Terrestrial Evidence for Two Greenhouse Events in the Latest Cretaceous

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ABSTRACT

We present a terrestrial record of stable carbon and oxygen isotopes from paleosol carbonate for climate interpretations between ca. 71.0 and 63.6 Ma. Isotopic ratios point to covarying and elevated atmospheric CO_2 pressures and temperatures between ca. 70.0 and 69.0 Ma and ca. 65.5 and 65.0 Ma. These two greenhouse episodes were characterized by atmospheric CO_2 levels between 1000 and 1400 ppm*V* (*V* = volume) and by mean annual temperatures in west Texas between 21 and 23 °C (~35°N paleo-latitude). Atmospheric CO_2 and temperature relations indicate that a doubling of pCO_2 was accompanied by an ~0.6 °C increase in temperature. A temperature gradient of ~0.4 °C per degree of latitude is proposed for North America across the Cretaceous-Tertiary boundary when comparing temperature proxies from west Texas with paleobotanical work in North Dakota. Our data demonstrate strong coupling between terrestrial climates and ocean temperatures that were possibly forced by Deccan trap volcanic degassing, leading to dramatic global climate changes.

INTRODUCTION

Characterizing Late Cretaceous (Maastrichtian) and early Tertiary (Danian) climates across the time of the Cretaceous-Tertiary (K-T) boundary (65.0 Ma) can be important for assessing mechanisms governing greenhouse climates, for providing better empirical data for general circulation models, and for detecting potential marine-terrestrial environmental coupling.

An abundant record suggests increased ocean temperatures between ca. 69.5 and 68.5 Ma and between ca. 65.5 and 65.0 Ma based on stable oxygen (O) isotopes of foraminifera (Li and Keller, 1998a, 1998b; Barrera and Savin, 1999; Keller, 2001; Olsson et al., 2001; Wilf et al., 2003). Terrestrial records during this time are less abundant, but recent evidence from Cojan et al. (2000) and Nordt et al. (2002) strongly indicate that stable carbon (C) and O isotopes from upper Cretaceous paleosol carbonates track shifts in the marine foraminifera isotopic record. They, along with the paleobotanical work of Wilf et al. (2003), provide compelling evidence for both elevated atmospheric CO_2 levels and temperatures between ca. 65.5 and 65.0 Ma coinciding with a well-documented warm ocean excursion, possibly forced by Deccan trap volcanism (see also Keller, 2001; Olsson et al., 2001). In contrast, no marine-terrestrial correlations have been assessed for the warm ocean excursion near 69 Ma, and doing so would further improve our understanding of marine-terrestrial linking and greenhouse events. It is also unclear whether continental ice sheets persisted during the Late Cretaceous because of conflicting ocean temperature estimates (Miller et al., 1999; Stoll and Schrag, 2000; Huber et al., 2002; Miller et al., 2003) and the inability of general circulation models to simulate empirically derived climate data (Upchurch et al., 1999).

To enhance our understanding of climate conditions near and across the K-T boundary, this study constructs atmospheric CO_2 and temperature curves between ca. 71.0 and 63.6 Ma from stable C and O isotopic compositions in paleosol carbonate. These results facilitate a better understanding of potential coupling between atmospheric pCO_2 and temperatures and between terrestrial and marine environments during this important time period.

SETTING

The study area is located adjacent to Dawson Creek within the Tornillo Basin of Big Bend National Park, Texas (29.30°N, 103.52°W). From base to top, the study interval includes the Aguja, Javelina, and Black Peaks Formations, previously documented as a relatively conformable succession of Upper Cretaceous to lowermost Tertiary overbank-dominated alluvial deposits and associated paleosols (Lehman, 1985, 1990, 1991) (Fig. 1). The paleosols commonly contain carbonate nodules and exhibit well-structured surface horizons (A horizons) and subsoils that are weakly developed (Bw horizons), carbonate enriched (Bk horizons), slickensided (Bss horizons), or clay enriched (Bt horizons) (Fig. 1).

METHODS

Initial Age Estimates

To bracket the stratigraphic section, we assigned the base an age of 71.0 Ma (Campanian-Maastrichtian boundary) as supported by a putative latest Campanian to earliest Maastrichtian age (Lehman, 1985). The K-T boundary was placed ~70 m below the section top, coincident with a weak iridium anomaly 5 m above the highest dinosaur remains and 26 m below Tertiary fauna (Lehman, 1990). Although the study interval experienced magnetic overprinting, Lehman (1990) concludes that the section top, within the Black Peaks Formation, coincides with polarity Chron C28R. If correct, then the section top is no younger than 63.6 Ma.

