces reasonably accurate pCO_2 estimates when used with the carbonate CO_2 paleobarometer. Applying a –1‰ correction to the $\delta^{13}C$ of occluded OM also produces accurate pCO_2 estimates, but the extreme variability in $\delta^{13}C$ of plant matter leads to inaccurate pCO_2 estimates, even when samples are averaged.**

INTRODUCTION

Since its introduction more than 20 years ago (Cerling 1991), the carbonate CO_2 paleobarometer, which uses carbon isotope analysis of paleosol carbonates to estimate CO_2 concentration in the ancient atmosphere, has become one of the most widely used methods for producing quantitative estimates of atmospheric pCO_2 (e.g., Ekart et al. 1999). Recently, this approach has been utilized to determine soil pCO_2 as a proxy for primary productivity in ancient terrestrial environments (Myers et al. 2012a). Several different equations may be used with the carbonate CO_2 paleobarometer (Yapp and Poths 1996; Retallack 2009; Breecker and Retallack 2014), but the most common formulation is that presented by Cerling (1999; also see Ekart et al. 1999). All equations require similar input parameters, including the $\delta^{13}C$ values of pedogenic calcite, soil-respired CO_2, and atmospheric CO_2, and the concentration of either soil CO_2 or soil-respired CO_2. Recent work has focused on refining the carbonate CO_2 paleobarometer by improving the accuracy of various input parameters. These efforts have attempted to develop more effective methods for estimating the depth-dependent soil CO_2 production function *S(z)* (Retallack 2009; Cotton and Sheldon 2012; Montañez 2013; Breecker and Retallack 2014) and the temperature of formation for pedogenic carbonate (Cotton and Sheldon 2012; Quade et al. 2013).

Although the carbonate CO_2 paleobarometer is especially sensitive to variation in the $\delta^{13}C$ value of soil-respired CO_2, this input parameter has received less attention of late. The $\delta^{13}C$ value of soil-respired CO_2 can be estimated indirectly (Ekart et al. 1999), but it is most often determined from $\delta^{13}C$ measurements of organic matter (OM) associated with pedogenic calcite (e.g., Montañez et al. 2007; Sheldon and Tabor 2009; Tabor et al. 2013; Tabor and Myers 2015). In most cases, the $\delta^{13}C$ value of fossilized OM is assumed to accurately reflect the $\delta^{13}C$ value of soil OM during pedogenesis. However, OM can be sampled from a variety of sources, including (1) horizons in carbonate-bearing paleosol profiles (Cerling 1992), (2) strata adjacent to carbonate-bearing paleosols (Tabor et al. 2004; Myers et al. 2012a), and (3) occlusions in pedogenic carbonate structures (Cotton and Sheldon 2012; Gastaldo et al. 2014; Schaller et al. 2015). Oxidation during pedogenesis usually destroys most OM in the soil profile (e.g., Prochnow et al. 2006), so the only OM present in stratigraphic successions with carbonate-bearing paleosols typically occurs in pedogenically unmodified strata adjacent to the paleosol profiles. Unfortunately, using measurements of allochthonous OM preserved in deposits adjacent

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to paleosols to estimate the $\delta^{13}C$ value of soil-respired CO_2 can produce unrealistically high estimates of soil pCO_2 (Myers et al. 2012a). Use of OM occluded within pedogenic carbonates collected from paleosol profiles to estimate the $\delta^{13}C$ of soil OM and soil-respired CO_2 was first suggested over 20 years ago (Cerling 1992), and this approach has been used increasingly in pCO_2 studies that employ the carbonate CO_2 paleobarometer (e.g., Montañez et al. 2007; Cotton and Sheldon 2012), despite models and measurements of modern soil systems that suggest occluded soil OM may undergo stable-carbon-isotope fractionation due to microbially mediated decomposition (Bowen and Beerling 2004; Wynn et al. 2005, 2006; Wynn 2007). This study uses data from modern and ancient soils to investigate the effects of different OM sources on estimates of soil pCO_2 and evaluate whether occluded OM provides a reasonable approximation of soil OM $\delta^{13}C$ values in the context of the carbonate CO_2 paleobarometer.

Initial investigations using carbon isotope analysis of paleosol calcite to estimate soil CO_2 concentrations in Late Jurassic terrestrial environments of North America, Western Europe, and Central Africa yielded unexpectedly high pCO_2 estimates that are useful only for broad, relative comparisons of primary productivity among those sites (Myers et al. 2012a). The input value of soil OM $\delta^{13}C$ was derived from carbonized wood and comminuted plant material in deposits stratigraphically adjacent to the paleosols sampled for carbonate (Myers et al. 2012a). The relatively positive $\delta^{13}C$ values of this allochthonous OM (averaging –22‰ to –21‰) produced soil pCO_2 estimates that exceeded 100,000 ppmV in some instances (Myers et al. 2012a). The carbonate CO_2 paleobarometer may even produce negative soil pCO_2 estimates when OM $\delta^{13}C$ values are extremely positive. Negative pCO_2 values have no physical meaning and indicate a lack of chemical equilibrium among the $\delta^{13}C$ compositions of materials under consideration. When this dataset is re-evaluated using occluded OM derived from paleosol carbonate accumulations to determine soil OM $\delta^{13}C$ values, the resultant soil pCO_2 estimates are much lower than the earlier estimates based on allochthonous OM (Myers et al. 2012a). These problems highlight the importance of soil OM $\delta^{13}C$ to the carbonate CO_2 paleobarometer.

In order to better understand the effects of different OM sources on pCO_2 estimates derived from pedogenic carbonate, the carbon-isotope composition of pedogenic calcite, plant material, and occluded OM in a modern soil profile are examined in detail. Estimates of atmospheric pCO_2 are calculated using (1) vascular plant OM and (2) occluded OM in soil calcite accumulations sampled from a modern soil and are compared with measurements of pre-industrial atmospheric CO_2 levels to determine which OM source produces the most accurate results. Information gleaned from studying various OM components of the modern soil system is used to evaluate a dataset of Upper Jurassic paleosols (expanded beyond that of Myers et al. 2012a) and further constrain Late Jurassic soil pCO_2. This expanded paleosol dataset includes additional Morrison Formation localities in Utah and New Mexico, as well as samples from the Upper Jurassic portion of the Tendaguru Formation in Tanzania (Bussert et al. 2009; Schrank 2010). The Tendaguru Formation samples provide important new information about Late Jurassic paleoclimatic conditions in the southern-hemisphere terrestrial environments of Gondwana.

METHODS

Field Sampling of Paleosol Carbonate

A total of 91 pedogenic carbonate samples were collected from three study areas (Fig. 1). This dataset is expanded numerically and geographically relative to earlier published results from the Upper Jurassic Morrison and Lourinhã formations (Myers et al. 2012a). Thirty-nine carbonate samples were collected from five different localities in the Morrison Formation. Seventeen samples were collected near Ghost Ranch, in northern New Mexico; six near Acoma Pueblo, in western New Mexico; 10 near Shell, in northern Wyoming; three near Bridger, in southern Montana; and three near Green River in eastern Utah (Fig. 1A). All of the 46 carbonate samples from the Lourinhã Formation were collected from coastal cliff exposures located west of the town of Lourinhã, between São Bernardino and Porto Novo, Portugal (Fig. 1B). All of the six samples from the Tendaguru Formation, which were picked from matrix encased in plaster jackets used to collect vertebrate fossil material, are derived from the upper Kimmeridgian Middle Dinosaur Member near the stratotype locality at Tendaguru Hill (Bussert et al. 2009; Schrank 2010) (Fig. 1C). All samples consist of discrete pedogenic nodules—stage II carbonate accumulation of Gile et al. (1966)—or calcareous rhizoliths that were collected from depths greater than 50 cm below the ancient soil surface where the concentration and isotopic composition of soil CO_2 are essentially constant (Cerling and Quade 1993; Ekart et al. 1999).

Sampling Modern Pedogenic Carbonate

Soil samples were procured by N.J.T. from the California "Soil Series Pedolarium" in the Department of Land, Air and Water Resources at the University of California, Davis. The DeStazo soil series was selected for intensive subsampling because it is a well-drained Aridisol formed on alluvium, contains a thick calcic horizon with abundant carbonate nodules, and shows no evidence of hydromorphic or redoximorphic conditions (e.g., gleying, mottling; Soil Survey Staff 2010). The type location of the DeStazo series is in the western Mojave Desert in southern California, northeast of Los Angeles. The samples from the DeStazo profile collected from the pedolarium are a mixture of matrix, carbonate masses, and small roots and fragments of plant material. Fourteen carbonate nodules ($\sim$ 1 cm diameter) were sampled from three intervals in the calcic horizon, which extends from 28 to 132 cm according to the official USDA description of the profile. Exact depths of carbonate and OM samples in the DeStazo profile are not available because these samples were initially collected over a range of depths in individual soil horizons, so depths of samples reported here are averages for each sampled horizon. Sampling procedures for carbonates were intended to replicate sample selection techniques used for paleosols. Therefore, only discrete stage II carbonate morphologies (*sensu* Gile et al. 1966) were selected for analysis, and the average depths of carbonate samples used to estimate soil pCO_2 are all $>$ 40 cm below surface (41 cm, 67 cm, 107 cm), which approximates the 50 cm minimum sampling depth used in paleosols in order to avoid the mixing zone of atmospheric and soil-respired CO_2 (Cerling and Quade 1993; Ekart et al. 1999).

