



# Influence of temporally varying weatherability on CO<sub>2</sub>-climate coupling and ecosystem change in the late Paleozoic

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**Abstract.** Earth's penultimate icehouse period, the late Paleozoic ice age (LPIA), was a time of dynamic glaciation and repeated ecosystem perturbation, which was under conditions of substantial variability in atmospheric  $p\text{CO}_2$  and  $\text{O}_2$ . Improved constraints on the evolution of atmospheric  $p\text{CO}_2$  and  $\text{O}_2/\text{CO}_2$  ratios during the LPIA and its subsequent demise to permanent greenhouse conditions are crucial for better understanding the nature of linkages between atmospheric composition, climate, and ecosystem perturbation during this time. We present a new and age-recalibrated  $p\text{CO}_2$  reconstruction for a 40 Myr interval ( $\sim 313$  to  $273$  Ma) of the late Paleozoic that (1) confirms a previously hypothesized strong  $\text{CO}_2$ –glaciation linkage, (2) documents synchronicity between major  $p\text{CO}_2$  and  $\text{O}_2/\text{CO}_2$  changes and compositional turnovers in terrestrial and marine ecosystems, (3) lends support for a modeled progressive decrease in the  $\text{CO}_2$  threshold for initiation of continental ice sheets during the LPIA, and (4) indicates a likely role of  $\text{CO}_2$  and  $\text{O}_2/\text{CO}_2$  thresholds in floral ecologic turnovers. Modeling of the relative role of  $\text{CO}_2$  sinks and sources active during the LPIA and its demise on steady-state  $p\text{CO}_2$  using an intermediate-complexity climate–carbon cycle model (GEOCLIM) and comparison to the new multi-proxy  $\text{CO}_2$  record provides new insight into the relative influences of the uplift of the Central Pangean Mountains, intensifying aridification, and increasing mafic rock to granite rock ratio of outcropping rocks on the global efficiency of  $\text{CO}_2$  consumption and secular change in steady-state  $p\text{CO}_2$  through the late Paleozoic.

## 1 Introduction

Earth's penultimate and longest-lived icehouse period (340 to 290 Ma) occurred under the lowest atmospheric  $\text{CO}_2$  concentrations of the last half-billion years (Foster et al., 2017) and, potentially, the highest atmospheric  $p\text{O}_2$  of the Phanerozoic (Glasspool et al., 2015; Krause et al., 2018; Lenton et al., 2018). Anomalous atmospheric composition, along with 3 % lower solar luminosity (Crowley and Baum, 1992), may have primed the planet for a near-miss global glaciation (Feulner, 2017). Notably, Earth's earliest tropical forests assembled and expanded during this icehouse period (the late Paleozoic ice age; LPIA), leading to the emergence of large-scale wildfire. Paleotropical terrestrial ecosystems underwent repeated turnovers in composition and architecture, culminating in the collapse of wetland (coal) forests throughout tropical Pangea at the close of the Carboniferous (Cleal and Thomas, 2005; DiMichele, 2014), possibly promoting the diversification and ultimate dominance of amniotes (Pardo et al., 2019). In the marine realm, global rates of macroevolution (origination, extinction) decreased, in particular among tropical marine invertebrates, and genera with narrow latitudinal ranges went extinct at the onset of the LPIA (Stanley, 2016; Balseiro and Powell, 2019; Powell, 2005). Low marine macroevolutionary rates continued through to the demise of the LPIA in the early Permian (Stanley and Powell, 2003; McGhee, 2018).

Reconstructions of late Paleozoic atmospheric  $p\text{CO}_2$  document a broad synchronicity between shifts in  $\text{CO}_2$ , glacia-

tion history, glacioeustasy, and restructuring of paleotropical biomes, underpinning the hypothesized greenhouse gas forcing of sub-million-year glacial–interglacial cycles (Montañez et al., 2016) and the terminal demise of the LPIA (Montañez et al., 2007). For late Paleozoic  $p\text{CO}_2$  (and  $p\text{O}_2$ ) reconstructions, however, broad intervals of low temporal resolution and significant uncertainties limit the degree to which mechanistic linkages between atmospheric composition, climate, and ecosystem change can be further evaluated. Moreover, the potential impact of large-magnitude fluctuations in atmospheric O<sub>2</sub>/CO<sub>2</sub>, which characterized the late Paleozoic, on the biosphere has been minimally addressed. On longer timescales ( $\geq 10^6$  years), the relative roles of potential CO<sub>2</sub> sinks and sources on secular changes in late Paleozoic atmospheric CO<sub>2</sub>, and in turn as drivers of glaciation and its demise, remain debated (McKenzie et al., 2016; Goddard et al., 2017; Macdonald et al., 2019).

Here, we present a multiproxy atmospheric  $p\text{CO}_2$  reconstruction for a 40 Myr interval (313 to 273 Ma) of the late Paleozoic, developed using new leaf-fossil-based estimates integrated with recently published age-recalibrated Pennsylvanian  $p\text{CO}_2$  estimates of 10<sup>5</sup>-year resolution (Montañez et al., 2016) and re-evaluated fossil-soil-based (paleosol) CO<sub>2</sub> estimates for the early Permian (Montañez et al., 2007). Our new multiproxy record offers higher temporal resolution than existing archives while minimizing and integrating both temporal and CO<sub>2</sub> uncertainties. This  $p\text{CO}_2$  reconstruction, together with new O<sub>2</sub>/CO<sub>2</sub> estimates of similar temporal resolution, permits refined interrogation of the potential links between fluctuations in atmospheric composition, climate shifts, and ecosystem events through Earth's penultimate icehouse period. Moreover, comparison of the new 40 Myr CO<sub>2</sub> record with modeled steady-state  $p\text{CO}_2$  and seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  over the same interval provides new insight into the relative importance and evolution of CO<sub>2</sub> sinks and sources during late Paleozoic glaciation and its turnover to a permanent greenhouse state.

## 2 Materials and methods

A brief account of the methods is presented here; more details are presented in the Supplement. Primary data generated or used in this study are deposited in the Dryad Digital Repository (Richey et al., 2020) and can be accessed at <https://doi.org/10.25338/B8S90Q>.

### 2.1 Sample collection and analysis

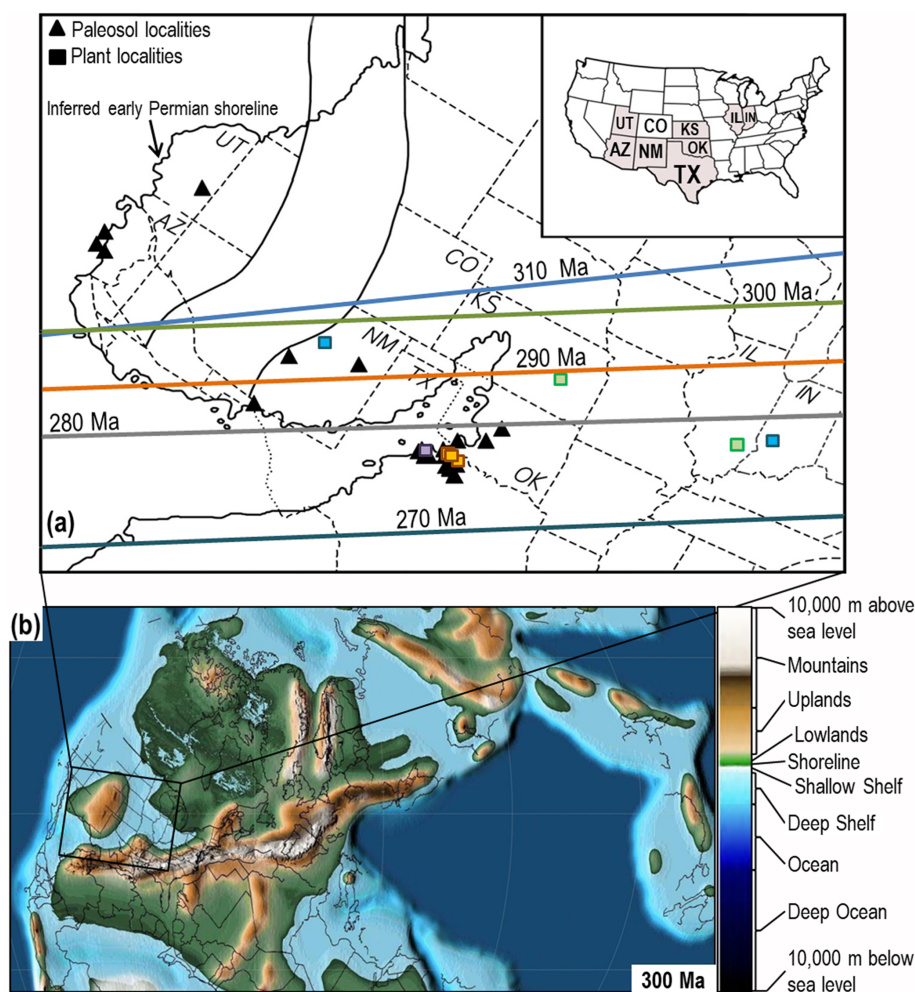
To build the  $p\text{CO}_2$  record, 15 plant cuticle fossil species/morphotypes were used, which were collected from eight localities in Illinois, Indiana, Kansas, and Texas, USA, including four well-studied Pennsylvanian interglacial floras (Sub-Minshall (313 Ma; Šimůnek, 2018), Kinney Brick (305.7 Ma; DiMichele et al., 2013), Lake Sarah Limestone (303.7 Ma; Šimůnek, 2018), and Hamilton