We calculated provisional paleosol ages first by assuming that virtually all of the bracketed geologic time (ca. 71.0 to 63.6 Ma) is accounted for by pedogenesis rather than by deposition and then by apportioning time among the paleosols based on soil maturity (see Retallack, 2001). The proportion of time estimated to account for each paleosol was plotted along a graphical linear scale as a cumulative succession within the age range of the study interval. A provisional age for each paleosol could then be assigned by comparing the midpoint location of its duration to the study interval age range (gray line on Fig. 2).

Sampling and Laboratory

Pedogenic carbonate nodules were collected in triplicate from Bk horizons below a depth of 50 cm in each of 33

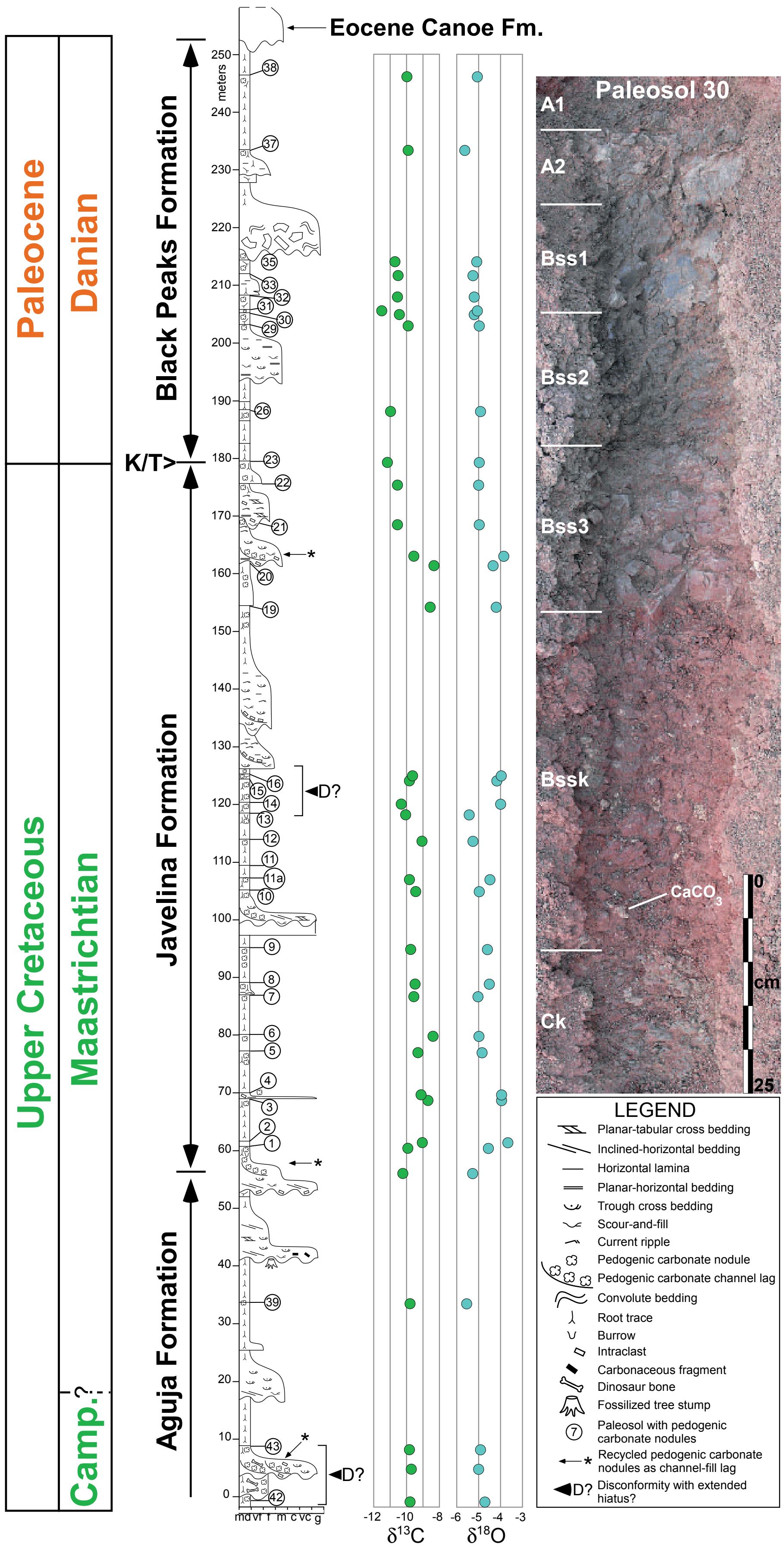

Figure 1. Stratigraphic correlation chart of the study area compiled from Lehman (1985, 1990, 1991), Gradstein et al. (1994), and Berggren et al. (1995); measured stratigraphic column with designations for the sampled paleosols; and photograph of paleosol 30 illustrating horizon designations and one of the sampled pedogenic carbonate nodules. Stable carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotopes from paleosol carbonate are plotted to show field distributions.

carbonate-bearing paleosols, with three additional triplicate pedogenic carbonate nodules collected from recycled channel-fill lag. The carbonate nodules were typically round to subround, 0.5–3.0 cm in diameter (Fig. 1), and composed of distinctive micrite (fine-grained) and sparry (coarse-grained) phases. We collected micritic calcite for $\delta^{13}C$ and $\delta^{18}O$ analysis under the assumption that it is a conservative tracer of climatic conditions during the time of paleosol formation (Driese and Mora, 1993). The triplicate isotopic values were averaged for each paleosol to assess internal variability versus long-term trends.

Approximately 5 mg of calcite was collected from each nodule using a 2.4 mm diameter drill bit. A 300 µg aliquot of this sample was digested in anhydrous phosphoric acid at 90 °C in a Micromass Multiprep Autosampler and the resulting CO_2 analyzed for ^{13}C and ^{18}O content on a VG PRISM II gas-source mass spectrometer. The laboratory standard error was <0.01‰ for both carbon and oxygen, with results reported relative to the Peedee belemnite (PDB) standard.

Atmospheric pCO_2 Estimates

For estimates of atmospheric CO_2 concentrations, we used the paleosol carbonate barometer, which permits calculation of the contributions of atmospheric CO_2 to the total soil CO_2 pool during soil formation (Cerling, 1999):

