Low CO₂ levels of the entire Pleistocene epoch

Jiawei Da¹, Yi Ge Zhang², Gen Li³, Xianqiang Meng¹ & Junfeng Ji¹*

Quantifying ancient atmospheric pCO₂ provides valuable insights into the interplay between greenhouse gases and global climate. Beyond the 800-ky history uncovered by ice cores, discrepancies in both the trend and magnitude of pCO₂ changes remain among different proxy-derived results. The traditional paleosol pCO₂ paleobarometer suffers from largely unconstrained soil-respired CO₂ concentration (S(z)). Using finely disseminated carbonates precipitated in paleosols from the Chinese Loess Plateau, here we identified that their S(z) can be quantitatively constrained by soil magnetic susceptibility. Based on this approach, we reconstructed pCO₂ during 2.6–0.9 Ma, which documents overall low pCO₂ levels (<300 ppm) comparable with ice core records, indicating that the Earth system has operated under late Pleistocene pCO₂ levels for an extended period. The pCO₂ levels do not show statistically significant differences across the mid-Pleistocene Transition (ca. 1.2–0.8 Ma), suggesting that CO₂ is probably not the driver of this important climate change event.
O

ver the last 3 million years (Ma), the Earth has cooled substantially and transitioned from a single-pole glaciation to a stage with major glaciations on both poles. In the past 1 Ma, the period of glacial cycles switched from ~41 thousand years (ky) to ~100 ky (mid-Pleistocene Transition, MPT), with the magnitude of the climate change associated with the glacial cycles significantly enhanced. What has ultimately driven these far-reaching climate changes is unclear. Atmospheric CO$_2$, the most important non-condensing greenhouse gas, plays an important role in global climate changes. However, although an overall decreasing trend has been documented, the available early Pleistocene (2.6–0.8 Ma) pCO$_2$ reconstructions, mostly from the marine realm, differ for both trends and absolute values.

As a terrestrial archive, the pedogenic carbonates found in paleosols have been widely applied for pCO$_2$ reconstruction, especially for the Paleozoic and Mesozoic eras when other proxies are often not available. In soils, the rate of carbonate crystallization is much slower than gas exchange, thus pedogenic carbonates precipitated in the vadose zone are thought to reach carbonate isotope equilibrium with CO$_2$ in soil pore space. This soil-pore CO$_2$ represents a mixture of two end members with distinct $\delta^{13}$C signatures: atmospheric CO$_2$ and soil-respired CO$_2$. Built on this isotopic end-member mixing principal and gas diffusion dynamics, previous studies have derived a complete solution to estimate ancient atmospheric pCO$_2$ from soil-associated parameters (i.e. the paleosol CO$_2$ paleobarometer).

Specifically, atmospheric pCO$_2$ levels can be expressed as

$$pCO_2 = S(z) \frac{\delta^{13}C_a - 1.00443 \delta^{13}C_c - 4.4}{\delta^{13}C_a - \delta^{13}C_c}$$  

(1)

where $\delta^{13}C_a$, $\delta^{13}C_c$, and $\delta^{13}C_c$ refer to the carbon isotopic compositions of total soil CO$_2$, soil-respired CO$_2$, and atmospheric CO$_2$, respectively, and $S(z)$ is the soil-respired CO$_2$ concentration at soil depth $z$ during the time of carbonate precipitation. Generally, the soil $\delta^{13}C_c$ is calculated from $\delta^{13}C_a$ (the carbon isotopic composition of pedogenic carbonate) using a temperature-dependent fractionation factor; the soil-respired $\delta^{13}C_c$ is approximated by $\delta^{13}C$ value of coeval soil organic matter (SOM) preserved in the same paleosol strata; and the carbon isotopic composition of atmospheric CO$_2$ ($\delta^{13}C_a$) can be estimated from marine carbonate records. This approach has been extensively applied to pedogenic carbonates worldwide to reconstruct pCO$_2$ over the geological past. Approaches to determine the carbon isotopic terms ($\delta^{13}C_a$, $\delta^{13}C_c$, and $\delta^{13}C_c$) have been well established. However, significant uncertainties still remain in this paleosol CO$_2$ barometer, which is mainly sourced from the $S(z)$ term that describes soil respiration.

$S(z)$ has been difficult to constrain. Early studies commonly treated $S(z)$ as a constant of 5000 ppm based on limited modern observations. However, accumulating evidence over the last decade has shown that $S(z)$ is highly variable both spatially and temporally. Studies of Holocene calcareous soils demonstrated that pedogenic carbonate precipitates under warm, dry climatic conditions, when soil productivity, and $S(z)$ are much lower than previously assumed. Besides, among different soil types and soil moisture regimes, $S(z)$ can vary by up to two orders of magnitude. The extensive variability of $S(z)$ across different climatic conditions and soil types leads to large uncertainties of the paleosol-based method, especially for the late Cenozoic when pCO$_2$ is low with small variations. Instead of treating $S(z)$ as a constant, recent works took into account the variability of $S(z)$ either by establishing empirical models equating $S(z)$ with other climatic parameters such as mean annual precipitation (MAP), or by defining soil order-specific ranges. Although a major step forward, both approaches have caveats. Estimates of $S(z)$ using MAP proxies such as CIA-K (chemical index of alteration without potassium) or DTC (depth to carbonate nodular horizon) are empirically developed based on modern soil systems, but have not been validated for applications in paleosols. $S(z)$ values of different soil types, for example, the aridisols, still vary from 500 to 2500 ppm, which would contribute to a five-fold spread in estimated $pCO_2$. Importantly, the calculated $pCO_2$ scales proportionately with $S(z)$ (Eq. (1)), making it a vital factor for the success of paleosol-derived CO$_2$ estimates.