Quarry (302.7 Ma; Hernandez-Castillo et al., 2009a, b, c); Figs. 1a and S2–4 in the Supplement; Richey et al., 2020; <https://doi.org/10.25338/B8S90Q>). The Pennsylvanian estimates were integrated into a previously published  $p\text{CO}_2$  reconstruction (313 to 296 Ma; Montañez et al., 2016) of 10<sup>5</sup>-year resolution built using pedogenic carbonates and wet-adapted seed fern fossils (Figs. 2b, S1b). The Permian estimates were integrated with previously published latest Carboniferous and early Permian pedogenic carbonate-based CO<sub>2</sub> estimates (Montañez et al., 2007), derived from paleosols from successions throughout Arizona, New Mexico, Oklahoma, Texas, and Utah, USA (Fig. 1a; Richey et al., 2020; <https://doi.org/10.25338/B8S90Q>). The pedogenic carbonates and leaf cuticle fossils span a broad region of Pennsylvanian and early Permian tropical Euramerica (Fig. 1b). Ages of samples used in Montañez et al. (2007, 2016) were recalibrated and assigned uncertainties using the latest geologic timescale (Ogg et al., 2016) and biostratigraphic and geochronologic controls (see the Supplement; Richey et al., 2020; <https://doi.org/10.25338/B8S90Q>).

Plant cuticle and organic matter occluded within pedogenic carbonates (OOM) were rinsed in 3 M HCl to remove carbonates and analyzed at the Stable Isotope Facility, University of California, Davis, using a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20-20 IRMS (isotope-ratio mass spectrometer). External precision, based on repeated analysis of standards and replicates, is  $< \pm 0.2\text{‰}$ . For Hamilton Quarry (HQ), all material was previously mounted on slides for taxonomic analysis (Hernandez-Castillo et al., 2009a, b, c). Because of this, biomarker  $\delta^{13}\text{C}$  values of bulk stratigraphic sediment samples were used (Richey et al., unpublished data; see the Supplement). HQ  $n\text{-C}_{27-31}$   $n$ -alkane  $\delta^{13}\text{C}$  was analyzed using a Thermo Scientific GC Isolink gas chromatograph connected to a Thermo Scientific MAT 253 mass spectrometer. Standard deviation of  $n$ -alkane  $\delta^{13}\text{C}$  was  $\pm 0.3\text{‰}$ . For biomarker  $\delta^{13}\text{C}$ , a  $+4\text{‰}$  correction was used to account for fractionation during biosynthesis (Diefendorf et al., 2015), and the standard deviation of all values was used as the uncertainty (1.6‰, which is five times the analytical precision).

### 2.2 Models

The MATLAB model Paleosol Barometer Uncertainty Quantification (PBUQ; Breecker, 2013), which fully propagates uncertainty in all input parameters, was used to derive pedogenic carbonate-based CO<sub>2</sub> estimates (Figs. 2a, S1a). For each locality, paleosols of inferred different soil orders were modeled separately. We applied improved soil-specific values for soil-respired CO<sub>2</sub> concentrations ( $S_{\text{z}}$ ; Montañez, 2013) and the  $\delta^{13}\text{C}$  of organic matter occluded within carbonate nodules ( $\delta^{13}\text{C}_{\text{OOM}}$ ; Fig. S5) as a proxy of soil-respired CO<sub>2</sub>  $\delta^{13}\text{C}$ . For samples where OOM was not recovered, estimates were revised using PBUQ and the plant fossil organic matter  $\delta^{13}\text{C}$  used in Montañez



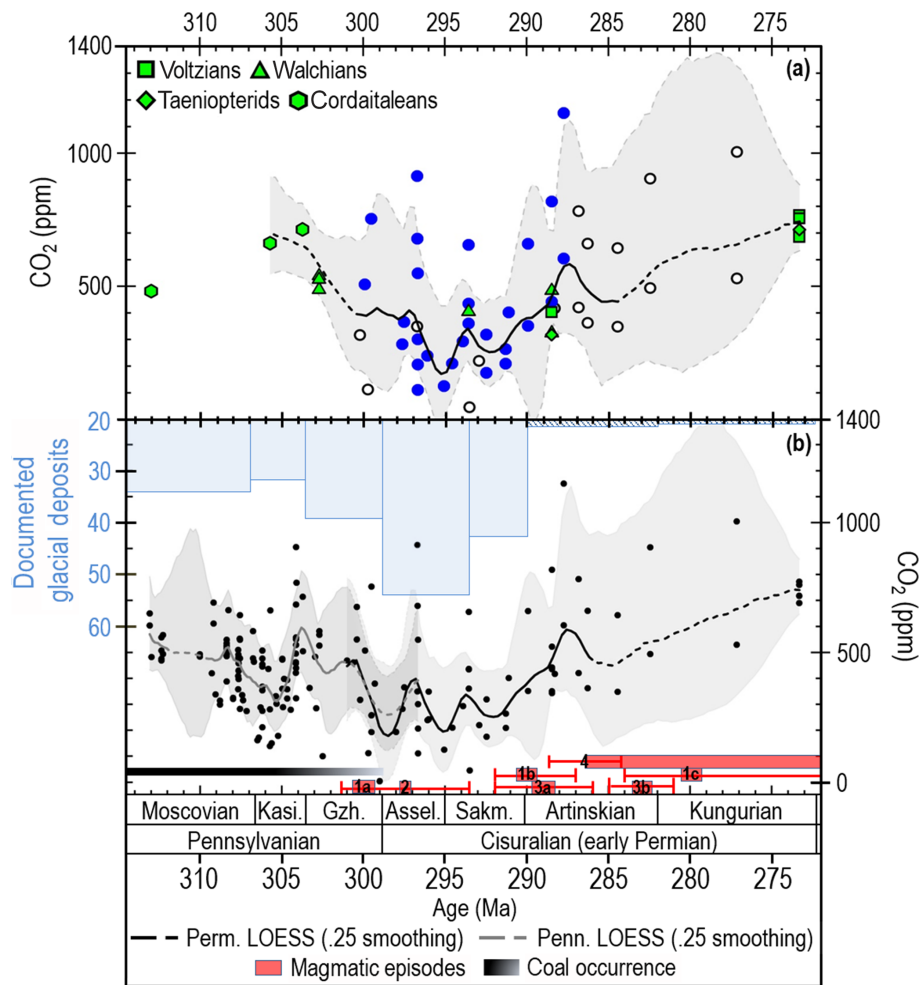
**Figure 1.** Sampling localities in present-day and late Paleozoic geographic context. **(a)** Sampling locations of pedogenic carbonates and plant fossils and their position relative to the late Pennsylvanian (310 and 300 Ma) and early Permian (290 to 270 Ma) equator (the colors of the flora localities correspond to that of the paleo-equator at that time). White band traversing NM (New Mexico) and CO (Colorado) is the area of inferred shortening during the Laramide and Sevier orogenies. Map modified from Montañez et al. (2007). **(b)** Earliest Permian (290 Ma) paleogeography (Scotese, 2016); shading corresponds to paleotopographic/bathymetric scale on the right. Inset box is the location of panel (a).

et al. (2007) ( $\delta^{13}\text{C}_{\text{POM}}$ ; Fig. S5). Because of the limited amount of carbonate nodules remaining after study by Montañez et al. (2007),  $\delta^{13}\text{C}_{\text{OOM}}$  was substituted for  $\delta^{13}\text{C}_{\text{POM}}$  for localities that occur in the same geologic formation, and a large error ( $\pm 2\%$ ) was used to account for the uncertainty in this approach. PBUQ model runs conducted in this study resulted in a small subpopulation of biologically untenable CO<sub>2</sub> estimates (i.e.,  $\leq 170$  ppm; Gerhart and Ward, 2010). To limit estimates below that threshold, two changes to the PBUQ MATLAB code were made (see the Supplement for details). All other input parameters remained unchanged from Montañez et al. (2007).

For cuticle fossil-based (Figs. S2–4) CO<sub>2</sub> estimates (Figs. 2a, S1a), we utilized a mechanistic (non-taxon-specific) gas-exchange model (Franks et al., 2014). For some

fossil cuticles, pore length (PL) was measured directly; for others, PL was inferred from guard cell length (GCL; Table S1 in the Supplement). Guard cell width was estimated via GCL using the prescribed gymnosperms and ferns scaler (0.6; Franks et al., 2014; Table S1).