Sampled carbonate nodules were sonicated in deionized water to remove adhering matrix and crushed with a mortar and pestle. A small fraction of the sample powders was used for $\delta^{13}C$ analysis of carbonate, and the larger portion was processed to isolate occluded OM for $\delta^{13}C$ analysis of organics. Of the 14 carbonate samples selected for $\delta^{13}C$ analysis of calcite, only five were large enough to yield sufficient amounts of occluded OM for $\delta^{13}C$ analysis. Processing techniques used to isolate and analyze occluded OM from modern pedogenic carbonates are identical to those described for paleosol carbonates above. Plant material (n = 11) was isolated from five intervals in the profile, beginning near the surface in the A horizon and ranging down to 132 cm depth. These plant OM samples were soaked in dilute 10% HCl overnight and washed thoroughly with deionized water. Plant OM samples that were sufficiently large and robust were loaded directly into Vycor combustion tubes for pyrolysis and offline extraction and purification of CO_2. Samples that were too small or too fragile to load directly were first loaded into Vycor sample boats and then inserted into the combustion tubes.

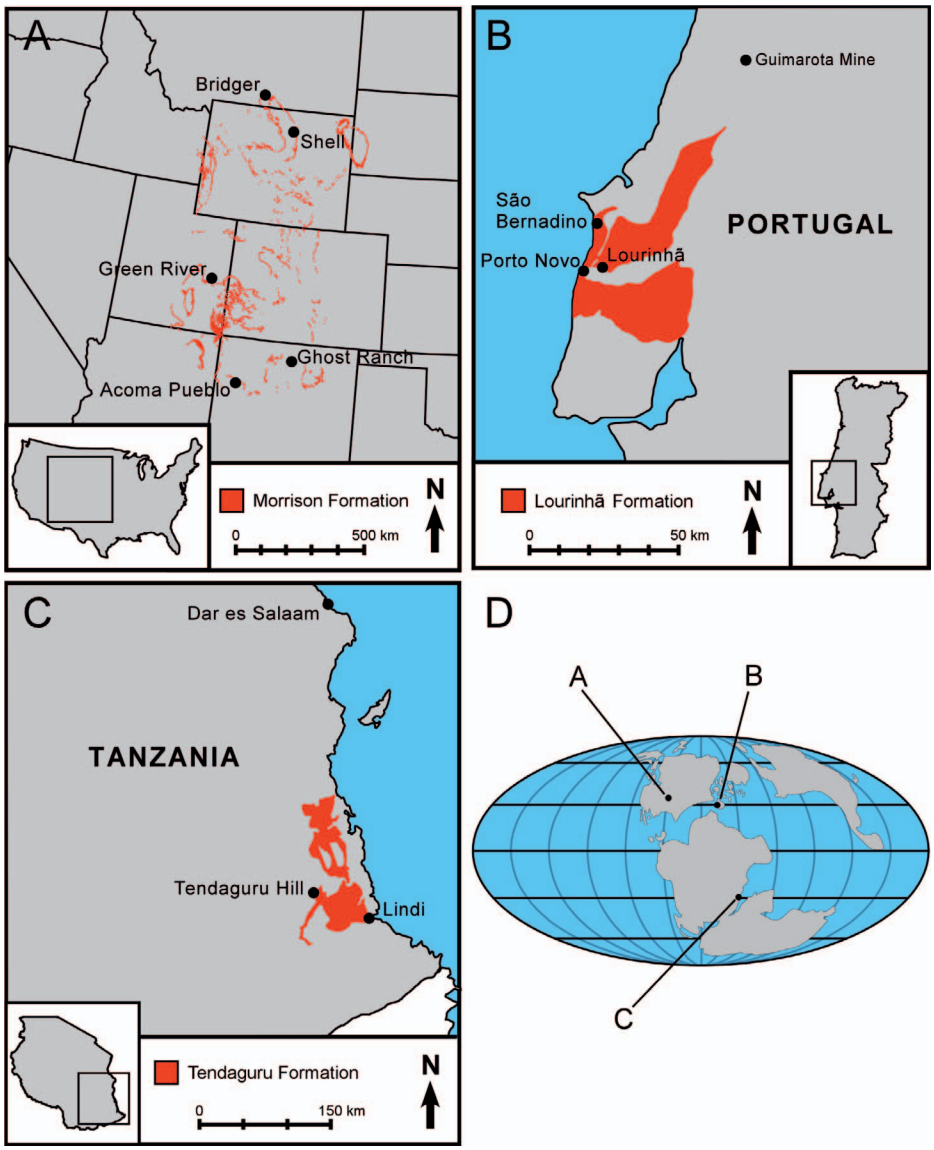

FIG. 1.—Maps showing study areas and sampling localities. **A)** Map of the Western United States showing outcrop distribution of the Morrison Formation and locations of the five sampling localities. **B)** Map showing outcrop distribution of the Lourinhã Formation in central Portugal with several towns for geographic reference. **C)** Map showing the distribution of the Tendaguru Formation in eastern Tanzania. Several towns and the stratotype locality at Tendaguru Hill are included for reference. **D)** Paleogeographic reconstruction showing the positions of all three study areas during the Late Jurassic. Modified from Smith et al. (1994).

Evaluating Diagenetic Alteration in Paleosol Carbonate

All 76 samples collected from the Lourinhã Formation and the Ghost Ranch, Shell, and Bridger localities in the Morrison Formation were thin-sectioned and examined for textural evidence of diagenesis with a petrographic microscope. Micritic calcite was sampled from thin sections with a Merchantek Micromill for $\delta^{13}C$ analysis. The 15 samples collected from the Tendaguru Formation and the Acoma Pueblo and Green River localities in the Morrison Formation were either drilled from hand samples or entire nodules were crushed and used for $\delta^{13}C$ analysis when little material was available. Greater amounts of material were required for acidification and isolation of occluded organic matter, so these sample fractions were drilled directly from billets or hand samples or subsampled from crushed whole nodules. Samples that were examined petrographically possess textures similar to the alpha-type microfabric described by Wright (1990), with micrite or microspar groundmasses that may contain quartz grains, spar-filled veins, or glaebules with circumgranular cracks. Micrite and microspar fabrics with crystals < 20 μm were sampled for $\delta^{13}C$ analysis, but coarse sparry fabrics with crystals > 20 μm were avoided because these textures typically represent groundwater or burial-diagenetic cements (Courty et al. 1987; Mora et al. 1993; Quast et al. 2006).

Laboratory Analyses of Modern and Ancient Samples

The Jurassic calcite samples drilled from thin section were analyzed at the University of California (UC), Davis. These samples were loaded into a GVI Optima Stable Isotope Ratio Mass Spectrometer equipped with an automated carbonate reaction device and reacted with 100% H_3PO_4 at 90°C. The evolved gases were cryogenically purified to isolate CO_2 and moved into the mass spectrometer to determine $\delta^{13}C$ values. All other calcite samples were analyzed at Southern Methodist University (SMU). These samples were reacted with 100% H_3PO_4 at 25°C for 12–24 h and cryogenically purified to produce CO_2 (McCrea 1950). The carbon isotope composition of the CO_2 gas was then measured with a Finnigan MAT 252 or MAT 253 isotope-ratio mass spectrometer. Average reproducibility for calcite $\delta^{13}C$ samples analyzed at UC Davis and at SMU is ± 0.1‰.

Occluded OM was isolated by digesting the carbonate samples in dilute HCl. Powdered samples were sonicated in 10% HCl until they no longer effervesced, then approximately 1 mL of 35% HCl was added to insure

complete reaction of any remaining refractory carbonate. The resultant residue of siliceous material and organics was rinsed with deionized water until the pH of the solution reached that of the rinsing agent and was then dried in an oven at 40–50°C. Procedures for extraction of CO_2 from the organic residues were based on the methods outlined by Boutton (1991). Samples were sealed under vacuum in Vycor tubing with 1 g wire-form CuO and 0.5 g Cu metal, then pyrolized at 900°C for 2 h. The temperature was reduced incrementally and then maintained at 650°C for an additional 2 h. Gases evolved during pyrolysis were cryogenically purified to isolate CO_2, the $\delta^{13}C$ value of which was measured at SMU using a Finnigan MAT 252 or MAT 253 isotope-ratio mass spectrometer. Average reproducibility for $\delta^{13}C$ analyses of organic-matter samples is ±0.1‰. Delta values (δ) for both calcite and OM samples are reported here in per mil (‰) units relative to the Peedee Belemnite (PDB) international standard:

$$\delta^{13}C = \frac{^{13}C/^{12}C\ \text{sample}}{^{13}C/^{12}C\ \text{standard}} - 1) \times 1000 \quad (1)$$

Estimating Soil pCO2

We use a reformulated version of a two-component mixing equation (Yapp and Poths 1996) to describe the relative contributions of atmospheric and soil-respired CO_2 in soils characterized by one-dimensional Fickian diffusion,

$$C_S = C_A \frac{\delta^{13}C_{Acc} - \delta^{13}C_{Occ}}{\delta^{13}C_{Scc} - \delta^{13}C_{Occ}} \quad (2)$$

where C_S is the concentration of soil CO_2 in ppmV, C_A is the concentration of atmospheric CO_2 in ppmV, $\delta^{13}C_{Acc}$ is the $\delta^{13}C$ value of calcite precipitated in equilibrium with only atmospheric CO_2, $\delta^{13}C_{Occ}$ is the $\delta^{13}C$ value of calcite precipitated in equilibrium with only soil-respired CO_2, and $\delta^{13}C_{Scc}$ is the measured $\delta^{13}C$ value of pedogenic calcite that precipitated in equilibrium with soil CO_2, which is a mixture of atmospheric and soil-respired CO_2.

