Atmospheric $p$CO$_2$ Reconstruction of Early Cretaceous Terrestrial Deposits in Texas and Oklahoma Using Pedogenic Carbonate and Occluded Organic Matter

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Abstract: Pedogenic carbonate samples collected from three Lower Cretaceous (Aptian–Albian) fossil localities in Texas and Oklahoma were analyzed to develop paleoatmospheric $p$CO$_2$ estimates by measuring the stable carbon isotopes of pedogenic calcite and their co-existing occluded organic matter. Calcite $\delta^{13}$C values ranged from $-10.9\, %$ to $-4.4\, %$ while occluded organic matter $\delta^{13}$C values ranged from $-27.3\, %$ to $-21.1\, %$. These stable carbon isotope measurements combined with temperature (30 °C) and soil-respired CO$_2$ concentration (839–6047 ppmV) values provided atmospheric $p$CO$_2$ estimates ranging from 67 ppmV to over 1100 ppmV. These estimates show a significant increase in atmospheric $p$CO$_2$ during the late Aptian followed by a decrease in atmospheric $p$CO$_2$ during the late Aptian to early Albian transition period, roughly correlating with the OEA1b event. Given the lack of chronostratigraphic constraints of the Lower Cretaceous geologic units in the study area, these data provide further evidence for the approximate age of the units as well as pertinent paleoclimate insights into greenhouse climate conditions.

Keywords: paleosol; pedogenic carbonate; organic matter; $\delta^{13}$C values; $\delta^{18}$O values; Albian; Aptian

1. Introduction

The Cretaceous climate has long been an area of keen interest as computer-based models and proxy-based paleoclimatic studies aim to understand this “greenhouse” period. Recently, the terrestrial carbon isotope record has become a major contributing factor in discovering the correlation between shifts in Earth’s near-surface global carbon $\delta^{13}$C compositions, including oceanic anoxic events (OAEs), and its relationship to changes in climate during the Early Cretaceous [1–5]. Here, we present data from paleosol calcite from the Aptian–Albian terrestrial units of Texas and Oklahoma in an effort to understand changes in atmospheric $p$CO$_2$ and its correlation(s) with regional and potentially global climatic changes, as deduced from independent geochemical proxies within these paleosols, including paleoprecipitation and paleotemperature, as well as other paleoenvironmental and paleoclimatic information offered by previously published work on Lower Cretaceous deposits. Furthermore, we aim to understand the correlation between changes in estimated atmospheric $p$CO$_2$ levels and global ocean–atmospheric events identified during the Aptian–Albian period.

2. Materials and Methods

2.1. Geologic Setting

Three localities were sampled for this study, spanning the Lower Cretaceous (Aptian–Albian) stratigraphy of North Central Texas and southern Oklahoma. The precise correlation of these localities is difficult as the succession includes the time-transgressive...
progradational and retrogradational sequences of the Western Interior Seaway, which have produced a complicated succession of interfingering carbonates, mudstones, sandstones, and rare coals that are reflective of both continental and marine facies. Nevertheless, the stratigraphic analysis by Jacobs and Winkler [6] (Figure 1) provided sufficient constraints to place these localities within a framework that ensures chronological order and biostratigraphic separation at the geological stage scale, albeit without chronometric dates.

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Paleosols from the Twin Mountains Formation were sampled at two fossil localities: Proctor Lake and Jones Ranch (Figure 1, sites 1 and 2). Paleosols at the Proctor Lake locality were first discovered during the excavation of fossil material from Convulosaurus marri, a basal ornithopod dinosaur [14]. The locality lies in the lower Twin Mountains Formation, approximately 17 m above the Pennsylvanian contact and 35 m below the Glen Rose Formation contact [15]. Pedogenic carbonate nodules measuring 3–5 cm in diameter

![Figure 1](image-url)
were recovered from a single Bk horizon in the lower section of the 3.2 m paleosol profile. These samples were labeled PL-3, PL-6, and PL-8. The observed paleosols consisted of a series of stacked B horizons and were previously classified as vertic Calcisols that contain prismatic peds, highly reactive carbonate matrix, infill dikes, and vermicular mottles [16] (Figure 2).