For both stomatal- and pedogenic carbonate-based CO<sub>2</sub> modeling, we calculated  $\delta^{13}\text{C}$  of atmospheric CO<sub>2</sub> using the carbonate  $\delta^{13}\text{C}$  record generated from an open-water carbonate slope succession (Naqing succession, southern China; Buggisch et al., 2011), contemporaneous estimates of mean annual temperature (Tabor and Montañez 2005; Tabor et al., 2013), and temperature-sensitive fractionation between low-Mg calcite and atmospheric CO<sub>2</sub> (Romanek et al., 1992; Eq. S2; Table S1).



**Figure 2.** Late Paleozoic CO<sub>2</sub> estimates. (a) New and revised (Montañez et al., 2007)  $p\text{CO}_2$  estimates, bootstrapped LOESS trend, and 75 % confidence interval (CI). Revised pedogenic carbonate-based estimates were made using  $\delta^{13}\text{C}_{\text{OOM}}$  (blue filled circles;  $n = 28$ ; Fig. S1) and  $\delta^{13}\text{C}_{\text{POM}}$  (open black circles;  $n = 16$ ; Fig. S1). Trend line is the median of 1000 bootstrapped LOESS analyses; dashed intervals indicate low data density and higher uncertainty. See Fig. S1 for error bars on individual CO<sub>2</sub> estimates and the 95 % CI, and see Richey et al. (2020) (<http://doi.org/10.25338/B8S90Q>) for the full dataset. (b) Multiproxy CO<sub>2</sub> record and individual estimates (this study and age-recalibrated values by Montañez et al., 2016;  $n = 165$ ), documented glacial deposits (Soreghan et al., 2019), occurrence of peats (coal), and best estimate of timing (and uncertainties) of magmatic episodes: 1a = Tarim 1, China (~300 Ma); 1b = Tarim 2 (292–287, peak ~290 Ma); 1c = Tarim 3 (284–272, peak ~280 Ma; Chen and Xu, 2019); 2 = Skagerrak-centered, NW Europe (297.5 ± 3.8 Ma; Torsvik et al., 2008); 3a = Panjal Traps, NW India (289 ± 3 Ma; Shellnutt, 2018); 3b = Qiangtang Traps, Tibet (283 ± 2 Ma; Zhai et al., 2013); 4 = Choiyoi, W Argentina (beginning 286.5 ± 2.3 Ma, continuing for up to 39 Myr; Sato et al., 2015). Trend lines are as in (a); dashed intervals across the Carboniferous–Permian boundary (298.9 Ma) indicate overlap of the two LOESS trend lines.

We used the spatially resolved intermediate-complexity GEOCLIM model (Goddéris et al., 2014) to quantitatively evaluate how steady-state atmospheric CO<sub>2</sub> may have responded to changes in weatherability and the relative influences of different CO<sub>2</sub> sources and sinks. The spatial distributions of the mean annual runoff and surface temperature were calculated offline for five time increments (Goddéris et al., 2017), covering the period of interest, and for various atmospheric CO<sub>2</sub> levels using the 3-D ocean–atmosphere climate model FOAM and the approach as described in Donnadieu et al. (2006). GEOCLIM uses generated lookup ta-

bles to calculate steady-state atmospheric CO<sub>2</sub> for a given continental configuration and to account for paleogeography and relief. Although the GEOCLIM model does not include an explicit surface distribution of lithology, the weathering rate of mafic rocks and continental granites are calculated using different methods, and the impact of physical erosion on granite weathering is accounted for (Goddéris et al., 2017). For mafic surfaces, a simple parametric law is used, linking the surface of the considered grid cell, local runoff, and mean annual temperature to the local mafic weathering rate. The calibration of the GEOCLIM model was performed at the



continental-scale by tuning the parameters of the model so that 30 % of the alkalinity generated by the weathering of silicates originates from the weathering of mafic rocks (GEOCLIM REG; Dessert et al., 2001; Godd  ris et al., 2014).

### 2.3 O<sub>2</sub>/CO<sub>2</sub> ratio

O<sub>2</sub>/CO<sub>2</sub> ratios (Fig. 3a) were calculated using the 10 000 CO<sub>2</sub> estimates produced by our modeling and combined with O<sub>2</sub> estimates obtained using geochemical mass balance and biogeochemical models (Krause et al., 2018; Lenton et al., 2018). Unreasonably high O<sub>2</sub>/CO<sub>2</sub> ratios (generally those that correspond to CO<sub>2</sub> < 200 ppm) were removed from the resulting O<sub>2</sub>/CO<sub>2</sub> dataset.

### 2.4 Statistical analyses

We utilize a bootstrap approach that assesses uncertainties of both CO<sub>2</sub> (or O<sub>2</sub>/CO<sub>2</sub>) and age. Each age uncertainty was truncated to ensure no overlap in locality ages, which were constrained by their relative stratigraphic position to one another (Richey et al., 2020; <https://doi.org/10.25338/B8S90Q>). The 10 000 modeled CO<sub>2</sub> estimates were trimmed by 28 % to remove anomalously high or low values. The means of the resulting 7200 CO<sub>2</sub> estimates were compared to the trimmed means of the 10 000 CO<sub>2</sub> estimates to ensure that trimming did not alter the central tendency of the data. Locality ages were resampled and perturbed, assuming that the individual ages and truncated age uncertainties represent the mean and standard deviation of the ages. Similarly, the trimmed CO<sub>2</sub>–O<sub>2</sub>/CO<sub>2</sub> datasets were resampled with replacement, and the resampled ages and estimates were used to build 1000 resampled datasets. Each resampled dataset was subjected to LOESS analysis (0.25 smoothing), and the median and 95 % and 75 % confidence intervals of the LOESS analyses were calculated (Figs. 2, 3a, b, S1). The Pennsylvanian and Permian portions of the record were analyzed separately due to differing data density, with significant overlap across the Pennsylvanian–Permian boundary interval (Figs. 2b, 3b, S1b).

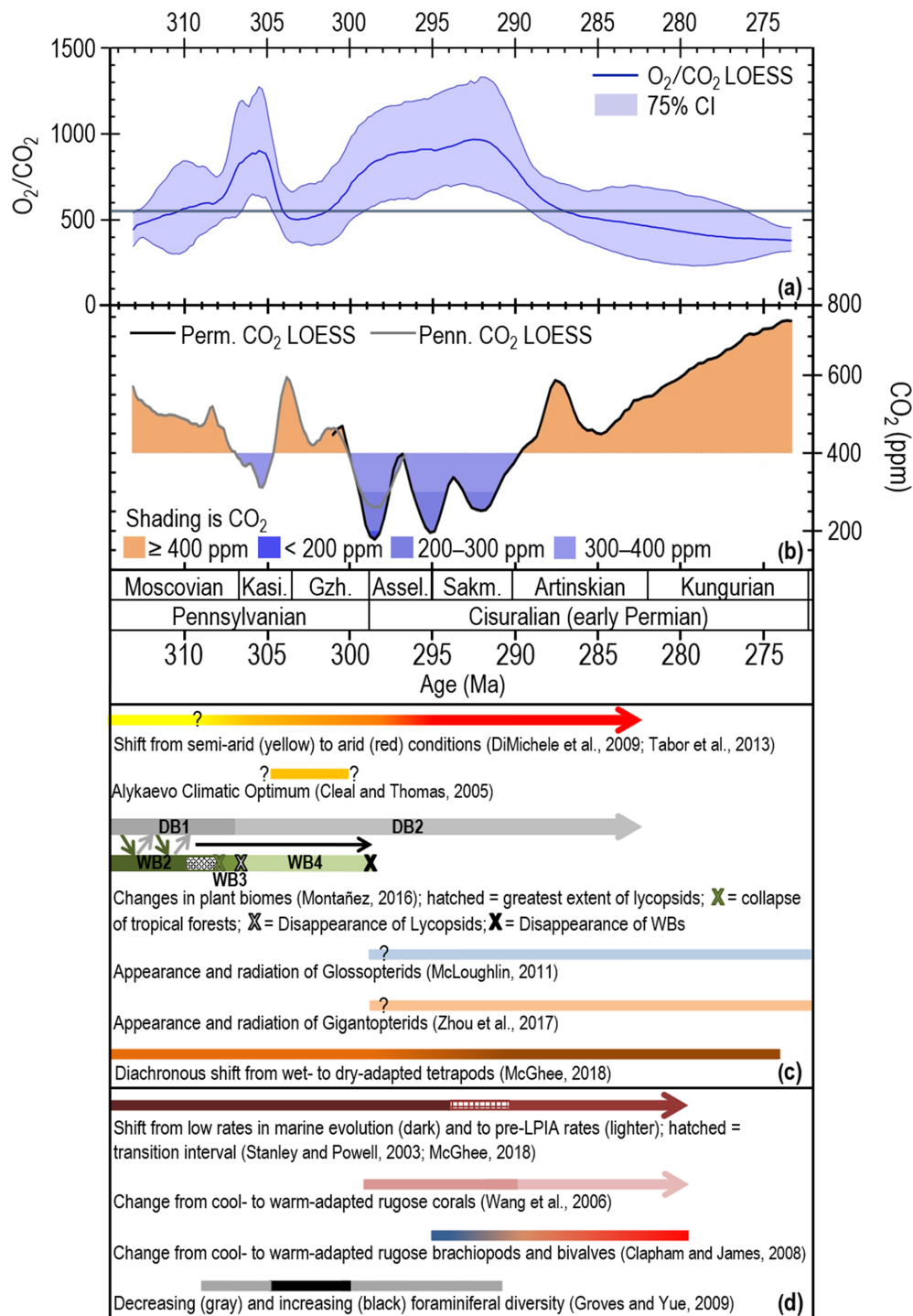
To test the validity of short-term fluctuations in the LOESS CO<sub>2</sub> trend, we undertook further analysis of the raw Monte Carlo data produced by PBUQ and the mechanistic stomatal model in several short-term increments. Eleven short-term highs or lows (A–K in Fig. 4a) were designated and used to form bins of ±0.5 to ±1 Myr. Within an individual bin, each shown “bootstrapped” CO<sub>2</sub> data point is the trimmed mean of 10 000 Monte Carlo model runs. The Monte Carlo model runs for each data point were sorted from lowest to highest CO<sub>2</sub> value, and the lowest CO<sub>2</sub> values for each data point within the bin were averaged. This averaging was repeated sequentially for each of the 10 000 values creating 10 000 means for each bin ( $n = 11$ ). To evaluate whether a visually perceived rise or fall (e.g., A to B decrease or B to C