$$C_a = S_z\left[\frac{\delta^{13}C_s - 1.0044\delta^{13}C_r - 4.4}{\delta^{13}C_a - \delta^{13}C_s}\right]$$

where C_a is atmospheric CO_2 concentration (ppm*V*), S_z is soil respired CO_2 concentration (ppm*V*), and $\delta^{13}C_s$, $\delta^{13}C_r$, and $\delta^{13}C_a$ are isotopic compositions of soil CO_2, soil-respired CO_2, and atmospheric CO_2, respectively. Assuming that the soil-atmosphere-ocean isotopic system is in equilibrium, elevated atmospheric CO_2 concentrations are isotopically recorded in the soil CO_2 pool and, ultimately, pedogenic carbonate.

After constructing a five-point running average of the $\delta^{13}C$ of planktic foraminifera from Deep Sea Drilling Project (DSDP) core 525A from the South Atlantic (Li and Keller, 1998a, 1998b) and DSDP 577 from the North Pacific (Shackleton and Bleil, 1985), and assuming a −8.5‰ isotopic equilibrium fractionation between ocean and atmospheric CO_2 (Lynch-Stieglitz et al., 1995), we estimated the $\delta^{13}C$ of atmospheric CO_2 ($\delta^{13}C_a$) for the model equation. Given low levels of paleosol organic carbon in the study area, we estimated the $\delta^{13}C$ of respired soil CO_2 ($\delta^{13}C_r$) by an empirical equation relating the $\delta^{13}C$ of atmospheric CO_2 to paleosol organic carbon ([$\delta^{13}C_{atm} = (\delta^{13}C_{organic} + 18.67)/1.10$]) (Arens et al., 2000). This equation yields results in agreement with measured isotopic organic carbon values across the K-T boundary in other localities (Grocke, 1998; Arens and Jahren, 2000), with measured isotopic fractionation between modern atmospheric CO_2 and plants during photosynthesis (Buchmann et al., 1998), and with an average isotopic value of ~−24.0‰ measured from three charcoal samples collected from the Aguja Formation in the study area. Temperatures determined from paleosol stable O isotopes were used to calculate the temperature-dependent carbonate equilibria fractionation (Romanek et al., 1992) in order to estimate paleosol $\delta^{13}CO_2$ ($\delta^{13}C_s$) from measured isotopic values of paleosol carbonate. Based on sedimentological interpretations at paleo-latitude of ~35°N, Robinson-Roberts and Kirschbaum (1995) suggest the presence of a subtropical climate during paleosol pedogenesis. Consequently, we used a range of 5000 to 7000 ppm*V* for soil CO_2 concentration (Sz) (see also Brook et al., 1983; Ekart et al., 1999). Isotopically, it is assumed that the primary photosynthetic pathway across the K-T boundary was from C3 plants (Grocke, 1998).