The Jones Ranch fossil locality occurs stratigraphically higher in the Twin Mountains Formation than the Proctor Lake locality, correlating with localities that are latest Aptian–early Albian in age (~113 Ma) [6,15,17,18]. A previous sedimentological study of the strata associated with the Jones Ranch fossil quarry interpreted the dinosaur-bearing strata as having been a broad and shallow ephemeral fluvial channel that occurred ~9.7 m below the Twin Mountains Formation’s upper contact with the Glen Rose Formation [18]. The dinosaur-bearing strata at the quarry consist of a lower, 40-cm thick bed that scours the underlying unfossiliferous stratum and fines upward from a basal concretionary sandstone with clay rip-up clasts to trough cross-bedded sandstone and an upper, 30-cm thick bed of cross-bedded sandstone with lenticular mud drapes and abundant fossil charcoal, wood, tree trunks up to 6 m in length, and plant debris. The 80-cm thick unit of fine-grained sandstones overlying the bone-bearing strata has a massive to single-grain soil texture and preserves the calcareous nodules and tubules that are interpreted to be the products of pedogenesis in a semi-arid climate (i.e., a paleosol, [18], Figure 2). These calcareous tubules from the paleosol profile were collected for geochemical study. The tubules are concentrated in 50 cm of outcrop and occur as irregular but continuous cylinders of micritic calcite with a uniform diameter of ~5–8 mm and common, small (1–2 mm diameter) channels of carbonate that extend outward along the length of and perpendicular to the main cylinder. The 13 calcareous tubules, labeled CR1–CR13, that were collected from the outcrop all had similar diameters (~5–8 mm) but ranged in length from ~20 mm to 75 mm. These tubules were interpreted as being root petrifactions (i.e., rhizoliths, [19]) that formed around and replaced root systems in the soil during Early Cretaceous pedogenesis.

The Twin Mountains and Paluxy Formations, both of which are interpreted as representing littoral to continental sedimentary deposits, are separated by the marine-dominated sedimentary rocks of the Glen Rose Formation in the southern part of the study area (Figure 1). To the north, the marine-dominated Glen Rose Formation pinches out and

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**Figure 2.** Paleosol outcrops and pedogenic features: (A) a cross section of the vertic Calcisols documented at the Proctor Lake locality with an arrow scale bar of 10 cm (Twin Mountains Formation); (B) a cross section of the outcrop at the Jones Ranch locality (Twin Mountains Formation); (C) pedogenic carbonate nodules recovered from the Oklahoma locality (Antlers Formation).
the continental-dominated Twin Mountains and Paluxy Formations combine to form the Antlers Formation (Figure 1), which contains claystone layers with unconsolidated sandstone lenses and carbonate concretions that have been interpreted as representing fluvial, deltaic, and strandplain settings [17,20]. The vertebrate fauna of the Antlers Formation is similar to that of the Twin Mountains and Paluxy Formations [21].

The precise stratigraphic positions of localities within the Antlers Formation are difficult to determine because of the absence of the Glen Rose Formation as a marker. The locality sampled in Oklahoma is stratigraphically equivalent with sections measured at fossil locality OMNH V706, which is considered to be in the middle Antlers Formation, occurring ~87 m above the base [22] (Figure 1, site 3). The stable carbon isotope ratios from fossil wood at this site are consistent with those from the middle of the Glen Rose Formation, which is considered to be Early Albian in age, based upon a stable carbon isotope chemostratigraphic correlation between Cretaceous vascular plant organic matter and shallow marine calcite [23]. The paleosol profile, identified as a calcic Vertisol, measures 2.36 m in thickness with fine to medium wedge-shaped peds that collectively define large arcuate slickenplanes at depth within the profile [16]. Pedogenic carbonate nodules up to 5 cm in diameter were collected from a single Bk horizon and were labeled as Cross-C1, Cross-C9, and Cross-C10 (Figure 2). All discrete pedogenic nodules and calcareous rhizoliths were collected from depths greater than 50 cm below the ancient soil surface, ensuring consistency in the isotopic composition and the pressure of soil CO₂ [24,25].

2.2. Laboratory Methods

Aliquots of each sample were ground separately with a corundum mortar and pestle to pass through a <62 µm sieve. To verify that the carbonate samples contained only low-Mg calcite, the samples were analyzed by powder X-ray diffraction using a Rigaku Ultima III X-ray diffractometer equipped with a Cu–Ka radiation X-ray source at Southern Methodist University (SMU). X-ray scans ranged from 2–70° 2θ with step lengths of 0.04° 2θ and at a rate of 1° 2θ/min. Another aliquot of each section was prepared as petrographic thin sections (~100 µm thick) and stained using alizarin red-S in order to confirm the presence of calcite. Each thin section was inspected with its matching billet under a reflected light microscope in order to verify that micrite (~<20 µm carbonate crystal size) was the only cement texture present and that later diagenetic textures, such as sparry calcite or dolomite cements, were absent. The samples selected for further analyses contained only micritic low-Mg calcite. The powders that were used for the X-ray diffraction analyses were then used as materials for the determination of pedogenic carbonate and co-existing occluded organic matter 13C values, as described below.