In this study, we seek to improve the paleosol CO$_2$ barometer by providing more robust constraints on $S(z)$. To achieve this, we focus on the finely disseminated carbonates (FDC) in bulk paleosols on the Chinese Loess Plateau (CLP). Field observations and scanning electronic microscopy (SEM) imaging together demonstrate a shallow formation depth of FDC (soil Bt/Bw horizon). Further, a suite of geochemical analyses are used to test the pedogenic origin of these carbonates, as well as the potential of diagenetic alterations. Rather than assuming a constant $S(z)$ for all samples, we explore the possibility of sample-specific $S(z)$ values by employing soil magnetic susceptibility (MS) as a proxy for $S(z)$. With this refined method and new data, we intend to provide a better assessment of the interglacial pCO$_2$ for the early Pleistocene epoch from a terrestrial perspective.

Results

Geological setting and sampling. The accumulation of eolian material on the CLP initiated during the early Miocene. In the Quaternary loess–paleosol sequence, paleosol units formed during interglacial episodes were characterized by slower eolian dust deposition, strengthened summer monsoonal rainfall, and enhanced pedogenesis relative to the glacials. Large seasonal changes in precipitation and evaporation contribute to the wide occurrence of pedogenic carbonates across the CLP. Unlike the more humid southeastern CLP (e.g. typical sites including Lantian, Baoji), where extensive leaching completely calcified the paleosols, or the more arid northwestern CLP (e.g. Huaxian, Jinyuan), where large amount of detrital carbonates remained due to insufficient rainfall, our sampling location, the Luochuan section (35.76°N, 109.42°E) located in the central CLP (Supplementary Fig. 1), is characterized by the appropriate level of pedogenesis. The detrital carbonates are mostly absent in paleosol samples, whereas authigenic carbonates are still preserved (Supplementary Fig. 2). Before sampling, we trenched the soil profile (>1 m deep) to avoid contamination of regolith, and monitored the MS values of bulk paleosols, which were compared to published data. Each sample was collected within a 10 cm interval. Paleosol samples used in this study mainly occur within the soil Bt/Bw horizons, characterized by subangular blocky structure with clay coatings attached on structural faces, and a 5–7.5 YR Munsell color.

Finely disseminated carbonates. In the field, the carbonates in our targeted paleosol samples have identifiable pedofeatures including finely disseminated cements filling the soil matrix, and carbonate hypocoatings (i.e. pseudomycelia) lining pores and tubules, which can be categorized as Stage 1 pedogenic carbonate. Therefore, we term this carbonate fraction as FDC. SEM imaging further reveals that our sampled FDC are mainly composed of 5–10 µm-long needle fiber calcite (NFC), and clustered nanoscale calcite nanofibers (Fig. 1a–d). The SEM results are consistent with previous findings that NFC is commonly associated with smaller carbonate fibers such as nanofibers, indicating similar formation conditions and a pedogenic origin. Importantly, NFC mostly appears between the humic horizon (O horizon) and subsurface C zone and vanishes with depth. The
location of NFC matches our field observations, which indicate the occurrence of FDC within the relatively shallow soil Bt/Bw horizon in comparison to the nodule-bearing Bk horizon. The origin of NFC is tied to both organic (fungal biominalization) and inorganic activities (physicochemical precipitation)\textsuperscript{29,30}. Whichever the case, it appears that the stable isotopic compositions (δ\textsuperscript{13}C and δ\textsuperscript{18}O) of NFC are indistinguishable from coeval calcite cements (rhombohedral calcite crystals)\textsuperscript{31}, making bulk measurements of FDC well representative of all encapsulated calcite phases.

Incomplete dissolution of the detrital carbonate components (calcite and dolomite) from parent material of the loess (e.g. eolian dust) would bias the δ\textsuperscript{13}C of the bulk soil carbonates. However, they appear to only impose very minor influence on our samples because we selected samples without the presence of any dolomite for subsequent analyses, as measured by the Fourier transform infrared spectrophotometry that is highly sensitive to carbonate minerals. However, we expect this process to have minimal influence on our carbonate samples for two reasons. Firstly, the long-term trend of δ\textsuperscript{13}C derived from the FDC fractions of our paleosol samples is almost identical with that determined from δ\textsuperscript{13}C of coeval calcite nodules throughout the Pleistocene, although the nodule record has a much lower resolution (Supplementary Fig. 3). Calcite nodules are usually considered to be buffered against diagenesis\textsuperscript{11,18}. Notably, the Pliocene paleosol formations in the CLP also show indistinguishable δ\textsuperscript{13}C and δ\textsuperscript{18}O values from mm-scale micrites to massive carbonate horizons\textsuperscript{34}, suggesting that the FDC could potentially be used to reconstruct pCO\textsubscript{2} beyond the Pleistocene. Secondly, numerous studies of paleosol carbonates from the CLP suggest that their geochemical signals are pristine and record near-surface conditions. For instance, trace metal compositions of fine-grained pedogenic carbonates from loess–paleosol sections in the CLP appear to preserve local precipitation signals\textsuperscript{33} and show high-frequency variations on orbital timescales\textsuperscript{35}. The Mn/Ca and Mg/Ca ratios of the FDC fractions are significantly lower than the carbonate samples from potential source regions of the loess— the deserts in Northern China (Fig. 1c)\textsuperscript{32}, providing additional evidence for the pedogenic origin of our bulk paleosol carbonates.