This equation requires assumptions for atmospheric pCO_2, the $\delta^{13}C$ of the atmosphere, and soil temperature. The soil pCO_2 estimates published by Myers et al. (2012a) used an atmospheric pCO_2 value of 3,200 ppmV (approximately 10 times pre-industrial atmospheric levels, PAL), based on independent geochemical analysis of pedogenic carbonates from the Morrison Formation (Ekart et al. 1999). However, the calculations of atmospheric pCO_2 by Ekart et al. (1999) utilized a value of 5000 ppmV for the soil CO_2 production function, which is probably too high to accurately reflect the concentration of soil-respired CO_2 in carbonate-bearing soils during periods of soil-moisture deficit when pedogenic carbonate forms (Breecker et al. 2009; Tabor et al. 2013). Estimates of atmospheric pCO_2 by Ekart et al. (1999) are on the high end of the range of estimates produced by mass-balance models (e.g., Berner 2008) and stomatal index proxies (Retallack 2001) for the Late Jurassic.

The Late Jurassic atmospheric pCO_2 value of 1450 ppmV (5 × PAL) used here is a compromise between high values produced by the carbonate CO_2 paleobarometer (Ekart et al. 1999) and the low values suggested by recent mass-balance models (Berner 2006; Berner 2008), and approximates atmospheric pCO_2 estimates based on stomatal index (Retallack 2001). As in the earlier study (Myers et al. 2012a), the $\delta^{13}C$ value used for the atmosphere (–6.7‰ PDB) is based on the average $\delta^{13}C$ value of Upper Jurassic shallow marine carbonates (Veizer et al. 1999), incorporating a –8‰ offset between the oceanic and atmospheric reservoirs (Ekart et al. 1999).

The soil temperatures used in this model (25°C, 30°C) are based on a combination of paleotemperature estimates derived from Late Jurassic general-circulation models (Rees et al. 2000; Sellwood and Valdes 2006; Sellwood and Valdes 2008) and estimates derived from oxygen and hydrogen isotope analysis of pedogenic phyllosilicates from the Lourinhã Formation (Myers et al. 2012b). The measured $\delta^{13}C$ of OM is equivalent to the $\delta^{13}C$ value of soil-respired CO_2 (Ekart et al. 1999), but upward diffusion of soil-respired CO_2 through the soil profile causes enrichment in ^{13}C. The isotopic effects of this diffusive process are described by the following equation (Yapp and Poths 1993; Yapp 2001; Tabor et al. 2004):

$$\delta^{13}C_{CO2} = 1.0044\delta^{13}C_{OM} + 4.4, \quad (3)$$

in which $\delta^{13}C_{CO2}$ is the diffusion-corrected $\delta^{13}C$ value of soil-respired CO_2, and $\delta^{13}C_{OM}$ is the $\delta^{13}C$ value of soil organic matter (i.e., uncorrected soil-respired CO_2). The diffusion-corrected $\delta^{13}C$ value of soil-respired CO_2 is then converted to $\delta^{13}C_{Occ}$ using the temperature-dependent, carbon-isotope calcite-CO_2 enrichment factor experimentally determined by Romanek et al. (1992):

$$\varepsilon_{cc-CO2} = 11.98 - 0.12T\,(°C). \quad (4)$$

The enrichment factors determined for 25°C and 30°C with this equation are used to calculate both $\delta^{13}C_{Acc}$ and $\delta^{13}C_{Occ}$ in the two-component mixing equation described above.

RESULTS AND DISCUSSION

Revisiting the Original Dataset of Jurassic Paleosols

Average estimates of soil pCO_2 calculated from both modern and Upper Jurassic samples are reported to the nearest 100 ppmV, and negative values are not reported or included in statistics. Previously published soil pCO_2 estimates derived from an earlier version of this dataset (Myers et al. 2012a) were calculated using a Late Jurassic atmospheric CO_2 concentration of 3200 ppmV, based on work by Ekart et al. (1999), and used the $\delta^{13}C$ of allochthonous, fossilized plant OM to estimate soil OM $\delta^{13}C$. The resultant estimates of soil pCO_2—many of which exceeded 60,000 ppmV—averaged 68,100 ppmV for the Morrison Formation and 39,500 ppmV for the Lourinhã Formation, assuming a soil temperature of 25°C (Myers et al. 2012a). These high estimates of soil pCO_2 are inconsistent with low pCO_2 levels observed in modern carbonate-bearing soils (e.g., Breecker et al. 2009). Recalculating the pCO_2 estimates for the earlier dataset of Jurassic paleosols using a lower atmospheric pCO_2 of 1450 ppmV produces somewhat lower values that are nevertheless too high to regard as accurate (Fig. 2). Average soil pCO_2 values are 24,100 ppmV for the Morrison Formation (n = 30, 1σ = 51,900) and 27,000 ppmV for the Lourinhã Formation (n = 38, 1σ = 25,000), assuming a soil temperature of 25°C (Fig. 2A). Seventeen of the Lourinhã samples used for calculations at 25°C either produced negative pCO_2 estimates, which have no physical meaning, or had no occluded OM $\delta^{13}C$ measurements associated with them. These samples are not comparable with other results presented here, and therefore are not included in the statistics reported here. If a higher soil temperature of 30°C is used in calculations, soil pCO_2 estimates decrease, yielding averages of 7,800 ppmV (n = 30, 1σ = 4,900) for the Morrison Formation and 29,600 ppmV (n = 48, 1σ = 63,700) for the Lourinhã Formation (Fig. 2B). With the higher soil temperature (30°C), only three Lourinhã samples yield negative pCO_2 estimates and are excluded from reported statistics. The apparent discrepancy in sample size for the Lourinhã Formation arises from the greater number of negative pCO_2 values produced by using a lower soil temperature (25°C) in the pCO_2 calculations.

When occluded-OM $\delta^{13}C$ values are used in conjunction with the same set of calcite-sample $\delta^{13}C$ values (including only those samples with comparable, non-negative pCO_2 values for a given soil temperature), the carbonate CO_2 paleobarometer yields much lower estimates of soil pCO_2

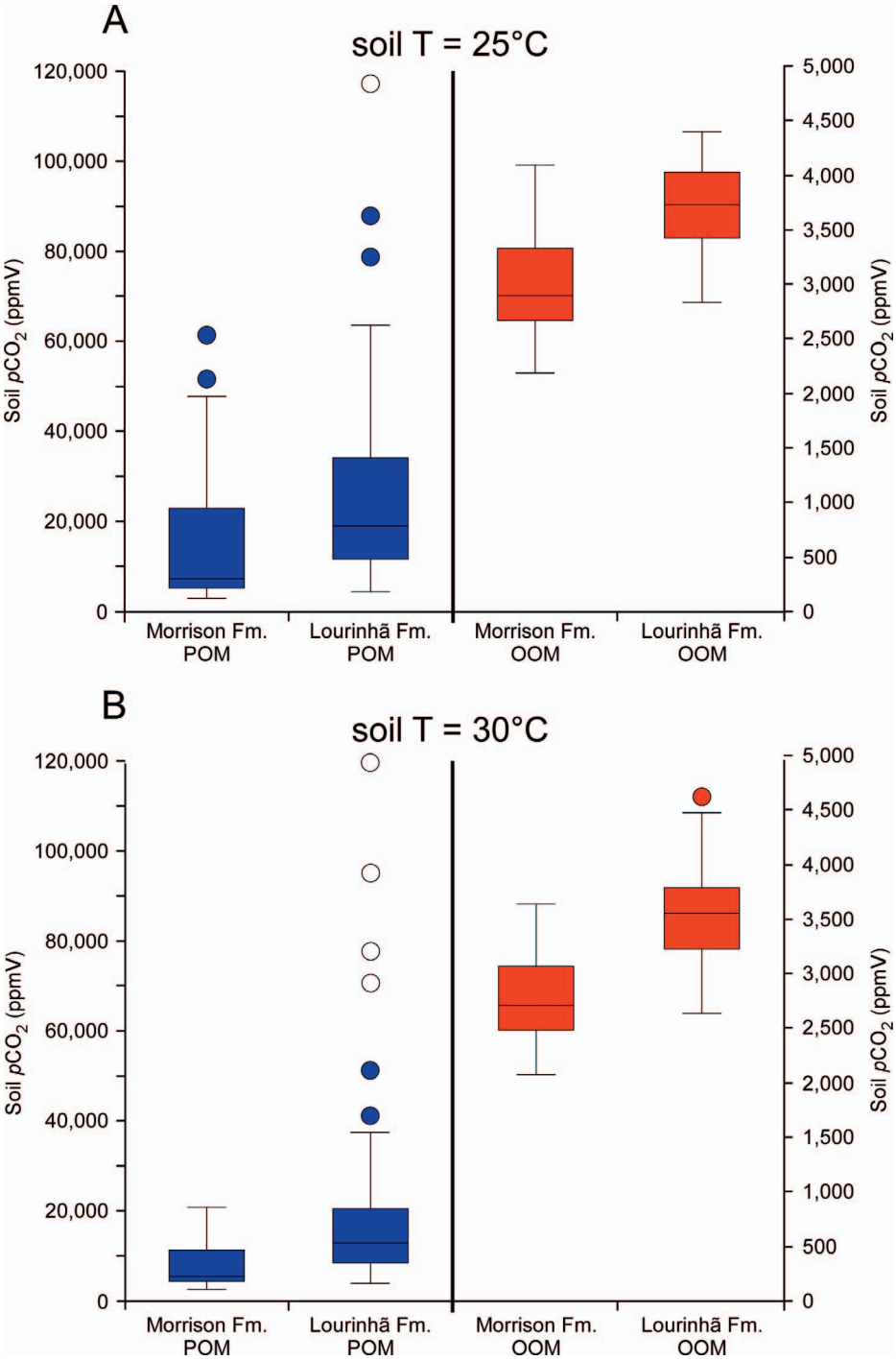

FIG. 2.—Box-and-whisker plots of soil pCO_2 estimates from Upper Jurassic localities in the Morrison and Lourinhã formations. **A)** Soil-pCO_2 estimates calculated using a soil temperature of 25°C. **B)** Soil-pCO_2 estimates calculated using a soil temperature of 30°C. Estimates plotted in blue are based on allochthonous plant OM, and the estimates plotted in red are based on occluded OM. Note the different scales for data on the left and right sides of the charts. In order to simplify figure scaling, one outlying data point of 429,800 ppmV is not shown on the plot of Lourinhã Formation estimates derived from allochthonous OM in Part B. The center line in the box-and-whisker plots represents the median, and the lower and upper limits of the box denote the first and third quartiles, respectively, which define the interquartile range (IQR). The whiskers represent the minimum and maximum values, unless these values are more than 1.5 × IQR beyond the first and third quartiles, respectively. Filled circles represent all values between 1.5 × IQR and 3.0 × IQR beyond the first and third quartiles. Outliers (values beyond 3.0 × IQR) are shown as open circles.