Paleosol carbonate powders from each sample were split into two fractions: one fraction that underwent no further chemical pretreatments, which was analyzed for calcite 13C and 18O values (see below), and a second fraction that was acidified in concentrated (~12 N) HCl solution. Each acid-treated fraction (Table 1) was kept in contact with ~12 N HCl solution for at least 24 h and fresh aliquots of ~12 N HCl solution were introduced to these fractions every 12 h until no effervescence could be detected. These acid-treated fractions were then rinsed with de-ionized H₂O until the rinse water remained at the original pH of the de-ionized H₂O (~5.6) after at least 10 min of contact with the acid-leached residue. The acid pretreatment of these fractions was designed to remove carbonate minerals from the samples and concentrate any finely disseminated occluded organic matter within the acid-treated residue. The carbon concentration and 13C values of these samples were determined from the CO₂ produced by the closed system combustion of the organic matter, following the methods of Boutton [26]. Gas samples produced by the combustion were cryogenically purified to isolate CO₂ and the CO₂ yields were measured via mercury manometry, with a precision of ± 0.2 µmol, using high-vacuum glass extraction lines at SMU.
Table 1. The paleosol carbonate stable isotopic values of the measured $\delta^{13}$C of calcite ($\delta^{13}$C$_\text{carb} \text{‰ VPDB}$), the measured $\delta^{13}$C of acid-treated residues containing occluded organic matter ($\delta^{13}$C$_\text{om} \text{‰ VPDB}$), the differences between paired calcite and co-existing occluded organic matter ($\Delta^{13}$C$_{cc-om}$), and the estimated $\delta^{13}$C of soil-respired CO$_2$ at the time of calcite crystallization ($\delta^{13}$C$_S$) based on the measured values of the occluded organic matter corrected for diffusion enrichment assuming a soil temperature of 30 °C ($\delta^{13}$C$_S$ ‰ VPDB, 30 °C). Replicate analyses are marked with “R”.

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<th>Location</th>
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<th>$\delta^{13}$C$_\text{carb}$ (‰ VPDB)</th>
<th>$\delta^{13}$C$_\text{om}$ (‰ VPDB)</th>
<th>$\Delta^{13}$C$_{cc-om}$ (%)</th>
<th>$\delta^{13}$C$_S$ (‰ VPDB, 30 °C)</th>
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For the determination of the calcite $\delta^{13}$C and $\delta^{18}$O values, between 10.0 and 19.2 mg of carbonate-bearing powders were loaded into reaction vessels and their atmospheric gases were evacuated. The samples were then dissolved in 100% H$_3$PO$_4$ in vacuo at 25 °C for ~16 h to produce CO$_2$. The CO$_2$ samples resulting from the acid dissolution of the calcite were cryogenically purified to isolate CO$_2$ and the CO$_2$ yields were measured via mercury manometry, with a precision of ± 0.2 µmol, using high-vacuum glass extraction lines at SMU. The CO$_2$ resulting from the combustion of acid-treated residue fractions, as well as all of the aliquots of the calcareous tubules, were analyzed for carbon and oxygen stable isotope ratios using a Finnigan MAT 253 isotope ratio mass spectrometer at SMU. The carbon and oxygen isotope values are reported in per mille notation and “std” corresponds to the Vienna Peedee Belemnite (V-PDB) standard [27,28].
2.3. Estimating Atmospheric CO₂

The atmospheric pCO₂ estimates were made using the δ¹³C values measured from the pedogenic calcite and occluded organic matter in combination with a reformulated version of a two-component mixing equation [29]:

\[
C_A = C_S \times \frac{\delta^{13}C_{m(\text{cc})} - \delta^{13}C_{O(\text{cc})}}{\delta^{13}C_{A(\text{cc})} - \delta^{13}C_{O(\text{cc})}}
\]

(1)

where \(C_A\) is the concentration of atmospheric CO₂ in ppmV, \(C_S\) is the concentration of soil CO₂ in ppmV, \(\delta^{13}C_{O(\text{cc})}\) is the δ¹³C of calcite precipitated in equilibrium with only soil-respired CO₂, \(\delta^{13}C_{A(\text{cc})}\) is the δ¹³C value of calcite precipitated in equilibrium with only atmospheric CO₂, and \(\delta^{13}C_{m(\text{cc})}\) is the measured δ¹³C value of pedogenic calcite that precipitated in equilibrium with soil CO₂, which is a mixture of atmospheric and soil-respired CO₂.

To calculate the atmospheric pCO₂ estimates, this equation required assumptions for the soil pCO₂, the δ¹³C of the atmosphere, and the soil temperature at the time(s) of calcite crystallization in the soil. A value of −6.5‰ was chosen for the δ¹³C value of Early Cretaceous paleatmospheric CO₂ [2,25,30–33]. A soil temperature of 30 °C was chosen based on paleotemperature estimates derived from the oxygen and hydrogen isotope analyses of pedogenic phyllosilicates from the paleosols associated with each locality considered here [16]. The measured δ¹³C of occluded organic matter was related to the δ¹³C of soil-respired CO₂ [25]; however, the δ¹³C of the occluded organic matter had to be corrected to account for the upward carbon isotope diffusion of the soil-respired CO₂ through the soil profile, which causes an enrichment in δ¹³C of at least 4.4‰ [34]. This was estimated using the following equation [35–38]:

\[
\delta^{13}C_{\text{CO}_2} = 1.0044\delta^{13}C_{\text{OM}} + 4.4
\]