Diagenetic alterations (i.e. the dissolution and reprecipitation of fine-grained carbonates) could also affect δ\textsuperscript{13}C and other geochemical signatures. However, we expect this process to have minimal influence on our carbonate samples for two reasons. Firstly, the long-term trend of δ\textsuperscript{13}C derived from the FDC fractions of our paleosol samples is almost identical with that determined from δ\textsuperscript{13}C of coeval calcite nodules throughout the Pleistocene, although the nodule record has a much lower resolution (Supplementary Fig. 3). Calcite nodules are usually considered to be buffered against diagenesis\textsuperscript{11,18}. Notably, the Pliocene paleosol formations in the CLP also show indistinguishable δ\textsuperscript{13}C and δ\textsuperscript{18}O values from mm-scale micrites to massive carbonate horizons\textsuperscript{34}, suggesting that the FDC could potentially be used to reconstruct pCO\textsubscript{2} beyond the Pleistocene. Secondly, numerous studies of paleosol carbonates from the CLP suggest that their geochemical signals are pristine and record near-surface conditions. For instance, trace metal compositions of fine-grained pedogenic carbonates from loess–paleosol sections in the CLP appear to preserve local precipitation signals\textsuperscript{33} and show high-frequency variations on orbital timescales\textsuperscript{35}. The Mn/Ca and Mg/Ca ratios of the FDC fractions are significantly lower than the carbonate samples from potential source regions of the loess— the deserts in Northern China (Fig. 1c)\textsuperscript{32}, providing additional evidence for the pedogenic origin of our bulk paleosol carbonates.

Diagenetic alterations (i.e. the dissolution and reprecipitation of fine-grained carbonates) could also affect δ\textsuperscript{13}C and other geochemical signatures. However, we expect this process to have minimal influence on our carbonate samples for two reasons. Firstly, the long-term trend of δ\textsuperscript{13}C derived from the FDC fractions of our paleosol samples is almost identical with that determined from δ\textsuperscript{13}C of coeval calcite nodules throughout the Pleistocene, although the nodule record has a much lower resolution (Supplementary Fig. 3). Calcite nodules are usually considered to be buffered against diagenesis\textsuperscript{11,18}. Notably, the Pliocene paleosol formations in the CLP also show indistinguishable δ\textsuperscript{13}C and δ\textsuperscript{18}O values from mm-scale micrites to massive carbonate horizons\textsuperscript{34}, suggesting that the FDC could potentially be used to reconstruct pCO\textsubscript{2} beyond the Pleistocene. Secondly, numerous studies of paleosol carbonates from the CLP suggest that their geochemical signals are pristine and record near-surface conditions. For instance, trace metal compositions of fine-grained pedogenic carbonates from loess–paleosol sections in the CLP appear to preserve local precipitation signals\textsuperscript{33} and show high-frequency variations on orbital timescales\textsuperscript{35}. The Mn/Ca and Mg/Ca ratios of the FDC fractions are significantly lower than the carbonate samples from potential source regions of the loess— the deserts in Northern China (Fig. 1c)\textsuperscript{32}, providing additional evidence for the pedogenic origin of our bulk paleosol carbonates.
Based on field observations, micromorphology, and geochemical characteristics, we conclude that the FDC fractions used in this study are of a pedogenic origin with minimal diagenetic alteration, thus suitable for paleosol-based pCO$_2$ reconstructions.

**Resolving S(z).** Rearranging Eq. (1) and we obtain

$$ S(z) = pCO_2 \times \delta^{13}C_a - \delta^{13}C_i - 1.0044\delta^{13}C_i - 4.4 \quad (2) $$

which provides a mathematical solution for S(z). Carbonate and SOM were measured for stable C isotopes to obtain δ$^{13}$C$_{a}$ and δ$^{13}$C$_{i}$ (see the “Methods” section). δ$^{13}$C$_{a}$ was obtained from marine carbonate δ$^{13}$C$_{CO_2}$ over the last 800 ky were derived from the ice core pCO$_2$ record34. Together they were used to compute S(z) of the Luochuan section over the last 800 ky. To estimate the uncertainties of the back-calculated S(z), we adopted Monte Carlo random sampling simulations to propagate errors from all input parameters (Supplementary Note 1). In brief, for each sample, we randomly sampled each parameter in Eq. (2) within its error range for 10,000 times and calculated a corresponding S(z) population. We report S(z) as the median values of the results from the Monte Carlo simulations, and define the associated uncertainties using the 16th and 84th percentiles of the simulated S(z) population (corresponding to the median value and the ±1σ error range in a standard Gaussian distribution).