(Fig. 2). Average estimates of soil pCO_2 derived using occluded OM are 3,000 ppmV for the Morrison Formation (n = 30, 1σ = 400) and 3,700 ppmV for the Lourinhã Formation (n = 48, 1σ = 400), with soil temperature equal to 25°C (Fig. 2A). For a soil temperature of 30°C, soil pCO_2 averages are 2,800 ppmV (n = 30, 1σ = 400) for the Morrison Formation and 3,500 ppmV (n = 48, 1σ = 500) for the Lourinhã Formation (Fig. 2B). The results obtained using occluded OM rather than allochthonous, fossilized plant material, indicates that using different sources of OM to determine soil OM $\delta^{13}C$ yields vastly different estimates of pCO_2.

Testing a Modern Soil System

Analyses of modern DeStazo soil profiles yield some surprising results. Models of modern soil systems predict that the $\delta^{13}C$ of soil CO_2 decreases with increasing depth in the mixing zone of atmospheric and soil-respired CO_2 (Mora et al. 1993). However, $\delta^{13}C$ analyses of calcite in the DeStazo profile (n = 14) do not fit the expected pattern. The $\delta^{13}C$ values of soil calcite from carbonate nodules in the DeStazo profile range from –6.4 to –2.9‰, with an overall average of –4.3‰. The range of $\delta^{13}C$ values of soil calcite in each of the sampling intervals varies between 1.0 to 3.5‰, with an average range of 2.0‰. When samples in each of the four sampling

intervals are averaged, there is a general trend of increasing $\delta^{13}C$ values with increasing depth (Fig. 3A), the opposite of the expected trend for soil carbonates formed in equilibrium with soil CO_2 (Cerling 1984; Cerling and Quade 1993; Breecker et al. 2009). Deviations from the expected relationship between $\delta^{13}C$ and depth in a soil may arise from (1) hydromorphic conditions in part of the profile (Tabor et al. 2013) or (2) disturbance of the stratigraphic continuity of the profile, but there is no evidence for either of these in the DeStazo soil (Soil Survey Staff 2010).

The $\delta^{13}C$ values of plant root material (n = 11), sampled from five intervals in the DeStazo profile, range from –26.7 to –20.8‰ with an average of –23.7‰. The range of $\delta^{13}C$ values in each sampling interval varies between 0.1 and 5.9‰, with an average range of 1.9‰; comparable to the range of $\delta^{13}C$ values within soil calcite. The average $\delta^{13}C$ value of each interval does not vary substantially with depth, with the exception of outlier values between 53 and 81 cm below surface that are approximately 3–4‰ more negative than the average values for the other sampling intervals (Fig. 3B). Disregarding the negative outlier values between 53 and 81 cm, there is a subtle positive shift in $\delta^{13}C$ of approximately 1‰ from the uppermost sampling interval (0–4 cm) to the lowermost (81–132 cm). Similar patterns of increasing soil OM $\delta^{13}C$ with depth have been documented in modern soils (e.g., Wynn 2007; Cotton et al. 2012). Some coarse-textured, sandy soils—like the DeStazo profile—permit mixing of soil organic carbon with different $\delta^{13}C$ values, and therefore exhibit nearly invariant soil OM $\delta^{13}C$ (Wynn et al. 2005; Wynn 2007). Coarse, sand-size particles in these soils do not stabilize ^{13}C-enriched decomposition products like fine, clay-size matrix (Wynn et al. 2005). The occasionally large and generally unpredictable variability within and among the sampling intervals in the DeStazo soil profile likely reflects $\delta^{13}C$ variation among different plant species and different types of plant tissue that contribute to soil OM in this environment. The significant variability in $\delta^{13}C$ values in the plant material in the DeStazo profile effectively highlights the need for multiple OM samples in order to accurately characterize the average soil OM $\delta^{13}C$ in paleosols.

The number of $\delta^{13}C$ analyses of occluded OM (n = 5) is constrained by available sample volumes, such that only three intervals in the DeStazo profile yield occluded OM $\delta^{13}C$ values, and one interval is represented by a single analysis. The $\delta^{13}C$ values of the occluded OM ranges from –22.4 to –21.2‰, with an average of –21.7‰. When values in each sampling interval are averaged, there is an increase of approximately 0.8‰ with increasing depth in the profile. Overall, the $\delta^{13}C$ variability within occluded OM is much lower than the variability in the plant root matter samples, and the occluded OM samples are enriched in ^{13}C by approximately 2‰, on average, relative to plant root matter in the soil (Fig. 3C). When average $\delta^{13}C$ values of plant matter and occluded OM are compared within sampling intervals, and the interval with the negative outlier values of plant matter (53–81 cm) is excluded, the offset between the $\delta^{13}C$ of plant root matter and occluded OM is $\sim$ 1.1‰. Although the relationship between $\delta^{13}C$ and depth is complicated by significant variation in the $\delta^{13}C$ of plant matter, the average $\delta^{13}C$ values of both plant root matter and occluded OM appear to loosely track one another and increase by $\sim$ 1‰ over the 1.3 m sampled thickness of the DeStazo profile. These results are consistent with soil OM–CO_2 modeling and measurements that suggest occluded OM sampled from depth in a paleosol profile will become enriched in ^{13}C during decomposition (Bowen and Beerling 2004; Wynn et al. 2005, 2006; Wynn 2007).

In order to evaluate the effects of using various types of OM in the carbonate CO_2 paleobarometer, estimates of atmospheric pCO_2 were calculated using $\delta^{13}C$ values of plant root matter, occluded OM, and corrected (occluded) OM from the DeStazo soil. Soil CO_2 concentrations are not reported for the DeStazo series, but estimates of 500 and 750 ppmV are used based on dry-season soil pCO_2 measurements reported for similar soil-forming environments (Breecker et al. 2009). The $\delta^{13}C$ used for recent pre-industrial atmospheric CO_2 is –6.5‰ (Leuenburger et al. 1992), soil temperature at the time of calcite crystallization is assumed to be 29°C based on the average July temperature reported for the DeStazo soil series (Soil Survey Staff 2010), and the measured $\delta^{13}C$ values of pedogenic calcite and OM used in the pCO_2 calculations are listed in Table 1. The resultant estimates of atmospheric pCO_2 calculated using soil CO_2 concentrations of 500 and 750 ppmV compare favorably with the pre-industrial atmospheric CO_2 concentration of 290 ppmV (Fig. 4). The average estimates of atmospheric pCO_2 calculated with a soil pCO_2 of 500 ppmV provide the closer approximation to preindustrial atmospheric pCO_2 than those based on soil pCO_2 of 750 ppmV, although both sets of estimates fall within the range of standard error typically associated with pCO_2 estimates derived from paleosol carbonate (e.g., Cotton and Sheldon 2012). Estimates of atmospheric pCO_2 calculated using occluded OM from the DeStazo profile are lower than pCO_2 estimates based on associated plant OM by less than 100 ppmV, on average. The $\delta^{13}C$ values of occluded OM that have been corrected by subtracting 1‰ yield pCO_2 estimates closer to those based on the $\delta^{13}C$ of plant matter in the soil profile.

Expanding the Jurassic Paleosol Dataset

Once the effects of using various OM sources in pCO_2 calculations have been explored for a modern soil system, the information gleaned from this exercise can be applied to paleosols in order to constrain soil pCO_2 estimates. The original dataset of Upper Jurassic paleosols from the Morrison and Lourinhã formations has been expanded with the addition of new Morrison Formation localities in Utah and New Mexico, as well as samples from the Tendaguru Formation in Tanzania. The average $\delta^{13}C$ of fossilized vascular plant material collected from the Morrison and Lourinhã formations is –22.3‰ (n = 70, $1\sigma = \pm 1.5$‰; Fig. 5). Fossilized vascular plant-material from the Tendaguru Formation could not be obtained for this study. In contrast to the plant material $\delta^{13}C$, the $\delta^{13}C$ values of occluded OM from paleosol carbonate accumulations in the Morrison and Lourinhã formations are much more negative, with an average of –27.3‰ (n = 87, $1\sigma = \pm 1.2$‰; Fig. 5). The $\delta^{13}C$ values of occluded OM from all three study areas (–28.5‰ to –22.2‰, avg. –27.0) compare favorably with measured values for modern C_3 plants, which range between approximately –37‰ and –20‰, with an average of about –27‰ (Kohn 2010). This congruence suggests that the occluded OM has not been substantially altered by diagenesis and that there may instead be diagenetic or environmental factors affecting the $\delta^{13}C$ values of the fossilized plant material reported previously (Myers et al. 2012a). The average $\delta^{13}C$ value of fossilized vascular plant material from the Morrison and Lourinhã formations (–22.3‰) falls just outside the upper end of the range of $\delta^{13}C$ values for modern C_3 plants, which suggests that the plants may have been affected by either environmental stress or taphonomic or diagenetic factors.