(2)

where \(\delta^{13}C_{\text{CO}_2}\) is the diffusion-corrected δ¹³C value of soil-respired CO₂ and \(\delta^{13}C_{\text{OM}}\) is the measured δ¹³C value of organic matter for the acid-treated residues (i.e., uncorrected soil-respired CO₂). The temperature-dependent, stable carbon isotope, calcite–CO₂ enrichment factor was then applied to the diffusion corrected δ¹³C of CO₂ to calculate δ¹³C of soil CO₂ using the following equation [39]:

\[
\varepsilon_{\text{cc}-\text{CO}_2} = 11.98 - 0.12 \times T(°C)
\]

This same enrichment factor was also applied to calculate the δ¹³C of soil-respired CO₂ (Cs) was a significant source of uncertainty when estimating atmospheric pCO₂. Various levels of soil pCO₂, ranging from 1000 ppmV to 6000 ppmV, have been used throughout the literature to estimate atmospheric pCO₂ levels in the Early Cretaceous [2,4,25,32]. We present two models that used the following soil pCO₂ values: 1250 ppmV and 2000 ppmV. This range was supported by applying methods outlined by Cotton and Sheldon [40], who estimated Cs using mean annual precipitation in modern soils with the following equation:

\[
Cs = 5.67 \times \text{MAP} - 269.9
\]

(3)

where soil-respired CO₂ (Cs) is in ppm and mean annual precipitation (MAP) is in mm/yr. Using CALMAG data [41] as proxy estimates for MAP, which were initially reported in Andrzejewski and Tabor [16] for the same localities that were sampled for this study, we estimated the minimum and maximum levels of soil-respired CO₂ using the MAP relationship reported by Cotton and Sheldon [40]. However, it was noted that the modern soil dataset used by Cotton and Sheldon [40] did not include humid climate soils, such as Vertisols, which are present in our dataset. Although changes in the soil pCO₂ affected the
estimated numeric value of atmospheric $pCO_2$, the trends and relative difference between
the locality estimates remained the same.

Additionally, the mean annual precipitation was estimated using the negative corre-
lation between the $\Delta^{13}C$ of paired calcite–occluded organic matter samples described in
Tabor et al. [42] using the following equation:

$$\Delta^{13}\text{C}_{\text{cc-om}} = -0.31 \times \text{MAP(cm)} + 25.43$$

where $\Delta^{13}\text{C}_{\text{cc-om}}$ is the measured difference between the $\delta^{13}\text{C}$ of measured pedogenic
calcite and the corresponding occluded organic matter of the analyzed samples. MAP is
the mean annual precipitation estimated in cm/yr. It was noted that this correlation was
only documented in soils where MAP was < 500 mm/yr [42].

3. Results

3.1. Pedogenic Carbonate

The results of the 33 analyses of $CO_2$ derived from the phosphoric acid dissolu-
tion of calcite powders among the 19 different calcareous tubules and nodules collected
from the Aptian–Albian paleosol profiles are presented in Tables 1 and S1 and Figure 3.
The $CO_2$ yields from these analyses indicated that the samples ranged from 57 to nearly
100 weight percent calcite, with a mean of $89 \pm 11$ wt.% (1σ). The calcite $\delta^{13}\text{C}$
values from the Proctor Lake profile ranged from $-8.0\%$ to $-7.8\%$ with a mean value of
$-7.9 \pm 0.2 \%$ (1σ), whereas the $\delta^{18}\text{O}$ values ranged from $-5.8\%$ to $-4.8\%$ with a mean
value of $-5.1 \pm 0.2\%$ (1σ). The calcite $\delta^{13}\text{C}$ values from the Jones Ranch profile ranged from
$-6.0\%$ to $-4.4\%$ with a mean value of $-5.4 \pm 0.4 \%$ (1σ), whereas the $\delta^{18}\text{O}$ values ranged from
$-4.9\%$ to $-4.0\%$ with a mean value of $-4.3 \pm 0.2\%$ (1σ). The calcite $\delta^{13}\text{C}$ values
from the Oklahoma profile ranged from $-10.9\%$ to $-10.8\%$ with a mean value of $-10.9 \pm 0.1 \%$
(1σ), whereas the $\delta^{18}\text{O}$ values ranged from $-5.8\%$ to $-5.5\%$ with a mean value of
$-5.6 \pm 0.2\%$ (1σ). The replicate analyses indicated minimal heterogeneity of the $\delta^{13}\text{C}$
(<0.2‰) and $\delta^{18}\text{O}$ (<0.2‰) values in the individual aliquots of calcite powder samples.
Similarly, there was minimal heterogeneity of $\delta^{13}\text{C}$ (<0.3‰) and $\delta^{18}\text{O}$ (<0.5‰) values
between separate aliquots from the same calcareous sample.