When pedogenic carbonate precipitates deep in the soil profile where soil-respired CO$_2$ dominates over atmospheric CO$_2$, back-calculated S(z) are inherently associated with sizable errors7. We therefore adopted the concept of an R factor, defined as the ratio between [CO$_2$]$_{atm}$ and S(z) ($R = (\delta^{13}C_a - 1.0044 \times \delta^{13}C_i - 4.4)/\delta^{13}C_i$), as a screening criterion. When atmospheric CO$_2$ constitute a minor portion of soil CO$_2$ (R < 0.3 according to ref. 7), the samples are thought to be dominated by soil-respired CO$_2$ thus discarded for subsequent analyses. Twenty-two paleosol samples passed this criterion, representing 78% of all the samples analyzed for S(z). The calculated median S(z) levels over the last 800 ky show variations from 356 to 815 ppm, with uncertainties on average of +96/−75 ppm (Fig. 2a).

**MS as a proxy for S(z).** Soil-respired CO$_2$ comes from two major sources—the respiration of autotrophs, such as plant roots, and heterotrophs, such as the soil microbes mediating the oxidation of SOM. Studies of modern soils have shown that S(z) as a measure of soil productivity, is strongly correlated to climate parameters, such as temperature, precipitation, and evapotranspiration37. Notably, among carbonate-bearing soils in semi-arid to arid regions, such as the CLP, S(z) is mainly controlled by precipitation18,37. To quantitatively constrain S(z), here we explore a potential proxy sensitive to precipitation changes—soil magnetic susceptibility (MS).

The MS of bulk soil samples is predominantly controlled by the presence of ultrafine magnetite38,39, which is efficiently produced in situ under well-drained soils with alternative wet (Fe$^{2+}$ produced) and dry (Fe$^{2+}$/Fe$_3^+$ oxide precipitated) cycles. The ultrafine ferromagnetic grains are either directly produced by magnetotactic bacteria, or formed by inorganic precipitation, mediated by the production of Fe$^{2+}$ through iron-reducing bacteria40. Similarly, modest precipitation increase would enhance microbial activities, the formation of magnetic iron oxides and consequently soil MS, but MS decreases under excessive rainfall (MAP > 1000 mm) as the production of ferrimagnet ceases41. MAP > 1000 mm probably never occurred in the Pleistocene history of the central to northern part of the CLP42. As a result, MS is regarded as a sensitive paleoclimate proxy of pedogenesis intensity and paleorainfall40, and has been widely used to address the evolution history of the East Asian summer monsoon23,43.

Intensified precipitation would facilitate the formation of magnetic iron oxides (i.e. MS), and increase soil productivity and S(z). Because rainfall regulates soil MS and S(z) in a similar manner on the CLP, these two parameters are expected to be correlated. Indeed, when the two parameters from the Luochuan samples covering the last 800 ky were plotted against each other, we observe a statistically significant correlation (Fig. 2a):

$$ S(z) = 2.66(±0.44) × MS + 114.9(±71.1) (r^2 = 0.64, p < 0.0001) \quad (3) $$

The fitting is done using the least-squares linear regression model, and the uncertainties on the slope and intercept represent 1σ standard errors. Extrapolating this relationship to the entire Pleistocene will enable sample-specific S(z) using measured MS, and consequently the calculation of pCO$_2$ from paleosols (MS–S(z) approach). By providing new constraints on S(z), this MS–S(z) approach potentially improves the paleosol method for reconstructing pCO$_2$.

---

**Fig. 2** The magnetic susceptibility (MS)–S(z) correlation of the Chinese Loess Plateau. a Back-calculated S(z) values plotted against MS from Luochuan paleosol samples spanning the last 800 ky. Error bars represent 1σ errors resulted from Monte Carlo simulations (Supplementary Note 1). The best fitting line, as well as 95% confidence interval are indicated by red solid and dotted lines, respectively. b Histogram of the mean relative differences ($\Delta$) between calculated and ice core pCO$_2$ when the sample numbers in the training group ($n$) is set to 10.
To validate the MS–$S(z)$ approach, we next recalculated the $S(z)$ of our 800-ky paleosol samples using the MS–$S(z)$ approach, and compare the derived $pCO_2$ to those documented in ice cores. Because the determination of the MS–$S(z)$ relationship relied on the ice core $CO_2$ record, to avoid circular reasoning, we adopted a resampling technique. Specifically, the 22 samples were divided into two subsets: a training sample group and a test sample group. A MS–$S(z)$ regression was established from the training group, and used to estimate $S(z)$ for the test group, the resulting $pCO_2$ of which were then compared to the ice core data. For a given training sample number $n$, a bootstrap sampling of 1,000,000 times was performed (each time, we obtained $22 - n$ $pCO_2$ values). We also varied the sample numbers in the training group from $n = 10$ to $n = 21$. During each run, the mean relative difference $\chi$ between the calculated $pCO_2$ and those from the ice core data was calculated:

$$\chi = \frac{1}{(22 - n)} \sum_{i=1}^{22-n} \left(1 - \frac{\text{Calculated } pCO_2}{\text{Ice core } pCO_2}\right)$$ (4)

The statistical distributions of $\chi$ (Fig. 2b and Supplementary Fig. 4) show that, across different training sample number $n$, $\chi$ is clustered around 0 with >70% of the data points falling within ± 10% difference. This consistent pattern among different $n$ values strongly supports our MS–$S(z)$ approach for $pCO_2$ reconstruction over the last 800 kyr.