Average soil pCO_2 values, calculated using occluded OM, are 3,000 ppmV for the Morrison Formation (n = 39, $1\sigma = 500$), 3,900 ppmV for the Lourinhã Formation (n = 48, $1\sigma = 600$), and 6,100 for the Tendaguru Formation (n = 6, $1\sigma = 2{,}200$), assuming a soil temperature of 25°C (Tables 2–4, Fig. 6A). When a soil temperature of 30°C is used, estimates of soil pCO_2 decrease, yielding averages of 2,800 ppmV ($1\sigma = 400$) for the Morrison Formation, 3,500 ppmV ($1\sigma = 500$) for the Lourinhã Formation, and 4,900 ppmV ($1\sigma = 1{,}400$) for the Tendaguru Formation (Tables 2–4, Fig. 6B). When occluded-OM $\delta^{13}C$ values are corrected by subtracting 1‰ in order to account for potential diagenetic enrichment during decomposition, the carbonate CO_2 paleobarometer yields slightly lower soil-pCO_2 estimates that, given the standard deviation reported here, are not significantly different from pCO_2 estimates calculated using uncorrected occluded-OM $\delta^{13}C$ values. Average soil pCO_2 estimates derived using corrected occluded OM (1‰ subtracted from measured values) are 2,800 ppmV for the Morrison Formation (n = 39, $1\sigma = 400$), 3,500 ppmV for the Lourinhã Formation (n = 48, $1\sigma = 400$), and 4,700 ppmV for the

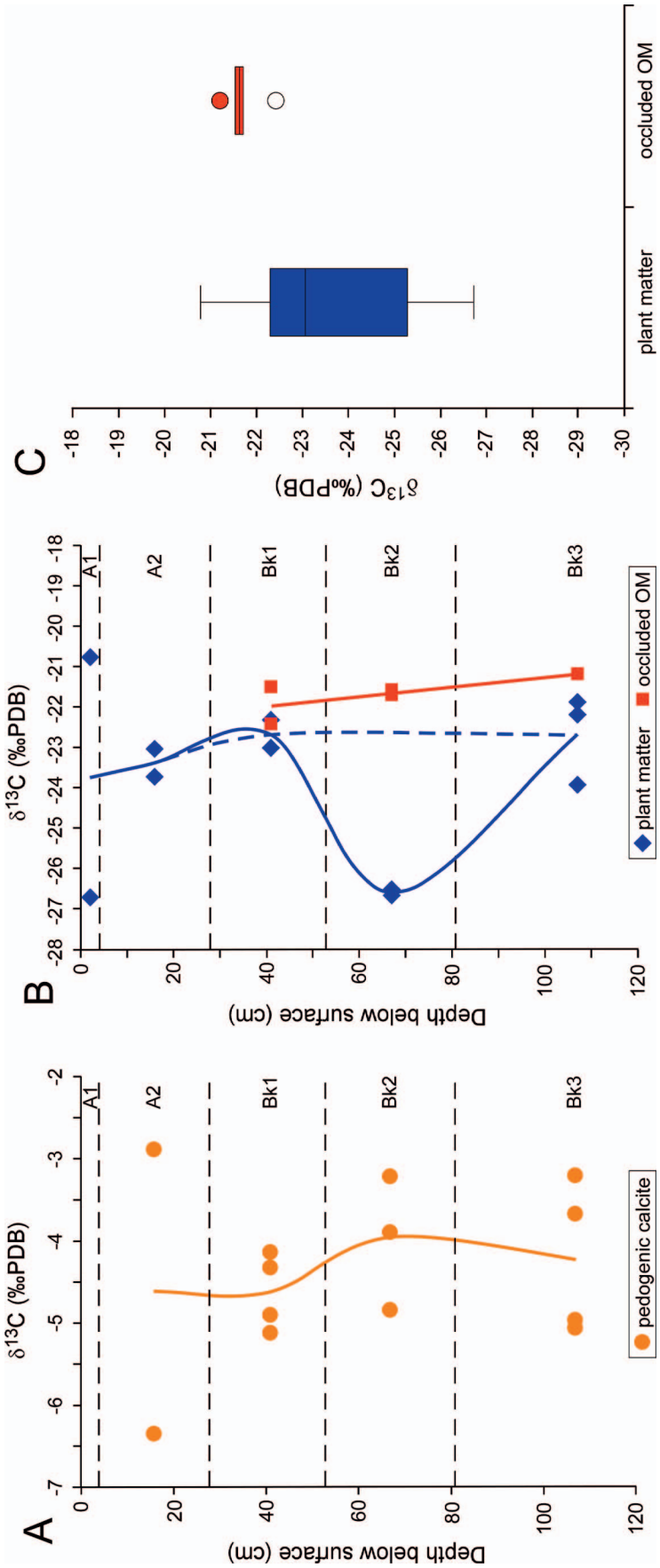

FIG. 3.—Plots of $\delta^{13}C$ values of pedogenic calcite and different sources of organic matter in the modern DeStazo soil profile. **A)** Plot of $\delta^{13}C$ values of calcite sampled from soil nodules (stage II carbonate accumulations *sensu* Gile et al. 1966) versus depth in the soil profile. Trend of mean values is denoted by solid orange line. **B)** Plot of $\delta^{13}C$ values of plant material and OM occluded in pedogenic carbonate nodules versus depth in the soil profile. Trends of mean values are denoted by solid blue and red lines. **C)** Box-and-whisker plots of $\delta^{13}C$ values of plant material and occluded OM collected throughout the entire DeStazo profile.

TABLE 1.—*Estimates of atmospheric* pCO_2 *from the DeStazo soil series (n = 5), calculated using soil temperatures of 29°C and the fractionation equation derived by Romanek et al. (1992).* $\delta^{13}C_{Atm} = -6.5‰$ *PDB,* $\delta^{13}C_{Acc} = 2.0‰$, $C_S = 500$ *ppmV, and 750 ppmV. In order to calculate* $\delta^{13}C_{Occ}$ *for each sample, add 12.9‰ to the measured* $\delta^{13}C$ *values of organic matter listed below. POM, plant organic matter; OOM, occluded organic matter; COR, corrected (occluded) organic matter.*

Sample	$\delta^{13}C_{Scc}$ (‰ PDB)	$\delta^{13}C_{POM}$ (‰ PDB)	$\delta^{13}C_{OOM}$ (‰ PDB)	$\delta^{13}C_{COR}$ (‰ PDB)	$C_{A\text{-}POM}$ (ppmV) (C_S = 500)	$C_{A\text{-}OOM}$ (ppmV) (C_S = 500)	$C_{A\text{-}COR}$ (ppmV) (C_S = 500)	$C_{A\text{-}POM}$ (ppmV) (C_S = 750)	$C_{A\text{-}OOM}$ (ppmV) (C_S = 750)	$C_{A\text{-}COR}$ (ppmV) (C_S = 750)
DS11-21C	–4.32	–22.7	–22.4	–23.4	232	225	247	348	338	371
DS11-21D	–4.91	–22.7	–21.5	–22.5	207	174	202	311	261	303
DS21-32C	–3.90	–26.6	–21.6	–22.6	312	224	248	468	336	372
DS21-32D	–3.21	–26.6	–21.7	–22.7	334	259	279	501	388	419
DS32-52C	–4.97	–22.7	–21.2	–22.2	205	162	192	307	242	287

Tendaguru Formation (n = 6, 1 = 1200) with soil temperature equal to 25°C (Fig. 6A). For a soil temperature of 30°C, mean soil-pCO_2 estimates calculated using corrected occluded OM are 2,600 ppmV ($1\sigma = 300$) for the Morrison Formation, 3,300 ppmV ($1\sigma = 400$) for the Lourinhã Formation, and 4,100 ppmV ($1\sigma = 900$) for the Tendaguru Formation (Fig. 6B).

In contrast to estimates obtained using allochthonous fossilized plant material, most of the soil-pCO_2 estimates calculated with both corrected and uncorrected occluded OM $\delta^{13}C$ fall within the range of CO_2 concentrations observed in modern carbonate-bearing soil systems (Retallack 2009 supplementary data; Montañez 2013; Tabor et al. 2013), although some are still higher than pCO_2 levels measured in some calcic soils (Breecker et al. 2009). Soil-pCO_2 estimates based on corrected occluded OM are anywhere from 200 to 2000 ppmV lower, on average, than estimates derived from uncorrected occluded OM. Given the results of the comparative tests of corrected and uncorrected occluded OM from the DeStazo profile, pCO_2 estimates based on either occluded OM input should provide a reasonably accurate approximation of actual soil CO_2 concentrations during pedogenic carbonate formation.

Both analytical uncertainties and uncertainties inherent to the carbonate CO_2 paleobarometer affect the precision of the pCO_2 estimates presented here. Analytical reproducibility for measurements of calcite ($\delta^{13}C_{Scc}$) and organic matter ($\delta^{13}C_{org}$) is no more than $\pm 0.1‰$. A change of 0.1‰ in both $\delta^{13}C_{Scc}$ and $\delta^{13}C_{org}$ results in a small uncertainty when estimated soil pCO_2 is small; however, the same 0.1‰ change produces a larger uncertainty when estimated soil pCO_2 is large. For example, an uncertainty of $\pm 0.1‰$ corresponds to a difference of < 100 ppmV in estimated soil pCO_2 for the sample associated with the lowest pCO_2 estimate calculated using uncorrected occluded OM (2,100 ppmV), whereas the same uncertainty induces a change of approximately $\pm 1{,}000$ ppmV for the sample with the highest pCO_2 estimate (9,100 ppmV). For the majority of the soil-pCO_2 estimates based on occluded OM, between 3000 and 4000 ppmV, the uncertainty associated with analytical variations of $\pm 0.1‰$ in $\delta^{13}C_{Scc}$ and $\delta^{13}C_{org}$ is approximately ± 100 ppmV.