![Figure 3](image-url)

**Figure 3.** A plot of the $\delta^{13}\text{C}$ values of pedogenic calcite from Lower Cretaceous localities in Texas
and Oklahoma. The data represent both the initial and replicate analyses conducted on samples from
each locality.

3.2. Organic Matter from Acid-Treated Residues

The results of the $\delta^{13}\text{C}$ analysis of organic matter occluded in calcareous tubules
and nodules collected from the Aptian–Albian paleosol profiles are presented in Table 1.
The CO$_2$ yields indicated that the acid-treated residues comprised 0.25 to 1.17 weight percent organic carbon (Table S1). The organic residue δ$^{13}$C values ranged from $-27.3$‰ to $-21.1$‰ with a mean value of $-24.8 \pm 1.4$‰, which was consistent with the C$_3$ vegetation that is known to have dominated Early Cretaceous paleolandsapes [43]. The lowest δ$^{13}$C values were from the Proctor Lake locality, averaging $-21.3 \pm 0.2$‰. This was isotopically heavy for C$_3$ vegetation but fell within the observed range of δ$^{13}$C values for C$_3$ plants [34]. Modern C$_3$ plants exhibiting isotopically heavier δ$^{13}$C values are typically water stressed, i.e., there is insufficient soil moisture to support efficient CO$_2$ uptake through photosynthesis [44]. This observation conformed with previous paleoclimatic studies of the Proctor Lake locality, suggesting it was a semi-arid environment with soil paleotemperatures averaging 30 °C and paleoprecipitation estimates of 330mm/yr [16], which might have induced moisture stress and the relatively heavy organic matter δ$^{13}$C values measured at that locality. In these regards, the δ$^{13}$C values of the occluded organic matter from the Proctor Lake locality are considered reasonable results and are used here to estimate atmospheric pCO$_2$ levels.

3.3. Mean Annual Precipitation Estimates

The stable carbon isotope differences between the calcite and co-existing occluded organic matter, ∆$^{13}$C$_{cc-om}$, ranged from 13.2 to 21.8‰. The resulting ∆$^{13}$C$_{cc-om}$ values were used as variables in Eqn. 4 in order to yield a corresponding range of MAP estimates from 117 ± 60 mm/yr to 401 ± 30 mm/yr (Table 2, Figure 4). The samples from the Proctor Lake locality averaged 391 ± 30 mm/yr, while samples from the Jones Ranch locality averaged 196 ± 50 mm/yr. The samples collected from the Antlers Formation in Oklahoma averaged 354 ± 40 mm/yr. This suggests that semi-arid climates persisted during the Early Cretaceous in Texas and Oklahoma. The paleoprecipitation estimates reported from these sample localities using CALMAG geochemical weathering indices, which were developed for paleosols, were in close agreement for the Texas localities of Proctor Lake and Jones Ranch; however, the ∆$^{13}$C$_{cc-om}$ based MAP estimate of ~350 mm/yr contrasted significantly with the CALMAG MAP estimate of ~1100 mm/yr for the Oklahoma locality (Table 2, Figure 4).