Temperature Estimates

Temperatures were calculated by simultaneous solution of two equations that relate the stable O isotopic composition of meteoric waters to ambient temperatures. These equations describe (1) the fractionation of oxygen isotopes from water into calcite during pedogenesis (Friedman and O'Neil, 1977), and (2) the correlation between oxygen isotopes of meteoric water and mean annual air temperature (Fricke and O'Neil, 1999). The resulting equation (3) uniquely describes mean annual air temperatures from measured oxygen isotopic compositions of pedogenic calcite:

$$\delta^{18}O_{calcite}(SMOW) - \delta^{18}O_{water}(SMOW) = 2.78\,(10^6\,T^{-2}) - 2.89 \qquad (1)$$

$$\delta^{18}O_{water}(SMOW) = 0.498\,(T\text{-}273) - 13.20 \qquad (2)$$

$$-0.498\,T^3 + (\delta^{18}O_{calcite}(SMOW) + 152.04)\,T^2 - 2.78 \times 10^6 = 0 \qquad (3)$$

where *T* is temperature in kelvin.

There is an inverse relationship between the $\delta^{18}O$ of meteoric water and latitude and between latitude and temperature ($r^2 = 0.60$ for mean annual temperatures) in continental North America today (Fricke and O'Neil, 1999). In addition, White

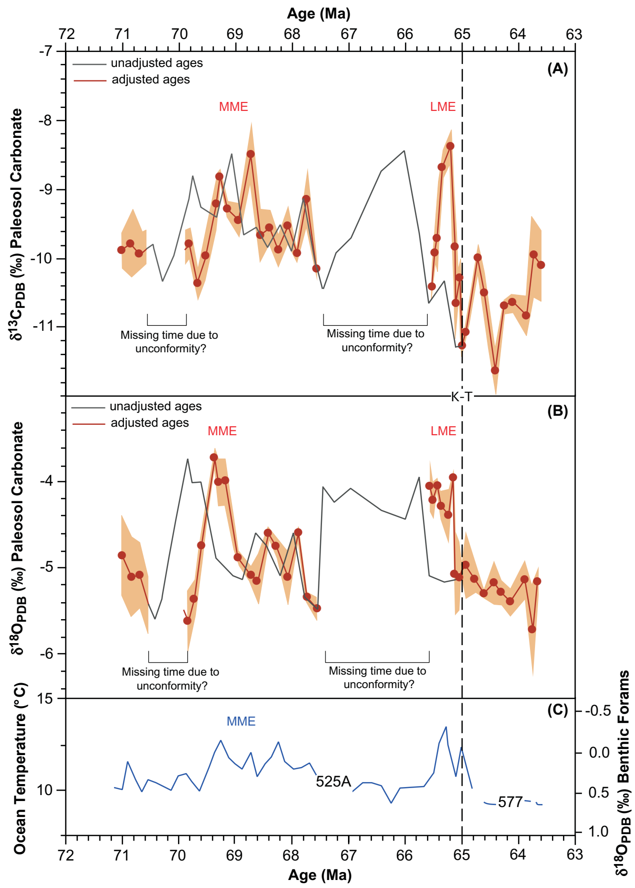

Figure 2. Stable carbon (**A**) and oxygen (**B**) isotope values measured from paleosol carbonate in the study area. Gray curves are the chronologically unadjusted isotopic data estimated by the techniques presented in "Methods" section. Brown curves are chronologically adjusted chemostratigraphically to fit the marine record and used for $\delta^{13}C$ values in the paleobarometer equation and for $\delta^{18}O$ values in the temperature equations. The one standard deviation window (shaded brown) is created from triplicate isotopic values from each paleosol. **C:** Stable O isotope curves from DSDP 525A from the South Atlantic (Li and Keller, 1998a, 1998b) and DSDP 577 from the North Pacific (Shackleton and Bleil, 1985). See Barrera and Savin (1999) for similar isotopic curves globally.