Reconstructing early Pleistocene $pCO_2$. The refined soil carbonate-$pCO_2$ approach was also applied to the samples from the lower section of the Luochuan profile spanning the early Pleistocene, beyond the available ice core records. Measured MS and stable carbon isotopes for those early Pleistocene samples were used to calculate $S(z)$ and $pCO_2$, assuming that the MS–$S(z)$ relationship remains (Eq. (3)). We calculated the uncertainties on $pCO_2$ by propagating the uncertainties associated with the analyses of all input parameters and the MS–$S(z)$ regression equation using PBUQ, a published MatLab-based program that adopts Monte Carlo random sampling simulations for uncertainty analysis. We report the median values of the calculated $pCO_2$, and define the uncertainties as the 16th and 84th percentiles (as ±1σ), and the 2.5th and 97.5th percentiles (as ±2σ) of $pCO_2$ distributions from Monte Carlo simulations (see the “Methods” section).

The calculated $S(z)$ during ~2.6–0.8 Ma vary between 276 and 644 ppm, with errors (1σ) ranging from 76 to 113 ppm (Fig. 3c). The $R$ values ($pCO_2$/$S(z)$) are generally higher (>0.3) during the early Pleistocene, suggesting that these samples are suitable for

---

**Fig. 3** Stable isotopes and calculated $S(z)$ and $pCO_2$. a $\delta^{13}C$ values of soil organic matter ($\delta^{13}C_{\text{SOOM}}$). b $\delta^{13}C$ values of finely disseminated carbonates ($\delta^{13}C_{\text{CN}}$). c $S(z)$ estimates based on the magnetic susceptibility (MS) proxy. d Reconstructed early Pleistocene $pCO_2$ (median levels of $pCO_2$ distributions, 2.6–0.8 Ma) and ice core $CO_2$ record (0.8–0 Ma)\(^{36}\). Horizontal gray line shows the pre-industrial $pCO_2$ level (280 ppm). Errors associated with $\delta^{13}C_{\text{CN}}$ and $\delta^{13}C_{\text{SOOM}}$ are standard deviations of all measurements within the same paleosol unit ($n > 3$). Error bars related to $pCO_2$ represent the 16th and 84th percentiles (1σ) based on PBUQ Monte Carlo simulations\(^7\), whereas errors associated with $S(z)$ were calculated based on Gaussian error propagations (Supplementary Note 1)
CO₂ reconstructions. This newly established interglacial CO₂ records show variations from 183 to 292 ppm (averaged median CO₂ levels for each interglacial episode) during 2.6–0.9 Ma (Fig. 3d). Except for some data points centered around the Pliocene–Pleistocene boundary (2.6–2.5 Ma) and the MPT showing relatively higher CO₂ exceeding 300 ppm, our paleosol-CO₂ estimates document overall low early Pleistocene CO₂ levels similar to those over the last 800 ky (Fig. 3d). The reconstructed CO₂ values have an 1σ error range of +92/–82 ppm when averaging the errors for all individual results.

To evaluate the role CO₂ played for the MPT, we performed a detailed comparison of MPT–CO₂ with those before and after the MPT (i.e. pre-MPT and post-MPT), the durations of which were considered to be 400 ky equivalent to the MPT itself (i.e. 0.8–0.4 Ma for post-MPT and 1.6–1.2 Ma for pre-MPT). Our paleosol-based CO₂ reconstructions provide 16 estimates during the MPT and 21 pre-MPT. CO₂ estimates during the MPT and pre-MPT were then converted into factor changes in CO₂ by normalizing CO₂ to the mean post-MPT CO₂ from ice cores, since our paleosol–CO₂ estimates are indistinguishable from ice core data (Fig. 2b and Supplementary Fig. 4). We calculated the probability density functions (PDFs) and cumulative distribution functions (CDFs) of the factor changes in CO₂ among different time periods (i.e. MPT/pre-MPT, MPT/post-MPT, pre-MPT/post-MPT) (Supplementary Note 2). As indicated by both absolute values and the factor changes, CO₂ level during the MPT (mean = 269 ± 38 ppm, 1σ = +105/–94 ppm) was ~15% higher than that of the post-MPT (mean = 231 ± 37 ppm), and ~20% higher than that of the pre-MPT (mean = 217 ± 25 ppm, 1σ = +73/–67 ppm) (Fig. 4a). Results from the PDFs and CDFs also confirm this distribution (Fig. 4b, c).

Discussion

The foundation of the refined paleosol-based CO₂ estimates lies in the premise that soil MS can be used to constrain S(z), with the rationale that on the CLP, both parameters are controlled by monsoon precipitation. However, soil residence time, or the duration of pedogenesis before they were deeply buried by the newly arrived eolian material, could potentially affect MS, thus hampering the application of our MS–S(z) approach. However, multiple lines of evidence suggest that since soil formation, soil MS quickly reaches a near-steady-state equilibrium status, insensitive to the duration of pedogenesis. For instance, the MS of modern surface soils across the CLP region (30–200) 44 are equivalent to those of the Pleistocene paleosols (60–220) from this study, even though the modern soils have undergone much shorter periods of pedogenesis.

Changes of the accumulation rate of dust supply could also modify soil properties. However, in the central CLP region (e.g. Luochuan in this study), the mean mass accumulation rate of loess remained relatively constant (ca. 5–8 g m⁻² yr⁻¹) without discernable trend during the interglacial cycles over the last 2.6 Ma 45. As a consequence, we render that the observed correlation between MS and S(z) over the last 800 ky can be applied to early Pleistocene paleosols.