Table 2. The mean annual precipitation estimates of Lower Cretaceous localities in Texas and Oklahoma using ∆$^{13}$C$_{cc-om}$ [42], which are newly presented here, and CALMAG weathering index [41] MAP estimates, as reported in Andrzejewski and Tabor [16]. Soil-respired pCO$_2$ was then estimated from the mean annual precipitation estimates using the equations derived by Cotton and Sheldon (Equation (3), [40]). C$_s^1$ calculated soil-respired pCO$_2$ using MAP derived from ∆$^{13}$C$_{cc-om}$. C$_s^2$ calculated soil-respired pCO$_2$ using MAP derived from the CALMAG weathering index.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Estimate</th>
<th>MAP mm/yr (± 55) Using ∆C$_{cc-om}$</th>
<th>C$_s^1$ (MAP-Derived)</th>
<th>MAP mm/yr (± 110mm) Using CALMAG</th>
<th>C$_s^2$ (MAP-Derived)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oklahoma</td>
<td>Min</td>
<td>338</td>
<td>1649</td>
<td>952</td>
<td>5128</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>366</td>
<td>1806</td>
<td>1210</td>
<td>6591</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>354</td>
<td>1736</td>
<td>1114</td>
<td>6047</td>
</tr>
<tr>
<td>Jones Ranch, TX</td>
<td>Min</td>
<td>117</td>
<td>392</td>
<td>288</td>
<td>1363</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>262</td>
<td>1215</td>
<td>444</td>
<td>2248</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>196</td>
<td>839</td>
<td>365</td>
<td>1800</td>
</tr>
<tr>
<td>Proctor Lake, TX</td>
<td>Min</td>
<td>380</td>
<td>1883</td>
<td>268</td>
<td>1250</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>401</td>
<td>2004</td>
<td>416</td>
<td>1811</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>391</td>
<td>1949</td>
<td>331</td>
<td>1607</td>
</tr>
</tbody>
</table>
There are two possible scenarios that explain the discrepancy between the CALMAG and ∆13C_{cc} based MAP estimates of paleoprecipitation from the Oklahoma locality. The first is that the bulk paleosol matrix that was collected and analyzed for the CALMAG analyses contained inherited minerals that were not representative of the original paleosol profile that produced the carbonate nodules. However, work conducted by Andrzejewski and Tabor [16] analyzed the clay mineralogy of the < 0.2 µm fraction of the paleosol matrix, which is thought to represent the authigenic fractions produced in situ, as pedogenic minerals and found substantial amounts of kaolinite in the samples from the Oklahoma locality. This suggests that an interval of increased chemical weathering, which is typically associated with higher rates of meteoric precipitation, supported the higher precipitation estimates produced using the CALMAG weathering index [16]. The second and more plausible scenario is that the paleosol profile recorded two paleoclimate events simultaneously. In this scenario, periods of significant rainfall caused increases in chemical weathering, producing chemically leached minerals, such as kaolinite, which recorded a more humid and high-precipitation paleoclimate, which was detected using the CALMAG weathering index. Additionally, paleosol carbonate precipitates in the soil during a subsequent, younger low-precipitation paleoclimate were detected by the ∆13C_{cc} based MAP estimates within the same paleosol profile; this is an example of soil polygenesis and is a common feature in Quaternary-aged modern surfaces [45]. This suggests that the Oklahoma locality might have experienced weather patterns with periods of significant paleoprecipitation that were later followed by much drier periods, during which carbonate precipitated in the paleosol profile. Given that both the CALMAG weathering index and the ∆13C_{cc} precipitation proxies provided plausible paleoprecipitation estimates, both were used to estimate soil-respired CO₂ in Table 2. The soil-respired CO₂ estimates were then used to estimate atmospheric pCO₂ in Table 3.

Figure 4. The average mean annual precipitation estimates for Lower Cretaceous localities in Texas and Oklahoma using ∆13C_{cc} based MAP estimates of paleoprecipitation from the Oklahoma locality. The circles represent the Jones Ranch locality. The triangles represent the Proctor Lake locality. The inverted triangles represent the Oklahoma locality. These estimates were produced using the CALMAG weathering index, as reported in Andrzejewski and Tabor [16] (open symbols, error bars ± 55 mm) and the CALMAG weathering index, as reported in Andrzejewski and Tabor [16] (open symbols, error bars ± 110 mm).
Table 3. The estimated atmospheric $p\text{CO}_2$ estimates calculated with the $C_s$ values of 1250 and 2000 ppmV. The estimated atmospheric $p\text{CO}_2$ values calculated using $C_s$ values based on average mean annual precipitation estimates using the $\Delta^{13}\text{C}_{\text{cc-om}}$ proxy [42] and CALAMG weathering index [41] are shown in the last two columns. The values show the minimum, maximum, and average $p\text{CO}_2$ calculated for each locality.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Estimate Range</th>
<th>$p\text{CO}_2$ ($C_s$) = 1250</th>
<th>$p\text{CO}_2$ ($C_s$) = 2000</th>
<th>$p\text{CO}<em>2$ ($C_s$) = $\Delta^{13}\text{C}</em>{\text{cc-om}}$ MAP avg.</th>
<th>$p\text{CO}_2$ ($C_s$) = CALMAG MAP avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oklahoma</td>
<td>Min</td>
<td>124</td>
<td>198</td>
<td>172</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>188</td>
<td>301</td>
<td>261</td>
<td>910</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>153</td>
<td>246</td>
<td>213</td>
<td>742</td>
</tr>
<tr>
<td>Jones Ranch, TX</td>
<td>Min</td>
<td>467</td>
<td>747</td>
<td>313</td>
<td>671</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>692</td>
<td>1108</td>
<td>465</td>
<td>997</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>592</td>
<td>947</td>
<td>397</td>
<td>852</td>
</tr>
<tr>
<td>Proctor Lake, TX</td>
<td>Min</td>
<td>67</td>
<td>108</td>
<td>105</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>115</td>
<td>183</td>
<td>179</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>88</td>
<td>141</td>
<td>138</td>
<td>114</td>
</tr>
</tbody>
</table>