increase) is statistically valid, the 10 000 means of two adjacent bins were compared sequentially with one another (i.e., the mean of the lowest values of one bin was compared to the mean of the lowest values of the adjacent bin) in order to calculate a percent change  $((V_2 - V_1)/V_1) \times 100$  for each of the 10 000 model runs, resulting in 10 000 percent changes for each set of adjacent bins. The percent of the 10 000 comparisons that confirm an increase or decrease between bins is reported (Fig. 4b–j) as a measure of the statistical significance of the short-term fluctuations in CO<sub>2</sub> concentration visually observed on the LOESS trend.

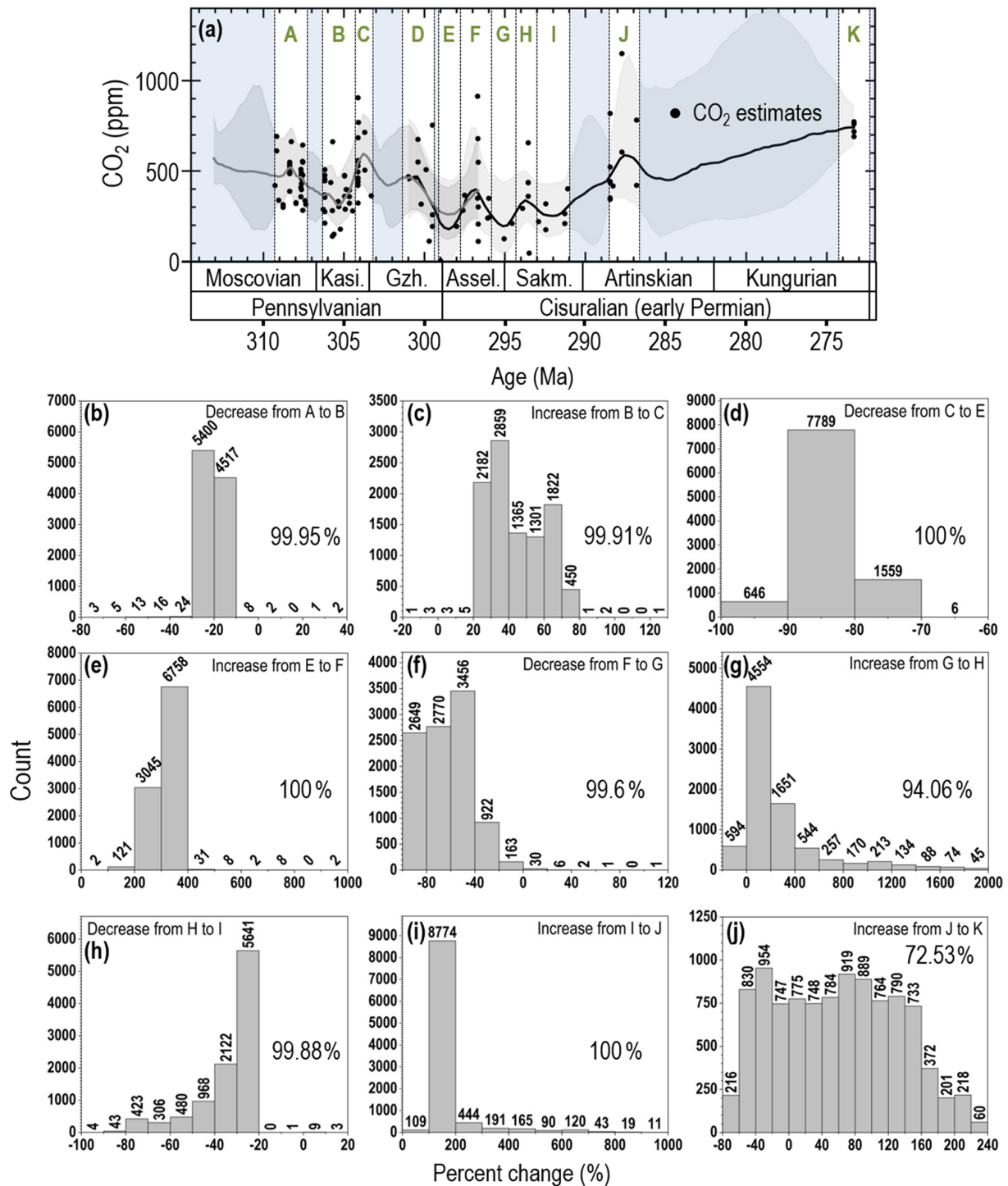
## 3 Results

Revised early Permian mineral-based CO<sub>2</sub> estimates define a substantially narrower range (45–1150 ppm; Fig. 2a) than previous estimates (175–3500 ppm) made using the same pedogenic carbonate sample set (Monta  ez et al., 2007) while maintaining the original trends and including fewer photosynthetically untenable concentrations ( $\leq 170$  ppm; Gerhart and Ward, 2010). New early Permian cuticle-based estimates show a high level of congruence by locality and broad plant functional type, falling within the revised pedogenic carbonate-based CO<sub>2</sub> range (Figs. 2a, S1a). Similarly, stomatal-based estimates for the four Pennsylvanian interglacial floras are within the estimated  $p$ CO<sub>2</sub> range defined by the pedogenic carbonates (Figs. 2a, S1a) and late-glacial wetland plant fossils (Monta  ez et al., 2016). Notably, the newly integrated record confirms elevated atmospheric CO<sub>2</sub> concentrations (482 to 713 ppm (−28/ + 72 ppm)) during Pennsylvanian interglacials in comparison to  $p$ CO<sub>2</sub> during glacial periods (161 to 299 ppm (−96/ + 269 ppm)), with interglacial durations on the order of thousands to tens of thousands of years given the inferred eccentricity scale duration of the glacial–interglacial cycles (Horton et al., 2012; Monta  ez et al., 2016; Fielding et al., 2020).

Overall, the new  $p$ CO<sub>2</sub> record documents declining CO<sub>2</sub> through the final 13 Myr of the Pennsylvanian into the earliest Permian, including a 2.5 Myr interval (307 to 304.5 Ma) of minimum CO<sub>2</sub> values (less than 400 ppm to as low as 200 ppm) in the Kasimovian (Figs. 2b, S1b). Declining  $p$ CO<sub>2</sub> in the late Carboniferous coincides with rising atmospheric  $p$ O<sub>2</sub> (Glasspool et al., 2015; Krause et al., 2018; Lenton et al., 2018); thus, O<sub>2</sub>/CO<sub>2</sub> ratios in the interval of minimum Pennsylvanian CO<sub>2</sub> are nearly 2 times those of present-day values ( $\sim 515$ ; gray line in Fig. 3a). A 10 Myr CO<sub>2</sub> nadir ( $\sim 180$  to  $< 400$  ppm) characterizes the first two stages (Asselian and Sakmarian; 298.9 to 290.1 Ma) of the early Permian, overlaps with the peak occurrence of glacial deposits in the LPIA (gray boxes in Fig. 2b; Soreghan et al., 2019), and defines a second interval of anomalously high O<sub>2</sub>/CO<sub>2</sub> ratios (up to 970 ppm; Fig. 3a). A subsequent long-term rise ( $\sim 17$  Myr) in  $p$ CO<sub>2</sub> to peak values up to  $\sim 740$  ppm (−190/ + 258 ppm) defines the remainder of the



**Figure 3.** Late Paleozoic O<sub>2</sub>/CO<sub>2</sub> ratios and pCO<sub>2</sub>, as well as a comparison to environmental and biotic events. **(a)** O<sub>2</sub>/CO<sub>2</sub> estimates made using CO<sub>2</sub> values of this study and averaged time-equivalent modeled O<sub>2</sub> (Krause et al., 2018; Lenton et al., 2018). Trend line is the median of 1000 bootstrapped LOESS analyses; gray horizontal line is present-day O<sub>2</sub>/CO<sub>2</sub>. **(b)** Bootstrapped Pennsylvanian and Permian LOESS analyses (from Fig. 2a), with significant overlap across the Pennsylvanian–Permian boundary interval. The shading indicates CO<sub>2</sub> above (orange) and below (shades of blue) the mean value for the 16 × 10<sup>6</sup>-year record through the late Pennsylvanian reported in Montañez et al. (2016). Temporal changes in terrestrial **(c)** and marine **(d)** ecosystems. Plant biomes from Montañez (2016): wetland biome (WB) 2 (i.e., cordaitalean/lycopsid co-dominance), WB 3 (i.e., lycopsid dominated with cordaitaleans decreasing and tree ferns increasing in occurrence and prominence), WB 4 (i.e., tree fern dominated), dryland biome (DB) 1 (i.e., cordaitalean dominated), DB 2 (i.e., walchian dominated). Diagonal arrows indicate 10<sup>5</sup>-year glacial–interglacial shifts between wet- and dry-adapted floras.