It is noteworthy that interglacial MS levels during the early Pleistocene (99 ± 28) are generally lower than those during the last 800 ky (154 ± 28), and most of the MS values (78 ± 11) of our 1.7–1.5 Ma samples fall below the MS range (99–227) over the last 800 ky. This translates to low S(z), low soil productivity, weak pedogenesis, and perhaps drier climate during the early Pleistocene, which is consistent with our current understanding of the early Pleistocene climate on the CLP 42.46. For instance, Fe minerals found in the CLP sequences are sensitive to climate changes, as high temperatures and limited seasonal rainfall would favor the formation of hematite over goethite. The hematite/goethite ratio of Luochuan section demonstrates a long-term, stepwise decreasing trend from 0.25 to 0.3, since the Pliocene/Pleistocene boundary, to as low as 0.2 towards the late Pleistocene, indicating reduced monsoonal precipitation during the early Pleistocene 47.

Previous estimates of the early Pleistocene pCO₂ mostly come from the applications of geochemical proxies to marine sediments (e.g. alkenone and boron proxies) 18–52. Although results from both boron and alkenone-based proxies suggest an overall decreasing trend since the early Pleistocene, discrepancies remain among individual records (Fig. 5). For instance, the composite view from two boron isotope records 18,49 indicates a sudden decline of pCO₂ at ~2.2 Ma, while the alkenone proxy suggests a gradual decline since ~2.5 Ma. Two alkenone-based results 17,50, however, show early Pleistocene pCO₂ values higher than 300 ppm, significantly elevated from the late Pleistocene levels recorded by ice cores. Both alkenone and boron proxies rely on certain assumptions, which could be invalidated by local physical, chemical, and biological processes 53. For example, marine-based pCO₂ reconstructions assume that an air–sea equilibrium of CO₂ is maintained for the entire studied interval, which does not
Fig. 5 $p$CO$_2$ and benthic $\delta^{18}$O data since 2.6 Ma. a Benthic $\delta^{18}$O stack$^{44}$. b–d Proxy-derived $p$CO$_2$ estimates (2.6–0.8 Ma) and ice core data (0.8–0 Ma)$^{36}$. Also shown is the blue ice record at ca. 1 Ma$^{56}$. Error bars are 1σ uncertainties. b Alkenone-derived $p$CO$_2$ records (red triangles (ODP 925)$^{17}$; green and gray triangles (ODP 806 and 1208)$^{50}$; yellow triangles (ODP 999)$^{51}$). c Boron-derived $p$CO$_2$ records (yellow circles (ODP 668)$^{49}$; green circles (ODP 999)$^{52}$; gray circles (ODP 999)$^{52}$; red circles (ODP 999)$^{48}$). Recently published high-resolution $p$CO$_2$ records across the MPT$^{62}$ are shown as the dark blue curve, with a lighter gray band representing the full 95% envelope of the sampled distribution. d Luochuan paleosol-based $p$CO$_2$ estimates. Horizontal dashed lines indicate the pre-industrial $CO_2$ level (280 ppm)

necessarily always hold. In addition, the boron method requires the knowledge of a second carbonate system such as alkalinity or dissolved inorganic carbon$^{54}$. Similarly, the alkenone method requires constraints on the physiological conditions of alkenone-producing haptophyte algae$^{55}$. Curiously, the recently studied blue ice which are outcrops of old ice from Antarctica show that $p$CO$_2$ remained <300 ppm for at least 1 million years$^{56}$ and possibly 2.7 million years$^{57}$, contradicting to some of the boron-based and alkenone-based results (Fig. 5b, c). In this respect, terrestrial archives free of the air–sea disequilibrium of CO$_2$ problem could weigh into the absolute values of Pleistocene $p$CO$_2$ problem.

Our terrestrial-based record shows that interglacial $p$CO$_2$ levels during 2.6–0.8 Ma varied between 183 and 292 ppm (averaged for each interglacial), with the lower $p$CO$_2$ levels within this range often associated with samples collected close to the paleosol–loess (i.e. interglacial–glacial) transitions. These $p$CO$_2$ estimates are similar to the ice core $p$CO$_2$ record of the last 800 ky (Fig. 5d), and consistent with the blue ice records which show <300 ppm $p$CO$_2$$^{56}$.

Coupled general circulation model/ice sheet model have suggested that, the $p$CO$_2$ has to drop below the threshold of 280 ppm to induce major Northern Hemisphere glaciations (NHG)$^{58}$. This is confirmed by this paleosol-based record, as well as a recently published high-resolution $\delta^{11}$B–$p$CO$_2$ record$^{48}$. However, some of the earlier estimates using marine archives showed >400 ppm of $p$CO$_2$ estimates prior to ca. 2.3 Ma$^{48,50}$. A recent study has identified that the traditional alkenone method tends to overestimate Pleistocene $CO_2$, which can be explained by the physiological parameter $b$ used that are on average, too large$^{59}$.

The gradual decline of $p$CO$_2$ over the last 3.0 Ma has been hypothesized to trigger the MPT transition$^{60,61}$. Recently published high-resolution $p$CO$_2$ record using $\delta^{11}$B proxy$^{62}$ documents an overall higher $CO_2$ level (241 ± 21 ppm) during the early part of the MPT (1.25–1.08 Ma) than that during 0.26–0 Ma (203 ± 14 ppm) (Fig. 5c). Our paleosol-based $p$CO$_2$ values also demonstrate a statistically significant decline of ~40 ppm from the MPT to the post-MPT period (Fig. 4a). However, the $p$CO$_2$ record presented in this study shows that the MPT itself was accompanied by a $CO_2$ rise of ~50 ppm (Fig. 4a). Calculation of factor changes in $CO_2$ among three time periods (i.e. pre-MPT, MPT, and post-MPT) also show a significant $CO_2$ peak during the MPT, and no apparent $CO_2$ difference before and after the MPT (Fig. 4). This analysis indicates that the low $CO_2$ condition was already established long before the MPT. As a consequence, our results do not support the supposition that the decline of $p$CO$_2$ lead to the onset of the MPT.