3.4. Soil-Respired CO$_2$ Estimates

Using CALMAG data reported from Andrzejewski and Tabor [16] and MAP estimates made using the $\Delta^{13}\text{C}_{\text{cc-om}}$ precipitation proxy, the minimum and maximum levels of soil-respired CO$_2$ ($C_s$) were estimated using the methods outlined by Cotton and Sheldon [40] (Table 2). The lowest reported CALMAG value from the three sampled localities was from the Proctor Lake locality. A measured CALMAG value of 31.0 corresponded to a MAP estimate of 268 mm/yr. By applying the reported relationship between the MAP and soil-respired CO$_2$, the minimum contribution of soil-respired CO$_2$ ($C_s$) was 1250 ppmV. The maximum reported CALMAG values were from the Oklahoma locality, with a CALMAG value of 72.5 producing an MAP estimate of 1210 mm/yr. This MAP estimate produced a maximum contribution of soil-respired CO$_2$ ($C_s$) of 6591 ppmV. The lowest MAP estimate produced using the $\Delta^{13}\text{C}_{\text{cc-om}}$ precipitation proxy was 117 mm/yr from the Jones Ranch locality, producing an estimated $C_s$ value of 392 ppmV. The maximum MAP estimate produced using the $\Delta^{13}\text{C}_{\text{cc-om}}$ precipitation proxy was 401 mm/yr from the Proctor Lake locality, producing an estimated $C_s$ value of 2004 ppmV. Given the estimated minimum and maximum values for soil-respired CO$_2$, we used two different models with $C_s$ values of 1250 and 2000 ppmV to estimate atmospheric $p\text{CO}_2$.

3.5. Atmospheric pCO$_2$ Estimates

The two models with fixed soil CO$_2$ values produced estimates of atmospheric $p\text{CO}_2$ ranging from 67 to over 1100 ppmV (Table 3, Figure 5). The largest reported values occurred in samples from the Jones Ranch locality, while lower estimates were produced from the Proctor Lake and Oklahoma localities (Figure 5). Although the absolute value of these estimates significantly changed with the varying estimates of soil-respired $p\text{CO}_2$, the trends were consistent between the two models with differences in atmospheric $p\text{CO}_2$ estimates between the localities remaining proportionally the same. This included an 8-fold increase in atmospheric $p\text{CO}_2$ from the Proctor Lake locality to the Jones Ranch locality, followed by a 4-fold decrease in atmospheric $p\text{CO}_2$ from the Jones Ranch locality to the Oklahoma locality.
values calculated using mean annual precipitation provided a more robust estimate of atmospheric pCO2, the estimates ranging from ~−8.0‰ to −3.0‰. Furthermore, the estimates of atmospheric pCO2 appear to also agree with Aptian–Albian atmospheric pCO2 estimates from these regions. More specifically, Ludvigson et al. [4] reported values of 600–1200 ppmV with a soil-respired value (Cs) of 2000 ppmV in the Cedar Mountain Formation in Utah. Li et al. [2] reported atmospheric pCO2 estimates ranging from 0–5676 ppmV for Cs levels of 2500–5000 ppmV in the Aptian–Albian deposits of southeast China. Moreover, Harper et al. [5] reported atmospheric pCO2 estimates of 42–1116 ppmV with Cs values ranging from 2427 to 4393 ppmV in the Aptian–Albian deposits of northwest China. Additionally, studies using the stomatal index to estimate atmospheric pCO2 during the Aptian and
Albian periods have reported similar estimates ranging from 450 to 2030 ppmV [46–50]. The significant increase in atmospheric pCO₂ during the late Aptian followed by a decrease in atmospheric pCO₂ across the Aptian–Albian boundary appears to correlate with ocean anoxic event 1b reported during ~113–109 Ma (OAE1b) [51]. While the absence of any true chronostratigraphic constraints in the Texas and Oklahoma stratigraphy prevents us from definitively identifying and assigning a specific isotopic excursion event to this dataset, we recognize that the general pattern of a significant buildup in atmospheric pCO₂ during the late Aptian followed by a decrease in atmospheric pCO₂ during the Aptian–Albian transition and this is strikingly similar to the C10 isotopic excursion identified in the Cedar Mountain Formation [4]. The similarity between these two datasets supports the relative ages assigned to the Texas and Oklahoma localities, as well as the preservation of a global atmospheric change recorded within these sedimentary strata, despite the lack of a true chronostratigraphic framework.

Previous sedimentological and paleoclimatic studies from the Aptian Proctor Lake and Jones Ranch localities have suggested warm, semi-arid environments with estimated soil paleotemperatures averaging 28.5 ± 3 °C and paleoprecipitation ranging from 268 to 444 ± 110 mm/yr (Andrzejewski and Tabor 2020). During this interval, paleosol carbonate data recorded evidence for a significant increase in atmospheric pCO₂, with up to an 8-fold increase between the two localities. The rapid buildup of atmospheric pCO₂ during the late Aptian appears to indicate a significant global event. Ludvigson et al. [4] suggested a strong correlation between the late Aptian C10 CIE and a peak in submarine volcanic activity in the Kerguelen Large Igneous Province in the southern Indian Ocean [51,52]. This is then proceeded by data from the Albian Oklahoma locality, with average soil paleotemperature estimates averaging 26.5 ± 3 °C and CALMAG weathering index paleoprecipitation estimates ranging from 952 to 1210 ± 110 mm/yr, suggesting a warm and humid environment [16]. The slight decrease in paleotemperature estimates and the significant increase in paleoprecipitation is accompanied by a decrease in atmospheric pCO₂ across the Aptian–Albian boundary. Significantly, this trend also correlates with the transgression of the Glen Rose Sea onto the Texas craton [53] and suggests a complex relationship between both global and regional paleoevents that combined to effect paleoclimatic factors, which dramatically changed the paleolandscape. It remains clear that more research is needed to explore these global and regional Cretaceous events, which appear to correlate with significant changes in paleoclimate.