**Figure 4.** Analysis of the statistical significance of short-term CO<sub>2</sub> fluctuations. **(a)** White intervals (A–K) delineate short-term highs or lows in the CO<sub>2</sub> LOESS trend used for binning ( $n = 11$ ; bins  $\pm 0.5$  to 1 Myr resolution). Raw stomatal-based and pedogenic carbonate-based CO<sub>2</sub> estimates generated by Monte Carlo analysis (10 000 model runs per CO<sub>2</sub> estimate; data in shaded intervals were not used). CO<sub>2</sub> between bins was compared by calculating the mean of the lowest through to the 10 000th (highest) Monte Carlo values for all CO<sub>2</sub> points in each bin and comparing the means of the two bins sequentially. **(b–h)** Histograms of the percent change between each of the 10 000 Monte Carlo means of the adjacent bins. Negative values indicate a decrease in value between bins and positive values an increase. The number above each histogram bar is the “percent change” values represented in each bar. The percent of the 10 000 model runs that confirm a given increase or decrease in the LOESS trend is indicated by the % value shown on the right side of each panel. See Sect. 2 for further details.

early Permian and coincides with multiple episodes of extensive and long-lived volcanism (Fig. 2b; Torsvik et al., 2008; Zhai et al., 2013; Sato et al., 2015; Shellnutt, 2018; Chen and Xu, 2019). This  $p\text{CO}_2$  rise is also coincident with a decline in O<sub>2</sub>/CO<sub>2</sub> to below present-day values (Fig. 3a, b).

Short-term intervals of rising or falling CO<sub>2</sub> in the LOESS trend, within dating uncertainties, coincide with a brief but acute glaciation in the Kasimovian and with repeated deglaciations in south-central Gondwana in the early Permian (Griffis et al., 2018, 2019), as well as with restructuring of marine and terrestrial ecosystems (Fig. 3b–d). The statistical significance of these short-term rises and falls in CO<sub>2</sub> was evaluated by analyzing the raw Monte Carlo estimates (10 000 model runs per data point shown on the LOESS trend) generated by the aforementioned CO<sub>2</sub> models (Breecker, 2013; Franks et al., 2014), from which the bootstrapped CO<sub>2</sub> estimates for 11 increments of short-term rise or fall were subsequently determined (Fig. 4a). The analysis of the Monte Carlo CO<sub>2</sub> estimates within these short-term intervals of rising or falling CO<sub>2</sub> indicates that 72.5 % to 100 % of the data confirm a visually observed increasing or decreasing trend (Fig. 4).

## 4 Discussion

### 4.1 Declining CO<sub>2</sub> through the main phase of the LPia

Atmospheric CO<sub>2</sub> concentrations in the final 13 Myr of the Carboniferous (the Pennsylvanian portion of our record) are generally higher than those of the earliest Permian (Fig. 2b) and overall decline through the later part of the Carboniferous. Higher  $p\text{CO}_2$  in the latter half of the Pennsylvanian is compatible with the hypothesized waning of large early-to-middle Pennsylvanian glaciers in the late Pennsylvanian (cf. Fielding et al., 2008), including widespread terminal deglaciation in a major glacial depocenter in south-central Gondwana (Parana Basin, Brazil) toward the close of the Carboniferous (Griffis et al., 2018, 2019). Declining  $p\text{CO}_2$  toward a nadir in the earliest Permian is also consistent with a renewed increase in the geographic distribution of glacial deposits in Gondwana beginning in the late Pennsylvanian and peaking in the earliest Permian (Fig. 2b; Soreghan et al., 2019).

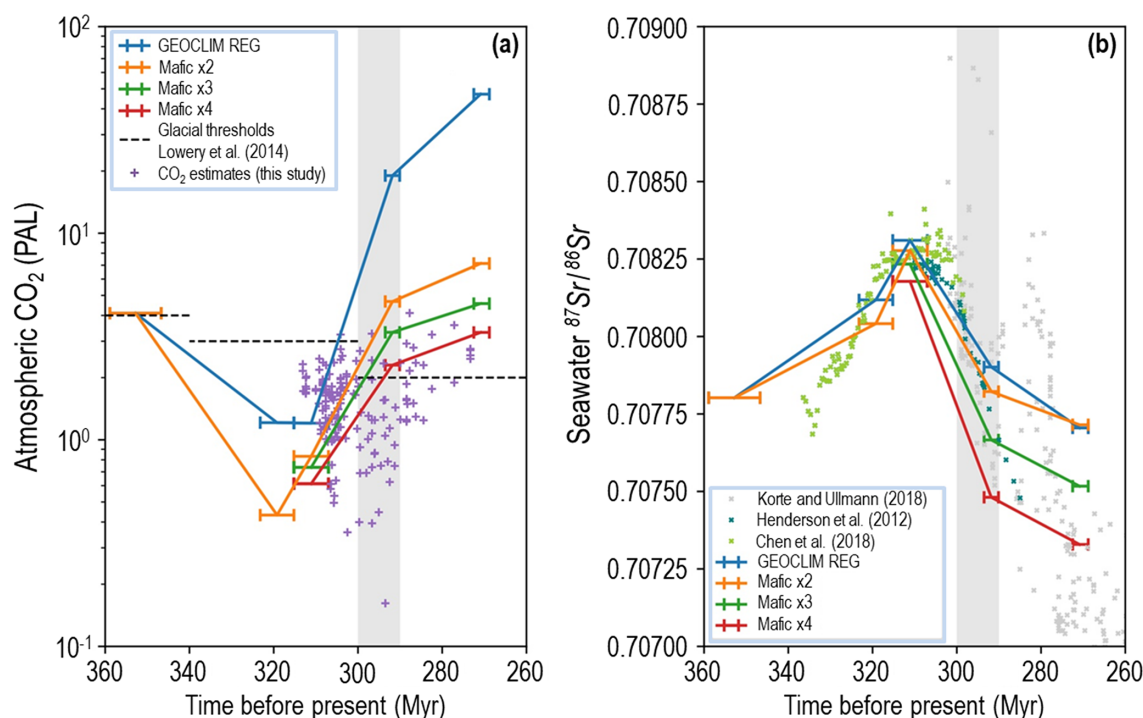
A tectonically driven increase in CO<sub>2</sub> consumption via a strengthening of the silicate weathering (“climate stabilizing”) negative feedback (Walker et al., 1981; Berner and Caldeira, 1997) has been proposed as the driver of the Pennsylvanian decline in  $p\text{CO}_2$  (Goddéris et al., 2017). The strength of the negative feedback varies with the degree of “weatherability” (i.e., the susceptibility to weathering), which, in turn, is predominantly controlled by the intensity of the hydrologic cycle (precipitation and surface runoff), with further influence by surface temperature and vascular plants (Dessert et al., 2001; Donnadiou et al., 2004; West, 2012; Maher and Chamberlain, 2014; Caves et al., 2016; Ibarra

et al., 2016). Uplift of the Central Pangean Mountains (CPM) through the Pennsylvanian would have increased weatherability in the tropics by inducing orographic precipitation and creating steeper slopes (Goddéris et al., 2017), thus providing a greater supply of fresh mineral surfaces and enhanced surface runoff with longer fluid travel paths (cf. Maher and Chamberlain, 2014). Consequently, CPM-induced increased weatherability and CO<sub>2</sub> consumption would have enhanced the global efficiency of weathering and created a tighter coupling between CO<sub>2</sub> and climate at this time (cf. Maher and Chamberlain, 2014; Caves et al., 2016).