et al. (2001) show that during the middle Cretaceous, stable O isotope ratios of rainfall, as estimated from sphaerosiderite in wetland paleosols, systematically decreased with increasing latitude along the Western Interior Seaway. We proceed under the assumption that these modern and middle Cretaceous trends hold for the latest Cretaceous in our study interval. However, effects of latitude, coastal setting, rainfall amount, and altitude can shift oxygen isotopic values out of equilibrium with meteoric water (Rozanski et al., 1993). Latitudinal effects are prominent between 20°N and 20°S latitude, where the source area for most global water vapor originates and does not vary isotopically. The west Texas study area, however, is outside of this latitudinal range. The coastal effect can enrich the heavier ^{18}O isotope in meteoric water of coastal settings, but during the K-T transition, the west Texas study area was typically at least 150 km away (Lillegraven and

Ostresh, 1990; Lehman, 1991; Davidoff and Yancey, 1993; Moran-Zenteno, 1994). The effect of precipitation amount is typical of monsoonal climates where rainwater becomes enriched in the heavier ^{18}O oxygen isotope from rain out of the lighter ^{18}O oxygen isotope, a situation not present in the study area during the K-T transition (Wolfe and Upchurch, 1987). There is no reason to believe that orographic or altitude effects were important (Lehman, 1991). Thus, the $\delta^{18}O$ of pedogenic carbonate should be a reasonable proxy for air temperature based on global relationships between the $\delta^{18}O$ of meteoric water and temperature.

Potential evaporative enrichment during pedogenesis and isotopic exchange with fluids after burial adds further uncertainty to temperature interpretations derived from oxygen isotopes in pedogenic carbonate (Cerling, 1984). Despite these potential problems, we use stable O isotopes and the Fricke and O'Neil (1999) relation for modern climates to estimate temperatures from west Texas paleosols based on the following observations: (1) shallow burial depth (<2 km) minimizes temperature effects on isotopic redistributions; (2) pedogenic depth functions of mobile constituents indicate minimal diagenetic alteration after burial; and (3) depth to carbonate (>50–150 cm) and deeply leached soil profiles strongly suggest the climate was humid subtropical, eliminating potential evaporative enrichment effects typical of arid climates (Cerling, 1984; Cerling and Quade, 1993).

TERRESTRIAL-MARINE CORRELATIONS

Stable C and O isotopes reveal covarying trends in the west Texas paleosol carbonate record (Fig. 2). Plotting of the chronologically unadjusted paleosol isotopic data (gray curves, Figs. 2A and 2B) against the marine $\delta^{18}O$ record of benthic foraminifera (blue curve, Fig. 2C) illustrates a close, yet imperfect, correlation. The two major paleosol isotopic peaks precede those observed in the marine record by ~0.8–1.0 m.y. The imprecise correlation between the alluvial and marine record may reflect the presence of two significant disconformities within the Dawson Creek succession. The two isotopic peaks occur above alluvial intervals characterized by the most mature and well-drained paleosols, an observation that is typically attributed to periods of lowered base level and associated channel incisement and prolonged interfluve weathering (e.g., Wright and Marriott, 1993; Retallack, 1998). We propose that these two zones of mature paleosols record unconformities such that the isotopic record is incomplete and can be reasonably shifted to younger ages to more precisely match the marine record. This shift is reflected in the chemostratigraphically adjusted isotopic curves (brown line, Figs. 2A and 2B).

The adjusted curves from west Texas place the two isotopic peaks in the Maastrichtian between ca. 70.0 and 69.0 Ma and ca. 65.5 and 65.0 Ma. Because covarying and elevated paleosol O and C isotopic proportions indicate relatively higher atmospheric CO_2 concentrations and terrestrial temperatures (see Methods), we conclude that these time intervals and associated warm ocean waters indicate the presence of two global greenhouse climates in the Maastrichtian. Carbon and oxygen isotopic values in the paleosols each decline appreciably immediately before and through the K-T boundary into the Danian, indicating a return to somewhat lower atmospheric CO_2 concentrations and a cooling trend.