The results of this study estimated that Albian–Aptian atmospheric pCO₂ ranged from 67 to 1108 ppmV and reflected the conditions of a “greenhouse” period that included higher than normal overall temperatures compared to modern Earth. The lower estimates of atmospheric pCO₂ recorded at the Proctor Lake and Oklahoma localities were slightly unexpected, given that increased atmospheric pCO₂ is often cited as the mechanism driving greenhouse conditions during the Cretaceous. Yet, some of the atmospheric pCO₂ estimates provided here suggested the possibility of a Cretaceous atmosphere with lower pCO₂ values than pre-industrial modern times, which was ~280 ppmV. This apparent contradiction may inform us of several possibilities as we move forward in paleoatmospheric pCO₂ reconstructions: (1) greenhouse climates persisted with low atmospheric pCO₂, such as values similar to pre-industrial modern values; (2) paleosol carbonate paleobarometer proxies may not effectively record atmospheric pCO₂ values at the time of soil formation, especially at lower atmospheric pCO₂ concentrations (~<500 ppmV; Sheldon and Tabor, 2009); (3) uncertainties in the parameters used in calculating atmospheric pCO₂, including the estimates of the contribution of soil pCO₂, may be producing inaccurate estimates; or (4) a combination of the above possibilities. The limited scope of this study was not sufficient to identify the solution and highlights the need for more extensive soil and paleosol carbonate analyses, as well as complimentary and new proxies for atmospheric pCO₂ to help to frame and more rigorously analyze the meaning of soil and paleosol Δ13Ccc-cow values.
5. Conclusions

The stable isotopic analysis of paleosol calcite and co-existing occluded organic matter from Aptian–Albian terrestrial deposits in Texas and Oklahoma provided a means of estimating changes in atmospheric $pCO_2$ during greenhouse conditions. These, combined with previous paleoclimate and paleoenvironment interpretations, allowed us to gain insight into the dynamic relationship between the ocean–atmosphere–climate system and the global carbon cycle. The estimates of soil-respired CO$_2$ combined with the stable carbon isotope analyses ($\delta^{13}C_{cc}$ from $-10.9\%$ to $-4.4\%$ and $\delta^{13}C_{OM}$ from $-27.3\%$ to $-21.1\%$) produced atmospheric $pCO_2$ estimates ranging from 67 to over 1100 ppmV. Soil-respired $pCO_2$ estimates were approximated using paleoprecipitation estimates from two different paleosol proxies, including a bulk matrix geochemical proxy and a paleosol carbonate–organic matter stable isotope proxy. Although the variations in soil $pCO_2$ changed the absolute value of the calculated atmospheric $pCO_2$ estimates, the trend produced in each scenario was similar. This included a significant increase in atmospheric $pCO_2$ in the late Aptian followed by a decrease in atmospheric $pCO_2$ during the Aptian–Albian transition. This appears to correlate with significant regional and global events, including the transgression of the Glen Rose Sea onto the Texas craton and a peak in submarine volcanic activity in the Kerguelen Large Igneous Province (southern Indian Ocean). Furthermore, the intervals of rapid increase in atmospheric $pCO_2$ correlated with warm, semi-arid paleoenvironments, while the interval of a drawdown in atmospheric $pCO_2$ transitioned to slightly cooler, humid paleoenvironments with a significant increase in paleoprecipitation. This dataset and similar terrestrial Cretaceous greenhouse records provide unique and key insights into the potential repercussions of the current rise in global atmospheric CO$_2$ on both the climate and the environment.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/geosciences12040148/s1. Table S1. Contains $\delta^{18}O$ data for the analyzed carbonates and weight% organic matter residue for the occluded organic material.

Author Contributions: Conceptualization, K.A. and N.T.; methodology, K.A. and T.M.; formal analysis, K.A. and T.M.; field investigation, K.A., N.T., D.W. and T.M.; data curation, K.A.; writing—original draft preparation, K.A.; writing—review and editing, N.T., D.W. and T.M.; supervision, N.T. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are fully reported in Tables 1–3 and S1.

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Conflicts of Interest: The authors declare no conflict of interest.

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