Sensitivity to changes in the concentration of atmospheric CO_2 (C_A) is also directly related to the magnitude of estimated soil pCO_2. For the range of soil-pCO_2 estimates presented here, changes of ± 500 ppmV in C_A, commensurate with the largest fluctuations modeled for the Late Jurassic (Royer et al. 2004; Berner 2008), induce soil-pCO_2 changes of approximately 700–3,100 ppmV, depending on the magnitude of the soil-pCO_2 estimate. For most of the soil-pCO_2 estimates calculated using occluded OM, uncertainties related to inaccuracies in the assumed value of C_A will be 1,000–1,400 ppmV. If atmospheric $\delta^{13}C$ is adjusted by –1‰ (from –6.7‰ to –5.7‰), estimated soil pCO_2 for the occluded-OM sample with the smallest associated estimate increases by 100 ppmV, whereas estimated soil pCO_2 for the sample with the highest associated soil-pCO_2 estimate increases by 800 ppmV. Although the soil-pCO_2 model is clearly sensitive to changes in atmospheric pCO_2, this problem may be mitigated by comparing contemporary sites with reasonably good age constraints, such as the study sites considered here. Constraints on atmospheric $\delta^{13}C$ values are considerably better in the Cenozoic, for which high-resolution data from planktonic and benthic foraminifera are readily available (e.g., Zachos et al. 2001).

Previous sensitivity analyses for this model indicate that soil-CO_2 concentrations above 60,000 ppmV are not resolvable with reasonable precision (Myers et al. 2012a), but soil-pCO_2 levels in this range are not typically found in modern carbonate-bearing soils (Cerling and Quade 1993; Ekart et al. 1999; Breecker et al. 2009; Retallack 2009; Sheldon and

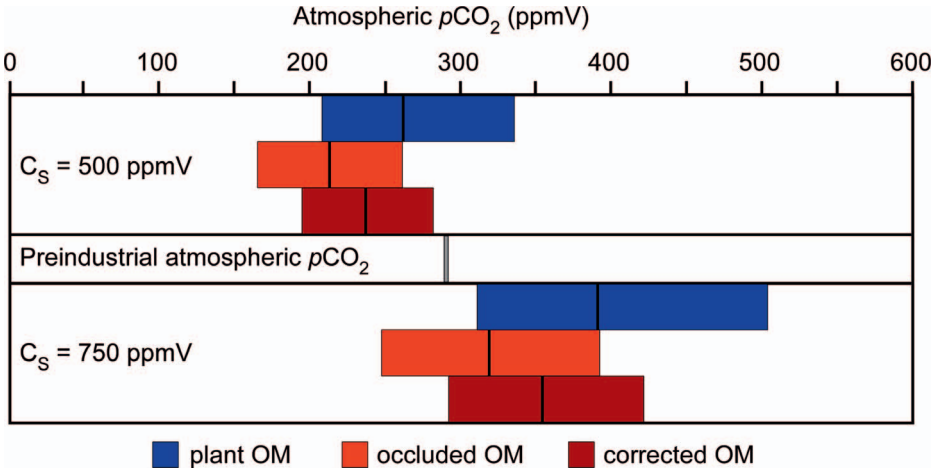

FIG. 4.—Plots of atmospheric-pCO_2 estimates derived from modern DeStazo samples compared with the measured, preindustrial atmospheric-pCO_2 value of 290 ppmV. Estimates of atmospheric pCO_2 were calculated using assumed soil-pCO_2 values of 500 and 750 ppmV. Colored bars denote range of data, and bold black lines represent mean values.

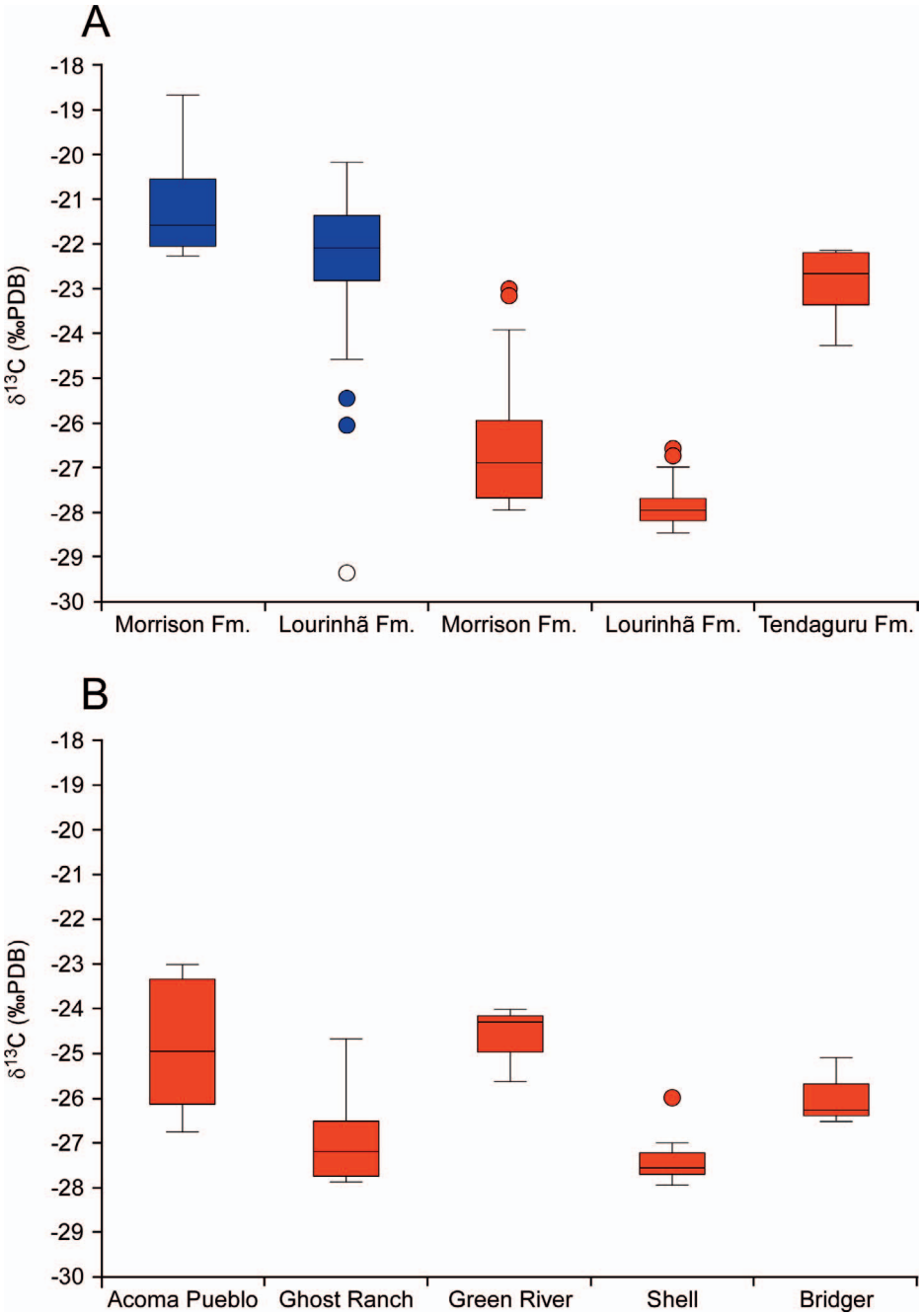

FIG. 5.—Box-and-whisker plots of $\delta^{13}C$ values of OM from various sources and localities. **A)** Plots comparing $\delta^{13}C$ values of allochthonous vascular plant OM (carbonized wood and disseminated plant fragments), in blue, and occluded OM isolated from pedogenic carbonates, in red. For the Morrison and Lourinhã formations, occluded OM is substantially more negative than allochthonous OM. Occluded OM from the Tendaguru Formation is more positive than that from the Morrison and Lourinhã formations. No fossilized plant material from the Tendaguru Formation was available for comparison. Averages for vascular-plant OM from the Morrison and Lourinhã formations are −21.0‰ (n = 4, 1σ = 1.6) and −22.3‰ (n = 66, 1σ = 1.4), respectively. Averages for occluded OM from each of the three study areas are −26.5‰ (n = 39, 1σ = 1.4) for the Morrison Formation, −27.9‰ (n = 48, 1σ = 0.4) for the Lourinhã Formation, and −22.9‰ (n = 6, 1σ = 0.9) for the Tendaguru Formation. Lourinhã Formation plant OM data are from Myers et al. (2012a). **B)** Plots comparing $\delta^{13}C$ values of occluded OM from various localities in the Morrison Formation, presented in order from south to north. Average values for each locality vary by as much as 2.7‰, but there are no clear geographic trends in the values. Averages are −24.8‰ for Acoma Pueblo (n = 6, 1σ = 1.7), −27.0‰ for Ghost Ranch (n = 17, 1σ = 0.9), −24.7‰ for Green River (n = 3, 1σ = 0.9), −27.4‰ for Shell (n = 10, 1σ = 0.6), and −26.0‰ for Bridger (n = 3, 1σ = 0.8).

Tabor 2009; Montañez 2013; Tabor et al. 2013). Modern carbonate-bearing soils are characterized by relatively low concentrations of soil-respired CO_2 during the warm, dry periods when carbonate precipitation occurs (Breecker et al. 2009; Retallack 2009; Breecker et al. 2010). Measurements of soil pCO_2 in Holocene soils suggest that a soil-respired CO_2 production value of 2500 ppmV more accurately reflects conditions during formation of pedogenic carbonate for many soils in arid and semiarid environments (Breecker et al. 2009; Retallack 2009; Breecker et al. 2010; Cotton and Sheldon 2012; Montañez 2013), although evidence exists for higher soil pCO_2 during calcite crystallization (Tabor et al. 2013). Comparison with these pre-industrial soil-pCO_2 measurements suggests that the Jurassic soil-pCO_2 estimates presented here, although much lower than previous estimates (Myers et al. 2012a) may still be somewhat high.