The marine record ca. 70–69 Ma is characterized by an abrupt reorganization of oceanic circulation and the first wave of Late Cretaceous extinctions, called the Mid-Maastrichtian Event (Frank and Arthur, 1999; Keller, 2001; Bralower et al., 2002). Based on chemostratigraphic correlation, the early greenhouse episode in the paleosol record from west Texas is also associated with the Mid-Maastrichtian Event (MME). The second greenhouse interval detected in the paleosol record, which we designate the Late Maastrichtian Event (LME), is chemostratigraphically correlated to warm ocean waters and the initiation of the most severe wave of end-Cretaceous mass extinctions before the K-T boundary (Li and Keller, 1998a, 1998b; Keller, 2001; Adatte et al., 2002).

TERRESTRIAL-CLIMATE CORRELATIONS

Conversion of the paleosol isotopic data into atmospheric CO_2 concentrations and terrestrial temperatures reveals further information about climate across the K-T boundary (Fig. 3). Atmospheric pCO_2 during the MME was between ~1000 and 1200 ppm*V*, with mean annual temperatures peaking near 22°C. This also coincides with an increase in ocean temperature of ~3 °C. Although this climate event appears to have emerged relatively rapidly, both the marine and associated terrestrial records indicate that the greenhouse condition subsided into background levels during a protracted transition. Following the MME, between ca. 68.5 and 67.5 Ma, atmospheric CO_2 levels ranged from ~400 to 600 ppm*V* and estimated temperatures from ~17.5 and 19 °C, before dropping further just prior to the unconformity at 67.5 Ma. Based on estimates from other localities, atmospheric CO_2 levels ranged from ~500 to 800 ppm*V* during the west Texas unconformity interval between ca. 67.5 and 65.5 Ma.

Figure 3 suggests that the greenhouse condition during the LME started at about the same rate-increase of atmospheric CO_2 and temperature as the MME, but dissipated more abruptly than the MME. The LME is characterized by calculated atmospheric CO_2 levels of ~1400 ppm*V* and temperatures of between 21 and 22 °C (Fig. 3). Elevated CO_2 levels from other studies corroborate this greenhouse interval, as do a temperature increase by ~5 °C in North Dakota (Fig. 3) and a temperature increase by ~3.5 °C in ocean water (Fig. 2). Immediately before the K-T boundary, CO_2 concentrations dropped dramatically to below modern levels, whereas temperatures declined by ~4–5 °C. The pCO_2 spike at the K-T boundary from Beerling et al. (2002) was estimated based on the effects of a bolide impact instantaneously transferring large quantities of carbon from the lithosphere into the atmosphere. In the Danian, near 64.6 Ma, a final pCO_2 peak of approximately 800 ppm*V* occurred in the west Texas study area, although temperatures remained relatively steady. Atmospheric CO_2 estimates from other areas confirm decreasing levels in the Danian, as do temperature data from North Dakota. When comparing the temperature proxy from North Dakota and west Texas, there is a temperature