We model a Himalayan-type mountain range (an analog for the CPM) using GEOCLIM, with the model parameterized such that 30 % of the alkalinity generated by silicate weathering originates from weathering of mafic rocks. This is referred to as the “reference” continental silicate weathering mineral assemblage or GEOCLIM REG. That modeling indicates steady-state CO<sub>2</sub> concentrations (blue lines in Fig. 5a) that are well below the middle-to-late Carboniferous (340 to 300 Ma) threshold for initiation of continental ice sheets (840 ppm; Lowry et al., 2014). A hypothesized primary influence of the CPM on CO<sub>2</sub> consumption through increased weatherability is further supported by the coincidence of modeled seawater and marine proxy <sup>87</sup>Sr/<sup>86</sup>Sr values that define a plateau of peak radiogenic values that is sustained for 15 Myr of the late Carboniferous (318 to 303 Ma; Fig. 5b). The proxy-based seawater <sup>87</sup>Sr/<sup>86</sup>Sr plateau has been long interpreted to record exposure and weathering of uplifted and metamorphosed crustal rocks of the CPM that had radiogenic Sr isotope compositions (Chen et al., 2018, 2020). Additionally, the burial of substantial organic matter as peat in swamp environments prone to preservation (ultimately as coal) during the Pennsylvanian would have partitioned global CO<sub>2</sub> consumption between silicate weathering and organic carbon burial, further driving steady-state  $p\text{CO}_2$  lower (D’Antonio et al., 2019; Ibarra et al., 2019). Our modeling, however, assumes a constant pre-Hercynian solid Earth degassing through the study interval, and it does not account for increased magmatic CO<sub>2</sub> during Hercynian arc-continent collision and potential widespread eruptive volcanism in the late Carboniferous (Soreghan et al., 2019), both of which could have increased steady-state CO<sub>2</sub>.

Short-term fluctuations in  $p\text{CO}_2$  are superimposed on the long-term decline through the latter portion of the Carboniferous. These short-term fluctuations have been confirmed as statistically significant (99.9 % to 100 % of estimates; Fig. 4b–d) and coincide with major environmental and biotic events. The brief interval of minimum  $p\text{CO}_2$  (an average of ~ 300 ppm but as low as 180 ppm) in the late Carboniferous (Kasimovian stage, 307 to 304.5 Ma; Fig. 3b) coincides with a short-lived but acute glaciation (306.5 to 305 Ma) recorded by prominent valley incision and large-scale regression recorded by cyclothemic successions in the US Appalachian Basin and Midcontinent basin, as well as Donets Basin, Ukraine (Belt et al., 2011; Eros et al., 2012;





**Figure 5.** Carboniferous through early Permian modeled (GEOCLIM) steady-state atmospheric CO<sub>2</sub> and seawater <sup>87</sup>Sr/<sup>86</sup>Sr for different surface areas of mafic rocks available for silicate weathering. In the model, maximum geographic extent and altitude (5000 m) of the CPM is reached in the Moscovian (320 Ma), with altitude decreasing to 3000 m at 290 Ma and 2000 m at 270 Ma. **(a)** Simulated (color lines) and proxy *p*CO<sub>2</sub> estimates (purple crosses, this study) are shown. Horizontal error bars on the colored lines represent the temporal uncertainty for simulated *p*CO<sub>2</sub> estimates. CO<sub>2</sub> thresholds for continental ice sheet initiation (360–340 Ma = 1120 ppm; 340–300 Ma = 840 ppm; 300–260 Ma = 560 ppm from Lowry et al., 2014) decrease in response to equatorward drift of Gondwana, favoring an overall reduction in ice sheet size through time. The reference surface area of outcropping mafic rocks (GEOCLIM REG) maintains steady-state atmospheric CO<sub>2</sub> below the ice initiation threshold from 350 to ~304 Ma. Steady-state atmospheric CO<sub>2</sub> for a 2-fold, 3-fold, or 4-fold increase in outcropping area of mafic rocks remains below the ice initiation threshold (560 ppm) up to ~300 Ma, crossing over at progressively later times in the early Permian. Threshold crossover of steady-state CO<sub>2</sub> at ~290 Ma for a 4-fold increase in mafic rock exposure coincides with the termination of the 10 Myr CO<sub>2</sub> nadir (gray vertical bar; both panels). **(b)** Seawater <sup>87</sup>Sr/<sup>86</sup>Sr modeled for the same set of varying surface areas of outcropping mafic rocks and <sup>87</sup>Sr/<sup>86</sup>Sr values of well-preserved biogenic calcites (gray X's) and conodont bioapatites (green and blue X's). Horizontal error bars on the colored lines represent the temporal uncertainty for modeled seawater <sup>87</sup>Sr/<sup>86</sup>Sr.

Montañez et al., 2016). Significant and repeated restructuring of wetland forests throughout tropical Euramerica, involving quantitative changes in floral composition and dominance, occurred during this 2.5 Myr *p*CO<sub>2</sub> minimum (and O<sub>2</sub>/CO<sub>2</sub> maximum; Fig. 3a–c). Before the short-term *p*CO<sub>2</sub> low, Euramerican tropical forests had expanded to their maximum aerial extent ( $\geq 2 \times 10^6$  km<sup>2</sup>) under CO<sub>2</sub> concentrations of ~500 ppm (Moscovian stage, Fig. 3b). The aerial extent of these forests dropped by half (green X in Fig. 3c; Cleal and Thomas, 2005) coincident with the decline in *p*CO<sub>2</sub> and near doubling of O<sub>2</sub>/CO<sub>2</sub> (Fig. 3a, b). Moreover, within this *p*CO<sub>2</sub> low (Fig. 3b), arborescent lycopods of the wetland forests went extinct throughout Euramerica (white X in Fig. 3c) and seasonally dry tropical floras shifted from cordaitalean dominance to walchian dominance (~307–306.8 Ma; Fig. 3c; DiMichele et al., 2009; Falcon-Lang et al., 2018). These restructuring events occurred at or proximal to CO<sub>2</sub> falling below 400 ppm, supporting a

previously hypothesized but untested CO<sub>2</sub> threshold for the Pennsylvanian ecologic turnovers (Fig. 3b, c; Beerling et al., 1998; Beerling and Berner, 2000; Montañez et al., 2016). In the oceans, foraminiferal diversity decreased substantially during the Kasimovian *p*CO<sub>2</sub> low with the loss of ~200 species (~58 % of all taxa; first gray bar in Fig. 3d; Groves and Yue, 2009), presumably due to decreasing seawater temperatures.

The interval of CO<sub>2</sub> minima was terminated by a rapid rise across the Kasimovian–Gzhelian boundary (303.7 Ma) to CO<sub>2</sub> concentrations above 600 ppm (Figs. 2b; S1b). The short-term interval of elevated *p*CO<sub>2</sub> (304 to 302.5 Ma) is coincident with a ~1.5 ‰ decline in seawater  $\delta^{13}\text{C}$  (Grossman et al., 2008; Chen et al., 2020), which is compatible with a decline in the CO<sub>2</sub> sink provided by terrestrial organic C (peats) burial (gray bar in Fig. 2b) and/or a peak in pyroclastic volcanism between ~310 and 301 Ma (Soreghan et al., 2019). This period of increased *p*CO<sub>2</sub> overlaps with

the Alykaevo Climatic Optimum (orange bar in Fig. 3c), defined by the invasion of tropical Euramerican vegetation into the *Ruffloria*-dominated midlatitude Angaran floral province (Cleal and Thomas, 2005). Terminal deglaciation in south-central Gondwana (Parana Basin, Brazil), U–Pb dated to between ~ 302 and 298 Ma (Cagliari et al., 2016; Griffis et al., 2018), may have been linked to the late Pennsylvanian interval of elevated CO<sub>2</sub>, although this requires further testing (Figs. 2b, 3b). Conversely to the Kasimovian CO<sub>2</sub> low, a significant change in global diversity of foraminifera involving a doubling of species occurred during this subsequent period of elevated CO<sub>2</sub> and presumed increase in seawater temperatures (black bar in Fig. 3d; Groves and Yue, 2009).

#### 4.2 An early Permian CO<sub>2</sub> nadir

Atmospheric *p*CO<sub>2</sub> dropped substantially across the Carboniferous–Permian boundary (i.e., 298.9 Ma) to a 10 Myr interval (300–290 Ma) of the lowest concentrations (175 to < 400 ppm) of the 40 Myr record (Fig. 2b). The CO<sub>2</sub> nadir, which spans the Asselian and Sakmarian stages, coincides with renewed glaciation and maximum ice sheet extent, marking the apex of LPIA glaciation (Fig. 2b; Fielding et al., 2008; Isbell et al., 2012; Montañez and Poulsen, 2013; Soreghan et al., 2019), as well as with a large-magnitude eustatic fall archived in paleotropical successions worldwide (Koch and Frank, 2011; Eros et al., 2012). Widespread glacial expansion temporally linked to this interval of lowest overall *p*CO<sub>2</sub> argues for CO<sub>2</sub> as the primary driver of glaciation rather than recently proposed mechanisms, such as the influence of the closing of the Precaspian Isthmus (Davydov, 2018) or a decrease in the radiative forcing resulting from increased atmospheric aerosols by explosive volcanism at this time (Soreghan et al., 2019). The very low greenhouse radiative forcing associated with this low CO<sub>2</sub> interval would have been amplified by 2.5 % lower solar luminosity (Crowley and Baum, 1992), reduced transmission of shortwave radiation (Poulsen et al., 2015) by the high *p*O<sub>2</sub> atmosphere of the early Permian (Krause et al., 2018; Lenton et al., 2018), and by increased atmospheric aerosols at this time (Soreghan et al., 2019).