Soil OM–CO_2 models and measurements suggest that soil OM sampled from depth in a paleosol profile, such as organic matter occluded in pedogenic carbonates, will be microbially enriched in ^{13}C during decomposition (Bowen and Beerling 2004; Wynn et al. 2005, 2006; Wynn 2007), resulting in underestimates or negative estimates of atmospheric pCO_2. Indeed, soil OM $\delta^{13}C$ increases during decomposition (Nadelhoffer and Fry 1988; Schweizer et al. 1999; Wynn 2007) and with increasing depth in modern soil profiles (Nadelhoffer and Fry 1988; Melillo et al. 1989; Wynn et al. 2005, 2006). In order to compensate for the increase in OM $\delta^{13}C$ with depth in modern soils and better approximate the $\delta^{13}C$ of soil-respired CO_2, some researchers advocate subtracting 1‰ from measured paleosol OM $\delta^{13}C$ values (Breecker and Retallack 2014).

TABLE 2.—*Estimates of soil* pCO_2 *for the Morrison Formation (n = 39), calculated using soil temperatures of 25°C and 30°C, the fractionation equation derived by Romanek et al. (1992), and* $\delta^{13}C$ *of uncorrected occluded organic matter.* $\delta^{13}C_{Atm} = -6.7‰$ *PDB,* $C_A = 1450$ *ppmV. AP = Acoma Pueblo, NM; GR = Ghost Ranch, NM; SH = Shell, WY; MD = Bridger, MT; RRM = Green River, UT.*

Sample	$\delta^{13}C_{Scc}$ (‰ PDB)	$\delta^{13}C_{OOM}$ (‰ PDB)	$\delta^{13}C_{Occ}$ (‰ PDB) (25°C)	$\delta^{13}C_{Occ}$ (‰ PDB) (30°C)	C_S (ppmV) (25°C)	C_S (ppmV) (30°C)
AP03	–3.19	–26.0	–12.7	–13.3	2286	2150
AP04	–5.57	–23.9	–10.6	–11.2	3716	3321
AP05	–5.24	–23.2	–9.9	–10.5	3795	3362
AP06	–4.83	–26.2	–12.9	–13.5	2729	2540
AP07	–4.64	–26.8	–13.5	–14.1	2583	2420
AP10	–4.09	–23.0	–9.7	–10.3	3101	2802
GR006A	–6.58	–25.9	–12.6	–13.2	3584	3260
GR006B	–6.77	–27.2	–13.9	–14.5	3289	3035
GR007	–6.94	–27.4	–14.1	–14.7	3317	3061
GR010	–5.60	–27.8	–14.5	–15.1	2733	2561
GR0013	–6.55	–24.7	–11.4	–12.0	4090	3640
GR018	–6.71	–25.7	–12.4	–13.0	3739	3383
GR020	–6.48	–26.5	–13.2	–13.8	3338	3065
GR021	–6.73	–26.9	–13.6	–14.2	3350	3082
GR023A	–4.97	–26.9	–13.6	–14.2	2669	2496
GR024	–4.92	–27.8	–14.5	–15.1	2542	2392
GR025A	–4.67	–27.7	–14.4	–15.0	2486	2342
GR028A	–5.07	–27.4	–14.1	–14.7	2631	2467
GR029A	–4.31	–27.7	–14.4	–15.0	2398	2264
GR030	–5.10	–27.9	–14.6	–15.2	2576	2423
GR034	–5.62	–26.2	–12.9	–13.5	3024	2794
GR035	–5.24	–27.2	–13.9	–14.5	2710	2534
GR046B	–6.68	–27.8	–14.5	–15.1	3112	2891
MD010A	–4.18	–25.1	–11.8	–12.4	2681	2486
MD013A	–6.73	–26.5	–13.2	–13.8	3469	3175
MD014	–6.35	–26.3	–13.0	–13.6	3333	3058
SH008	–6.96	–27.1	–13.8	–14.4	3408	3134
SH018	–6.12	–26.0	–12.7	–13.3	3301	3026
SH020	–6.67	–27.5	–14.2	–14.8	3172	2938
SH021	–5.81	–27.7	–14.4	–15.0	2815	2632
SH023	–5.93	–27.0	–13.7	–14.3	2983	2770
SH025	–4.78	–28.0	–14.7	–15.3	2482	2341
SH027	–5.41	–27.8	–14.5	–15.1	2678	2513
SH028	–5.79	–27.7	–14.4	–15.0	2809	2627
SH029	–5.40	–27.7	–14.4	–15.0	2688	2520
SH030	–3.28	–27.5	–14.2	–14.8	2190	2076
RRM01	–3.47	–24.0	–10.7	–11.3	2606	2407
RRM02	–5.77	–25.3	–12.0	–12.6	3325	3033
RRM03	–4.54	–24.3	–11.0	–11.6	2984	2730

TABLE 3.—*Estimates of soil* pCO_2 *for the Lourinhã Formation (n = 48), calculated using* $\delta^{13}C$ *of uncorrected occluded organic matter.* $\delta^{13}C_{Atm} = -6.7‰$ *PDB,* $C_A = 1450$ *ppmV.*

Sample	$\delta^{13}C_{Scc}$ (‰ PDB)	$\delta^{13}C_{OOM}$ (‰ PDB)	$\delta^{13}C_{Occ}$ (‰ PDB) (25°C)	$\delta^{13}C_{Occ}$ (‰ PDB) (30°C)	C_S (ppmV) (25°C)	C_S (ppmV) (30°C)
PL005A	–9.00	–27.3	–14.0	–14.6	4717	4213
PL005B	–8.61	–28.0	–14.7	–15.3	4038	3677
PL019	–8.18	–27.7	–14.4	–15.0	3884	3543
PL025	–8.79	–28.4	–15.1	–15.7	3988	3643
PL026	–8.61	–27.7	–14.4	–15.0	4169	3779
PL028	–8.55	–27.7	–14.4	–15.0	4128	3746
PL036	–7.98	–27.7	–14.4	–15.0	3761	3441
PL039	–9.39	–27.8	–14.5	–15.1	4750	4253
PL076	–9.28	–28.3	–15.0	–15.6	4372	3958
PL050	–8.72	–28.2	–14.9	–15.5	4024	3669
PL051	–8.86	–28.4	–15.1	–15.7	4032	3680
PL052	–7.74	–28.4	–15.1	–15.7	3421	3164
PL065	–7.67	–28.0	–14.7	–15.3	3501	3226
PL067	–8.57	–27.7	–14.4	–15.0	4140	3755
PL071	–8.81	–28.0	–14.7	–15.3	4176	3791
PL074	–7.54	–28.2	–14.9	–15.5	3384	3129
PL081	–8.46	–28.1	–14.8	–15.4	3901	3565
PL086	–8.74	–28.0	–14.7	–15.3	4126	3750
PL087	–8.43	–27.7	–14.4	–15.0	4049	3680
PL113	–7.25	–27.8	–14.5	–15.1	3353	3098
PL115	–8.24	–26.7	–13.4	–14.0	4399	3943
PL131	–6.26	–28.2	–14.9	–15.5	2883	2696
PL135	–9.37	–28.3	–15.0	–15.6	4440	4014
PL139	–8.02	–28.2	–14.9	–15.5	3617	3328
PT009	–7.27	–27.5	–14.2	–14.8	3446	3172
PT011	–7.64	–27.5	–14.2	–14.8	3640	3336
PT015	–7.90	–27.7	–14.4	–15.0	3718	3405
PT032AB	–7.89	–28.4	–15.1	–15.7	3492	3225
PT048	–8.36	–28.0	–14.7	–15.3	3879	3545
PT061AB	–7.11	–27.5	–14.2	–14.8	3369	3107
PT076	–8.26	–28.4	–15.1	–15.7	3680	3384
PT079	–6.20	–27.8	–14.5	–15.1	2931	2734
PT092	–9.46	–27.5	–14.2	–14.8	5033	4469
PT094	–8.52	–28.2	–14.9	–15.5	3900	3566
PT107	–9.56	–27.9	–14.6	–15.2	4847	4333
PT114	–9.16	–28.1	–14.8	–15.4	4385	3965
PT121	–9.20	–28.0	–14.7	–15.3	4469	4031
PT123	–9.43	–27.2	–13.9	–14.5	5233	4617
PT128	–7.63	–27.6	–14.3	–14.9	3603	3306
PT139A	–9.06	–28.2	–14.9	–15.5	4262	3866
PT137AB	–8.15	–28.0	–14.7	–15.3	3755	3441
PT098	–6.65	–28.4	–15.1	–15.7	2981	2784
PT144AB	–8.12	–28.0	–14.7	–15.3	3738	3427
PT149A	–8.14	–28.4	–15.1	–15.7	3617	3331
PT164	–5.86	–27.0	–13.7	–14.3	2957	2748
PT180	–5.31	–26.6	–13.3	–13.9	2828	2631
PT184	–6.99	–28.5	–15.2	–15.8	3084	2875
PT187	–8.51	–27.9	–14.6	–15.2	4017	3658

Modern data collected from the DeStazo soil profile (Fig. 3) indicate that the average $\delta^{13}C$ of occluded OM is approximately 1‰ more positive than that of plant matter in the same soil horizon. Therefore, subtracting 1‰ from measured $\delta^{13}C$ values of OM occluded in paleosol carbonates should more closely approximate the original $\delta^{13}C$ values of associated plant matter present during pedogenesis. Both corrected (1‰ subtracted from measured values) and uncorrected (measured values) occluded-OM $\delta^{13}C$ values appear to yield reasonable approximations of pCO_2, and differences between pCO_2 estimates derived from these two types of occluded-OM values are less than the uncertainties associated with the carbonate CO_2 paleobarometer. When using fossilized plant material to estimate soil-OM $\delta^{13}C$, it is important to remember that the $\delta^{13}C$ value of the plant matter may vary substantially, depending on which taxa or types of tissue are sampled (O'Leary 1981), not to mention natural variation between the same structures in a single plant (Leavitt and Long 1986). In contrast, the lower variability in $\delta^{13}C$ observed in OM occluded in pedogenic carbonate suggests that this material has undergone some homogenization, but identification of the specific chemical compounds that constitute occluded-OM samples can provide important information regarding decomposition processes.