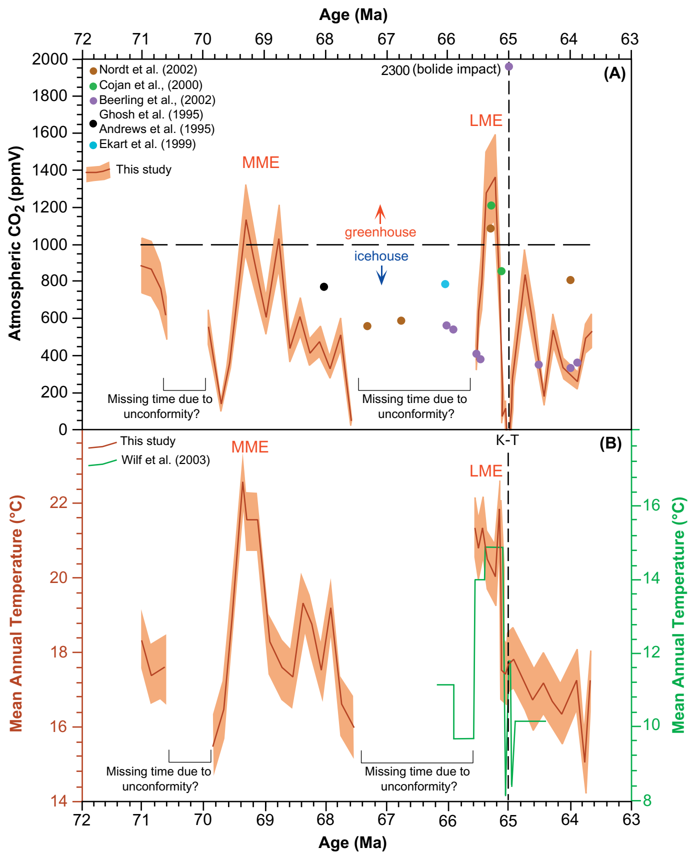

Figure 3. Calculated atmospheric CO_2 concentration and mean annual temperature curves in the study area. **A:** Data for pCO_2 from the west Texas study area shown with a range (shaded area) generated by varying S(z) from 5000 to 7000 ppm*V* typical of warm, low latitude settings (see Brook et al., 1983; Ekart et al., 1999). For India (Ghosh et al., 1995; Andrews et al., 1995) paleosol carbonate calculations are based on S(z) of 6000 ppm*V* for a latitude of 25–30°N. For paleosol carbonate data from France (Cojan et al., 2000) and Utah (Ekart et al., 1999), S(z) of 5000 ppm*V* was used for a latitude of 40–45°N. Paleosol carbonate data from Canada (Nordt et al., 2002) were calculated with an S(z) of 4000 ppm*V* for a latitude of 50°N. Atmospheric CO_2 estimates from Beerling et al. (2002) are from modeling of a stomatal index of land plant leaves. **B:** Temperature curve from the west Texas study area shown with a one-standard deviation window based on triplicate $\delta^{18}O$ values from paleosol carbonate. The temperature curve from Wilf et al. (2003) is from paleobotanical evidence in North Dakota (49°N).

gradient of ~0.4 °C per degree of latitude, which is approximately one-third less than the modern temperature gradient for North America.

Some workers interpret relatively high foraminiferal $\delta^{18}O$ values and accompanying low sea level as indicative of the formation of continental ice sheets in the Late Cretaceous (Miller et al., 1999; Stoll and Schrag, 2000; Miller et al., 2003). Other marine $\delta^{18}O$ interpretations for the same time interval argue for the presence of persistent greenhouse conditions (Huber et al., 2002). Excluding the two isotopic spikes, average atmospheric CO_2 concentration estimated from the west Texas study interval is ~500 ppm*V* with an average temperature of ~18 °C. Global circulation models predict that extensive continental ice sheets should begin to form below atmospheric CO_2 levels of 1000 ppm*V* when mean global temperatures fall below 20 °C (Oglesby and Saltman, 1990; DeConto and Pollard, 2003). Thus, our data cannot exclude the possibility of the presence of ice sheets during the K-T transition based on these climatic parameters.

Our data for the entire study interval reveal a relatively weak (r^2 = 0.30), but positive correlation between atmospheric CO_2 concentration and temperature, in which a doubling of CO_2 is accompanied by an ~0.6 °C increase in temperature. This is considerably less than the 2–4 °C temperature increase forecasted for a doubling of atmospheric CO_2 concentration in the next century (Adem and Garduno, 1998; Tett et al., 1999).

Ocean warming just prior to the K-T boundary has been noted to coincide with Deccan trap volcanism in India (Li and Keller, 1998a, 1998b; Barrera and Savin, 1999; Keller, 2001; Olsson et al., 2001; Wilf et al., 2003). Recent dating constrains two-thirds of Deccan trap flood basalt deposition to between 65.4 and 65.2 Ma (Hofmann et al., 2000), making it a strong candidate for CO_2 release causing the LME. Deccan trap volcanism began shortly after 69.0 Ma and lasted until 64.0 Ma (Hofmann et al., 2000), an interval that also brackets the MME and the atmospheric pCO_2 spike near 64.6 Ma.

CONCLUSIONS

Results from this investigation demonstrate that stable C and O isotopes from paleosol carbonate correlate well with the marine isotopic record and, when taken together, point to two intense greenhouse events in the Maastrichtian. These conclusions suggest that dramatic climate fluctuations were ongoing for several million years before the end-Cretaceous mass extinction. Further, they provide empirical evidence for atmospheric warming associated with elevated atmospheric CO_2 levels.

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