The 10 Myr *p*CO<sub>2</sub> nadir raises a paradox as to what was the primary CO<sub>2</sub> sink(s) at the time given that the CO<sub>2</sub> sinks of the Pennsylvanian were no longer prevalent. This paradox reflects the waning denudation rates of the CPM by the early Permian (Godd  ris et al., 2017), intensifying pantropical aridification, possibly driven by increasing continentality (yellow-to-red bar in Fig. 3c; DiMichele et al., 2009; Tabor et al., 2013) and the demise of the wetland tropical forests and associated loss of peats before the close of the Carboniferous (black-to-gray bar in Fig. 2b; Hibbett et al., 2016). In turn, surface runoff would have been inhibited and the supply of fresh silicate minerals decreased, thus lowering overall weatherability. Atmospheric CO<sub>2</sub> under the influence of these environmental factors should have equilibrated in

the earliest Permian at a new higher steady-state level, even if solid Earth degassing did not increase (cf. Gibbs et al., 1999), thus raising a paradox. If volcanism was increasing by this time (Fig. 2b and associated references; Soreghan et al., 2019), then this paradox is even greater.

Two mechanisms have the potential to resolve this paradox. The first, referred to as a delayed climate-controlled capacitor (Joshi et al., 2019), leads to a multi-million-year delay between the timing of peak orogenic uplift and maximum chemical weathering potential and CO<sub>2</sub> drawdown due to substantial differences in chemical weathering rates during the different phases of an orogenic cycle. In their study, the highest intensity of chemical weathering and capacity for CO<sub>2</sub> consumption occurs when mountains have been somewhat denuded rather than during peak uplift, reflecting the disproportionate influence of runoff temperature over hydrology and erosion on weathering potential. Notably, the coupled climate and geochemical modeling of the late Paleozoic ice age by Joshi et al. (2019) yields an evolution of simulated *p*CO<sub>2</sub> over the period of uplift and denudation of the CPM that corresponds to both absolute CO<sub>2</sub> concentrations and the magnitude of change over this period (~ 320 to 290 Ma). That said, in Joshi et al. (2019), the physical erosion parameter is not dependent on climate but rather is defined by the prescribed altitude. Thus, physical erosion is an external forcing in their model. The absence of runoff dependence for physical erosion (as is the case for GEOCLIM) and the strong dependence of weathering on temperature may be the trigger for their simulated delay between maximum uplift and the highest intensity of CO<sub>2</sub> consumption by silicate weathering. In GEOCLIM, the dependence of physical erosion on runoff does not allow for millions of years delay between maximum uplift of the CPM and lowest simulated *p*CO<sub>2</sub>. Further study is needed to interrogate the influence of this approach on the results.

The second mechanism, proposed here, is a substantial shift in the ratio of mafic-to-granite rocks available for weathering from the latest Carboniferous to the early Permian. This reflects the doubling or greater increase in weatherability of mafic mineral assemblages over granitic assemblages (Gaillardet et al., 1999; Dessert et al., 2003; Ibarra et al., 2016), thus enhancing weathering efficiency and CO<sub>2</sub> drawdown and creating a tighter coupling between CO<sub>2</sub> and climate. In turn, with tighter coupling between CO<sub>2</sub> and climate, the global silicate weathering flux needed to maintain homeostatic balance in the carbon cycle for a given scenario can be attained at a lower *p*CO<sub>2</sub> level.

Macdonald et al. (2019) hypothesized that increased weatherability provided by the exhumation of ophiolites along the ~ 10 000 km long Hercynian arc-continent suture zone, primarily situated in the paleotropics, was capable of lowering *p*CO<sub>2</sub> below the ice initiation threshold in the Carboniferous (i.e., Pennsylvanian), thus instigating the late Paleozoic ice age. Here, we used the GEOCLIM model to, first, interrogate this Carboniferous hypothesis further and,

second, to evaluate the potential of increased weatherability provided by increasing the ratio of outcropping mafic rocks to granite rocks available for weathering, as the predominant driver of the early Permian CO<sub>2</sub> nadir. Figure 5 illustrates the influence of a successive increase in the surface area of outcropping mafic rocks beginning with the reference continental silicate mineral assemblage (GEOCLIM REG), which was used to evaluate the influence of Pennsylvanian uplift of the CPM to an up to 4-fold increase in the outcropping of mafic rocks. In the GEOCLIM context, the weathering of mafic rocks is dependent on the surface of each grid cell (and on the associated local runoff and air temperature) multiplied by a calibration constant. Increasing the exposure area of mafic rocks is mathematically equivalent to multiplying by the calibration constant.

Between 300 and 290 Ma, when predominant Pennsylvanian CO<sub>2</sub> sinks were lost (terrestrial organic C burial) or waning (decreased precipitation and denudation rates of the CPM), modeled steady-state atmospheric CO<sub>2</sub> was maintained at or below the CO<sub>2</sub> threshold for initiation of continental ice sheets (560 ppm; Lowry et al., 2014) when the surface area of outcropping mafic rocks was greater than 2-fold that of GEOCLIM REG (Fig. 5a). Conversely, steady-state CO<sub>2</sub> rises well above the glacial threshold (to 3500 ppm) for the reference continental silicate rock assemblage (Fig. 5a). Although volcanism remained geographically extensive through the 10 Myr CO<sub>2</sub> nadir (Soreghan et al., 2019), the impact on atmospheric CO<sub>2</sub> would have been short lived ( $\leq 10^5$  kyr; Lee and Dee, 2019) and eclipsed on the longer term by the increased weatherability provided by increased exposure of mafic rocks along the Hercynian arc-continent suture zone, lowering steady-state CO<sub>2</sub> to, potentially, pre-volcanism levels (cf. Dessert et al., 2001).

Independent evidence for a substantial shift in the partitioning of silicate weathering to more mafic mineral assemblages in the earliest Permian exists in the late Paleozoic proxy-based seawater Sr isotope record, which documents a rapid ( $0.000043 \text{ Myr}^{-1}$ ) and near-linear decrease in seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  beginning in the latest Carboniferous ( $\sim 303$  Ma) and continuing into the middle Permian (Fig. 5b; Chen et al., 2020). The simulated trends in seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  for GEOCLIM REG (blue line on Fig. 5b) through a 2- to 4-fold increase in the area of exposed mafic rocks capture the rapid rise through the upper Carboniferous to peak values in the latter half of the Pennsylvanian and subsequent decline through the early Permian. The rapid rate of decline in proxy  $^{87}\text{Sr}/^{86}\text{Sr}$  values post-300 Ma, however, is best bracketed by simulated  $^{87}\text{Sr}/^{86}\text{Sr}$  for a 2- to 4-fold increase in mafic rock exposure. Moreover, the best fit of the simulated trends to the geochronologically well-constrained bioapatite data (blue and green crosses in Fig. 5b) suggests a progressive increase in mafic-to-granite ratio through the 10 Myr CO<sub>2</sub> nadir. This finding, together with the hypothesized need (the aforementioned second mechanism) for minimally a 4-fold increase in mafic-rock outcropping in order to maintain

CO<sub>2</sub> concentrations below the ice initiation threshold for a sustained period longer than that of hysteresis (i.e., throughout the interval of minimum CO<sub>2</sub> and apex of glaciation; Fig. 5), supports a change in weatherability through time. That is, the modeling results argue for a substantial increase in weatherability from the Carboniferous to early Permian driven by a compositional shift in outcropping rocks available for weathering from that of the reference continental silicate assemblage to one of higher mafic-to-granite ratio.

If peak ophiolite exhumation and maximum CO<sub>2</sub> consumption by their weathering occurred in the late Carboniferous, thus initiating the LPJA ( $\sim 330$  to 300 Ma) as has been suggested (Table S1 of Macdonald et al., 2019), then our modeling results suggest that a substantial increase in solid Earth degassing rate at this time would have been necessary. In our simulation, increasing the surface area of outcropping mafic rocks (2- to 4-fold) during the Pennsylvanian results in steady-state atmospheric CO<sub>2</sub> levels approaching “Snowball Earth” conditions given other operating influences on weatherability and CO<sub>2</sub> sequestration at the time and no change in degassing rate (Fig. S6). Such conditions are not compatible with proxy-inferred moderate surface conditions of the late Carboniferous (Montañez and Poulsen, 2013) and the radiation of forest ecosystems throughout the tropics (DiMichele, 2014). Rather, we hypothesize that the sustained CO<sub>2</sub> nadir and expansion of ice sheets in the first 10 Myr of the Permian record a major reorganization of the predominant factors influencing weatherability in the tropics across the Carboniferous–Permian transition, in particular a substantial shift in the ratio of mafic-to-granitic rocks available for weathering.