Methods
Chronology. The chronological framework of loess–paleosol sequences in Luochuan are based on the paleomagnetic reversal sequences, with the detailed information described in previous studies$^{43}$. The Brunhes–Matuyama reversal occurs among the transition of L8 (loess unit 8) and S8 (paleosol unit 8). The Jaramillo subchron is defined between the upper part of L10 and the base of S11, while the Olduvai subchron lies between the middle part of L25 and the lower part of S26. A basal age of ~2.6 Ma is estimated for the Chinese loess deposits, based on
δ13C and trace element analyses. Calcrete and dolomite contents of bulk soil samples were measured through Fourier transform infrared spectrophotometry, following procedures described in ref. 33. To ensure that our samples were free of detrital carbonates, only paleosol without dolomite were applied for subsequent analyses. In order to obtain δ13C, δ18O, and δ34S for pCO2 calculation, the δ13C values of pedogenic carbonates in bulk soil samples (i.e., FDC), and co-occurring SOM were measured. For carbonate isotope analyses, bulk soil samples were treated with 10% H2O2, the remaining of which were then oven-dried, crushed, and grinded into powder for homogeneous analysis. Samples were analyzed on a ThermoFinnigan MAT 253 isotope ratio mass spectrometer using a Kiel IV carbonate device (75 °C reaction in 100% H3PO4). For organic carbon isotope analyses, bulk soil samples were reacted with 1 M HCl to ensure complete dissolution of carbonates, and then ultrasonically rinsed with deionized water for multiple times until pH reached neutral. The oven-dried residues were grinded into powder, loaded into tin capsules and analyzed on the ThermoFinnigan MAT 253 isotope ratio mass spectrometer with a Costech elemental analyzer attached. Both carbonate and organic carbon isotopic results are reported in permil (‰) notation relative to the Vienna Pee Dee Belemnite (VPDB) standard with a precision better than ±0.2‰ from multiple analyses. Multiple samples (n = 3) from each paleosol unit were measured, with the averaged standard deviation for each paleosol unit about 0.47‰ (carbonate) and 0.43‰ (SOM). For trace element analysis of carbonate fractions, bulk samples were dissolved in 0.2 M acetic acid following the method described in ref. 33. Trace element concentrations of dissolved solutions were then measured on an ICP-OES 6300. Precisions are better than 0.3% for Mn/Ca, Mg/Ca, and Sr/Ca following ratio calculation method described in ref. 33.

Input parameters and error propagation. In this work, input parameters related to the pedobarometer equation were either directly measured or estimated. δ13C values can be solved by δ13C through a temperature-dependent fractionation equation. Previous work based on Pliocene pedogenic carbonates from the CLP revealed that the formation temperature of pedogenic carbonates is 1–2 °C lower than modern day summer air temperature (from June to September), and since Pliocene was globally warmer than Pleistocene, the formation temperature of pedogenic carbonates during the Pleistocene were probably not higher than the Pliocene. Therefore, we used a correction of −1.5 °C for the modern summer (JIAS) temperature (19.2 °C for Luochuan), to represent the formation temperature of our pedogenic carbonates throughout the study interval. Uncertainty associated with temperature was set to ±3 °C. Previous investigations have determined that δ13C fractionation between soil-respired CO2 and soil organic matter (SOM) and δ34S for pCO2 calculation. Therefore, δ13C values were approximated through δ13C of SOM from the same paleosol layer. However, carbon isotope fractionation occurs during decomposition of SOM, which could enrich the δ13C of bulk paleosol organic matter. Therefore, we applied a universal correction of −1 ± 0.5‰ for our δ13C values following the difference of δ13C values between the A and B horizon in an archived soil. Differences associated with the δ13C and δ18O were assigned based on the standard deviations of measured δ13C and δ18O in the same paleosol unit. Then, δ34S values were derived from measured δ34S values of contemporaneous marine benthic foraminifera carbonates. To calculate pCO2 and propagate errors associated with input variables, we used the Matlab-based PBuQ program. PBuQ calculates probability density functions for each variable based on input parameters and then uses Monte Carlo simulation, which are generated using 10,000 iterations. The program yields median R and pCO2 values with error bars extending to the 10th and 90th percentiles.

Data availability
All stable carbon isotope and magnetic susceptibility data from the Luochuan section of the Chinese Loess Plateau, as well as the calculated values can be solved by the pedobarometer equation: northern hemisphere ice sheets and North Atlantic Ocean. Paleogeography 4, 353–412 (1989).