Use of occluded OM in calculations of atmospheric pCO_2 sometimes yields negative pCO_2 estimates (Sinha and Stott 1994; Cotton and Sheldon 2012; Cotton et al. 2015), often due to precipitation of pedogenic carbonate under soil conditions where atmospheric and soil-respired CO_2 do not mix

TABLE 4.—*Estimates of soil* pCO_2 *for the Tendaguru Formation (n = 6), calculated using* $\delta^{13}C$ *of uncorrected occluded organic matter.* $\delta^{13}C_{Atm}$ *= –6.7‰ PDB,* C_A *= 1450 ppmV.*

Sample	$\delta^{13}C_{Scc}$ (‰ PDB)	$\delta^{13}C_{OOM}$ (‰ PDB)	$\delta^{13}C_{Occ}$ (‰ PDB) (25°C)	$\delta^{13}C_{Occ}$ (‰ PDB) (30°C)	C_S (ppmV) (25°C)	C_S (ppmV) (30°C)
WJ 3396	–6.64	–23.5	–10.2	–10.8	5088	4355
JG 61	–6.65	–24.3	–11.0	–11.6	4429	3893
Tin 7h	–4.92	–23.0	–9.7	–10.3	3640	3234
Tin 7h2	–7.01	–22.2	–8.9	–9.5	8601	6527
Tin 7i	–6.04	–22.2	–8.9	–9.5	5682	4696
Tin 7l2	–7.19	–22.3	–9.0	–9.6	9060	6803

freely (e.g., hydromorphic conditions) or because the difference between the estimated value of soil OM and the measured value of pedogenic calcite ($\Delta^{13}C_{cc-org}$) is too low (Cotton and Sheldon 2012; Tabor et al. 2013). Studies that employ alternative methods of estimating the $\delta^{13}C$ value of soil OM (e.g., allochthonous OM; Myers et al. 2012a) can also produce negative pCO_2 estimates that arise from low $\Delta^{13}C_{cc-org}$ values connected to inaccurate estimation of soil OM $\delta^{13}C$ rather than lack of two-component CO_2 equilibrium in the original soil profile. In addition to avoiding the use of external OM sources to approximate the $\delta^{13}C$ of soil OM, it is also imperative to carefully evaluate whether paleosols are suitable for use with the carbonate CO_2 paleobarometer before using pedogenic carbonate to estimate atmospheric or soil pCO_2 (Tabor and Myers 2015).

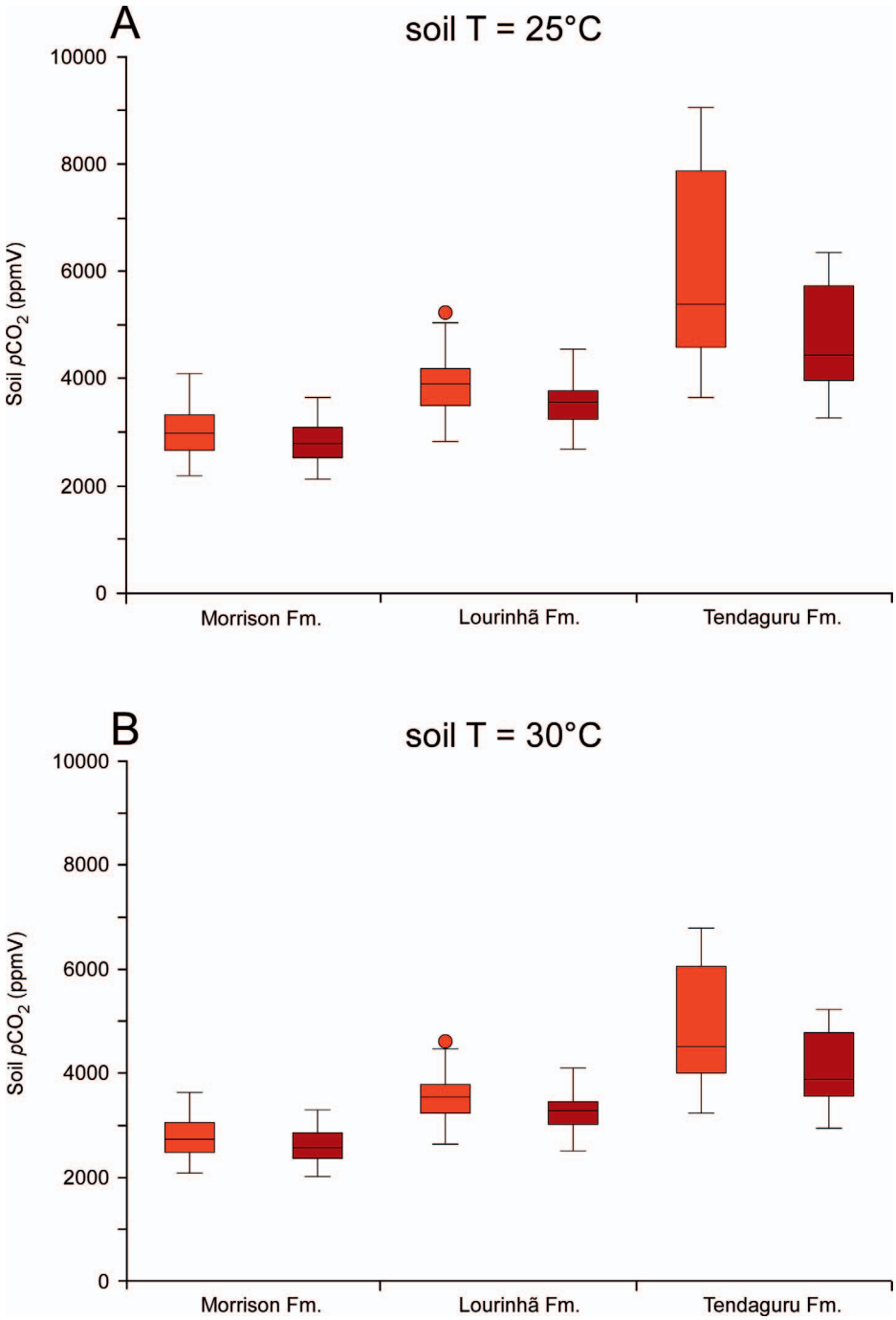

FIG. 6.—Box-and-whisker plots of soil pCO_2 estimates calculated using corrected (1‰ subtracted), in red, and uncorrected occluded OM, in dark red. **A)** Estimates of soil pCO_2 calculated assuming a soil temperature of 25°C. Average estimates for uncorrected occluded OM, rounded to the nearest 100 ppmV, are 3,000 ppmV for the Morrison Formation (n = 39, 1σ = 500), 3,900 ppmV for the Lourinhã Formation (n = 48, 1σ = 600), and 6,100 ppmV (n = 6, 1σ = 2,200) for the Tendaguru Formation. Soil-pCO_2 estimates for corrected occluded OM are 2,800 ppmV (1σ = 400) for the Morrison Formation, 3,500 ppmV (1σ = 400) for the Lourinhã Formation, and 4,700 ppmV (1σ = 1,200) for the Tendaguru Formation. **B)** Soil-pCO_2 estimates calculated assuming a soil temperature of 30°C. Average estimates are 2,800 ppmV (1σ = 400) for the Morrison Formation, 3,500 ppmV (1σ = 500) for the Lourinhã Formation, and 4,900 ppmV (1σ = 1,400) for the Tendaguru Formation. Estimates of soil pCO_2 for corrected occluded OM are 2,600 ppmV (1σ = 300) for the Morrison Formation, 3300 ppmV (1σ = 400) for the Lourinhã Formation, and 4,100 ppmV (1σ = 900) for the Tendaguru Formation.

CONCLUSIONS

The estimates of soil pCO_2 presented here indicate that Late Jurassic soil-forming environments of the Tendaguru Formation had the highest soil-pCO_2 levels, and samples from the Morrison Formation yield the lowest soil-pCO_2 estimates of the three study areas. Comparison of soil-pCO_2 estimates calculated using allochthonous and occluded OM demonstrates that appropriate OM sourcing is critical to producing reliable pCO_2 estimates with the carbonate CO_2 paleobarometer. The $\delta^{13}C$ values of plant material in a soil profile may vary substantially and may not provide the best approximation of soil-OM $\delta^{13}C$, especially with a small sample size. Even $\delta^{13}C$ values averaged from large samples of plant material, such as the allochthonous fossilized material collected from the Lourinhã Formation, are not necessarily suitable for use with the carbonate CO_2 paleobarometer. In contrast, OM occluded in pedogenic carbonates yields reasonable soil-pCO_2 estimates. Analysis of a modern soil system shows that occluded OM is enriched in ^{13}C by approximately 1‰, on average, relative to plant OM in the same horizon.

Future studies should focus on characterizing the composition of the OM occluded in modern and ancient pedogenic carbonates in order to better understand the origin and nature of this organic material. Recent studies suggest the soil-CO_2 concentration is positively correlated with primary productivity in terrestrial environments (Myers et al. 2012a), and soil-respired CO_2 levels are related to mean annual precipitation (Cotton and Sheldon 2012). Therefore, soil-pCO_2 measurements have the potential to become a valuable proxy for both floral biomass and moisture availability in ancient terrestrial ecosystems.

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