References
1. Ruddiman, W. F. et al. Pleistocene evolution: northern hemisphere ice sheets and North Atlantic Ocean. Paleogeography 4, 353–412 (1989).
2. Clark, P. U. et al. The middle Pleistocene transition: characteristics, mechanisms, and implications for long-term changes in atmospheric pCO2. Quat. Sci. Rev. 25, 3150–3184 (2006).
3. Da, J., Zhang, Y. G., Wang, H., Balsam, W. & Ji, J. An Early Pleistocene super-greenhouse pCO2 record from the Chinese loess deposits. Earth Planet. Sci. Lett. 426, 69–75 (2015).
4. Cerling, T. E. Carbon Dioxide in the atmosphere: evidence from Cenozoic and Mesozoic paleosols. Am. J. Sci. 291, 377–400 (1991).
5. Montañez, I. P. et al. Climate, pCO2 and terrestrial carbon cycle linkages during late Palaeozoic glacial-interglacial cycles. Nat. Geosci. 9, 824–828 (2016).
6. Cerling, T. E. The stable isotopic composition of modern soil carbonate and its relationship to climate. Earth Planet. Sci. Lett. 71, 229–240 (1984).
7. Breecker, D. O. Quantifying and understanding the uncertainty of atmospheric CO2 concentrations determined from calcic paleosols. Geochim. Geophys. Geosyst. 14, 3210–3220 (2013).
8. Romanek, C. S., Grossman, E. L. & Morse, J. W. Carbon isotopic fractionation in synthetic aragonite and calcite: effects of temperature and precipitation rate. Geochim. Cosmochim. Acta 56, 419–430 (1992).
9. Breecker, D. O. et al. Minor stable carbon isotope fractionation between respired carbon dioxide and bulk soil organic matter during laboratory incubation of topsoil. Biogeochemistry 123, 83–98 (2015).
10. Tolle, B. J., Meyers, S. R. & Pagani, M. Carbon isotope ratio of Cenozoic CO2: a comparative evaluation of available geochemical proxies. Paleoceanography 25, PA3202 (2010).
11. Eklart, D. D., Cerling, T. E., Montañez, I. P. & Tabor, N. J. A 400-million-year carbon isotope record of pedogenic carbonate: implications for paleoatmospheric carbon dioxide. Am. J. Sci. 299, 805–827 (1999).
12. Breecker, D. Improving paleosol carbonate-based estimates of ancient atmospheric CO2. Geochim. News 144, http://www.geochemsoc.org/publications/geochemical-news/14410e10/improvingpaleosolcarbonate (2010).
13. Solomon, D. K. & Cerling, T. E. The annual carbon dioxide cycle in a montane soil: observations, modeling, and implications for weathering. Water Resour. Res. 23, 2257–2265 (1987).
14. Breecker, D. O., Sharp, Z. D. & McFadden, L. D. Seasonal bias in the formation and stable isotopic composition of pedogenic carbonate in modern soils from central New Mexico, USA. Geol. Soc. Am. Bull. 121, 630–640 (2009).
15. Montañez, I. P. Modern soil system constraints on reconstructing deep-time atmospheric CO2. Geochim. Cosmochim. Acta 101, 57–75 (2013).
16. Amundson, R. G. & Davidson, E. A. Carbon dioxide and nitrogenous gases in the soil atmosphere. J. Geochem. Explor. 38, 13–41 (1990).
17. Zhang, Y. G., Pagani, M., Liu, Z., Bohaty, S. M. & Deconto, R. A 40-million-year history of atmospheric CO2. Philos. Trans. R. Soc. A 371, 20130096 (2013).
18. Cotton, J. M. & Sheldon, N. D. New constraints on using paleosols to reconstruct atmospheric pCO2. Geol. Soc. Am. Bull. 124, 1411–1423 (2012).
19. Retallack, G. J. Renifing a pedogenic-carbonate pCO2 pedobarometer to quantify a middle Miocene greenhouse spike. Palaeogeogr. Palaeoclimatol. Palaeoecol. 281, 57–65 (2009).
20. Breecker, D. O. & Retallack, G. J. Renifing the pedogenic atmospheric CO2 proxy and application to Miocene CO2. Palaeogeogr. Palaeoclimatol. Palaeoecol. 406, 1–8 (2014).
21. Shackleton, N. J. & Thompson, M. L. Sols (Cambridge University Press, 2015).
22. Guo, Z. et al. Onset of Asian desertification by 22 Myr ago inferred from loess deposits in China. Nature 416, 159 (2002).
23. Liu, T. S. Loess and the Environment, 1–251 (China Ocean Press, Beijing, 1985).
24. Meng, X. et al. Dolomite abundance in Chinese loess deposits: a new proxy of monsoon precipitation intensity. Geophys. Res. Lett. 42, 391–398 (2015).
25. Sun, Y., Clemens, S. C., An, Z. & Yu, Z. Astronomical timescale and palaeclimatic implication of stacked 3.6-Myr monsoon records from the Chinese Loess Plateau. Quat. Sci. Rev. 25, 33–48 (2006).
26. Gile, L. H., Peterson, F. F. & Grossman, R. B. Morphological and genetic sequences of carbonate accumulation in desert soils. Soil Sci. 101, 347–360 (1966).
27. Phillips, S. & Self, P. G. Morphology, crystallography and origin of needle fiber calcite in quaternary pedogenic calcrites of South Australia. Soil Res. 25, 429–444 (1987).
28. Barta, G. Secondary carbonates in loess–paleosol sequences: a general review. Open Geosci. 3, 129–146 (2011).
29. Wright, V. P. The role of fungal biominalization in the formation of Early Carboniferous soil fabrics. Sedimentology 33, 831–838 (1986).