Similar to the short-term fluctuations superimposed on the later Carboniferous long-term decline in CO<sub>2</sub>, two statistically significant (94 % to 100 % in Fig. 4e–h) short-term increases in  $p\text{CO}_2$  are superimposed on the early Permian nadir (Fig. 3b). The first (298 to 296 Ma) coincides, within age uncertainty, with a major deglaciation event in the Karoo (southern Africa) and Kalahari (Namibia) basins of south-central Gondwana (296.41 Ma  $\pm 0.27/-0.35$  Ma; Griffis et al., 2019). The second short-term rise in  $p\text{CO}_2$  (294.5 to 292.5 Ma) overlaps with the onset of widespread ice loss in several southern Gondwanan ice centers (Fig. 2b; Soreghan et al., 2019). This CO<sub>2</sub>–deglaciation link suggests that continental ice stability in the early Permian dropped substantially when  $p\text{CO}_2$  rose above  $\sim 300$  to 400 ppm and thus raises the question as to whether the ice sheet CO<sub>2</sub> threshold was even lower than modeled (560 ppm; Lowry et al., 2014) during the earliest Permian.

Notably, the early Permian  $p\text{CO}_2$  minimum (Figs. 2b, S1b), as well as the associated anomalously high O<sub>2</sub>/CO<sub>2</sub> ratios (700 to 960; Fig. 3a), is an interval of major ecosystem changes. The geologically rapid and large-magnitude drop in  $p\text{CO}_2$  prior to and across the Carboniferous–Permian boundary interval (Figs. 2b, S1b) coincides with a permanent shift in plant dominance from swamp-community floras to sea-

sonally dry vegetation (black X in Fig. 3c). That shift in plant dominance has been long attributed to intensification of an aridification trend that began in the mid-Pennsylvanian (yellow-to-red bar in Fig. 3c; DiMichele et al., 2009; Tabor et al., 2013). Analogous to the vegetation turnover and extinction during the Pennsylvanian CO<sub>2</sub> minimum, this permanent shift to seasonally dry vegetation is coincident with the earliest Permian drop in *p*CO<sub>2</sub> to concentrations below 400 ppm, suggesting a possible ecophysiological advantage of these plants over the wetland floral dominants that they replaced (Fig. 3a–c; cf., Wilson et al., 2017). The high water use efficiency of the seasonally dry plants would have made them water-stress tolerant and, in turn, would have amplified aridification through a modeled ~ 50 % decrease in canopy-scale transpiration (Wilson et al., 2017, 2020). The extreme habitat restriction of wetland floras was particularly consequential for tetrapods, leading to the acquisition of terrestrial adaptations in crown tetrapods and the radiation and eventual dominance of dryland-adapted amniotes, possibly shaping the phylogeny of modern terrestrial vertebrates (Fig. 3c; Pardo et al., 2019).

Moreover, the CO<sub>2</sub> decline at the Carboniferous–Permian boundary into the 10 Myr nadir and associated peak in O<sub>2</sub>/CO<sub>2</sub> also corresponds to the evolution and radiation of glossopterids and gigantopterids (McLoughlin, 2011; Zhou et al., 2017), with increasing vein density in the former (Fig. 3a–c; Srivastava, 1991). These plant groups had complex angiosperm-like venation (Melville, 1983; Srivastava, 1991), with gigantopterids having the only known pre-Cretaceous vessels in their stems (Li et al., 1996). The increased hydraulic capacity provided by these morphological characteristics would have conferred a significant ecological advantage to these plants under the low CO<sub>2</sub>, high O<sub>2</sub>, and elevated aridity conditions in which they evolved (cf. Gerhart and Ward, 2010; de Boer et al., 2016). In the oceans, a marked collapse in foraminiferal diversity with a notable fall in species to a minimum from a Pennsylvanian zenith (425 to 110 species; Fig. 3d, e; Groves and Yue, 2009) spanned the 10 Myr *p*CO<sub>2</sub> nadir, analogous to the diversity drop during the Pennsylvanian low-CO<sub>2</sub> interval.

#### 4.3 CO<sub>2</sub>-forced demise of the LPIA

The 10 Myr CO<sub>2</sub> nadir terminated at 290 Ma with the onset of a protracted CO<sub>2</sub> rise that persisted to the highest levels of the record (~ 740 ppm (−190/+258)) by the close of the early Permian (Fig. 2b). The onset of this protracted CO<sub>2</sub> rise overlaps with initiation of a period of large-magnitude magmatism (red bars in Fig. 2b). Widespread volcanism began around 297.4 Ma (±3.8 Ma) in northern Europe (Skagerrak-centered large igneous province), extending well into Germany (Rotliegend) (Torsvik et al., 2008; Käbner et al., 2019). The multistage Tarim magmatic episodes in China (292–272 Ma; with peaks at ~ 290 and 280 Ma; Fig. 2b; Chen and Xu, 2019), were likely associated with large-magnitude CO<sub>2</sub>

emissions given that the magma, which distributed basalt (400 m thick) over a  $2.5 \times 10^5$  km<sup>2</sup> region (Yang et al., 2013), intruded a thick succession of early Paleozoic marine carbonates (Gao et al., 2017). The Panjal Traps, NW India (289 ± 3 Ma; Shellnutt, 2018), and the compositionally similar Qiangtang dikes (283 ± 2 Ma; Fig. 2b; Zhai et al., 2013), albeit relatively small in extent, were an additional potential volcanic CO<sub>2</sub> source, along with contemporaneous volcanism in Oman. Furthermore, protracted Choiyoi volcanism, which began at 286.5 ± 2.3 Ma (Sato et al., 2015) and continued over ~ 39 Myr in western Argentina, may have contributed substantial pulses of greenhouse gases in the early Permian (Spalletti and Limarino, 2017). Once each magmatic episode waned, however, the mafic-dominated magmatic deposits would have served as longer-term regional sinks, leading to increased global CO<sub>2</sub> consumption (cf. Lee et al., 2015). Thus, for steady-state CO<sub>2</sub> to have increased through the remainder of the early Permian, the relative influence of CO<sub>2</sub> inputs must have outpaced that of these, and other, outputs (CO<sub>2</sub> sinks).

Our modeled (GEOCLIM) steady-state CO<sub>2</sub> for a 4-fold increase in outcropping of mafic rocks surpasses the ice-sheet initiation threshold at the termination of the CO<sub>2</sub> nadir (~ 290 Ma; red line in Fig. 5a) despite no change in solid Earth degassing. The fact that low CO<sub>2</sub> concentrations could no longer be maintained, despite a 4-fold increase in mafic rock exposure, reflects overall intensifying aridification, denudation of the CPM, and a shift from dense forests to savanna-like vegetation in Euramerica at this time. However, given that the magmatic CO<sub>2</sub> flux likely increased already by the earliest Permian (summarized in Fig. 2b), our model results indicate that maintaining low steady-state CO<sub>2</sub> concentrations during the earliest Permian 10 Myr CO<sub>2</sub> nadir would have required an increasingly greater proportion of mafic rock weathering over the reference continental silicate mineral assemblage of the Pennsylvanian, possibly well beyond a 4-fold increase.

A CO<sub>2</sub>-forced demise of the late Paleozoic ice age after 290 Ma is supported by the loss of continental ice from the main ice depocenters in south-central Gondwana by 282.17 ± 0.32/−0.44 Ma (Griffis et al., 2018, 2019) and a 6-fold drop in documented glacial deposits overall between the Sakmarian and Artinskian stages (Fig. 2b; Soreghan et al., 2019). The long-term CO<sub>2</sub> rise through the remainder of the early Permian coincided with substantial marine and terrestrial ecosystem perturbation (Fig. 3b–d; Chen and Xu, 2019). In the marine biosphere, the uniformly low rates of global macroevolution in marine organisms (brown bar in Fig. 3d) were reversed, and narrowly adapted and distributed genera reappeared, thus restoring marine ecosystems to their pre-LPIA rates (Stanley and Powell, 2003; Powell, 2005). Pennsylvanian rugose corals (pink bar in Fig. 3d) underwent a major turnover in composition to those that dominated until the end-Permian extinction, and cold-adapted marine bivalves and brachiopods turned over to warm-adapted forms syn-



chronous with the onset of the long-term increase in  $p\text{CO}_2$  (290.1 Ma; blue to red bar across the Sakmarian–Artinskian boundary in Fig. 3d; Wang et al., 2006; Clapham and James, 2008). On land, the loss of pelycosaur families (three in the late Artinskian and four in the early Kungurian; Kemp, 2006) coincided with CO<sub>2</sub> sustained at > 500 ppm. By the close of the Kungurian and the time of highest CO<sub>2</sub> (740 ppm), basal synapsids largely disappeared and were replaced by more derived therapsids, tetrapod diversity decreased significantly (Benton, 2012; McGhee, 2018), plant extinction rates reached a level comparable to that associated with the extinction of arborescent lycopsids in the early Kasimovian (Cascales-Miñana et al., 2016), and extinction and origination rates increased in fishes (Friedman and Sallan, 2012).

## 5 Conclusions

Glacial–interglacial climate cycles and large-scale glacioeustasy, as well as repeated ecosystem change analogous to that of the Pleistocene, characterized Earth's penultimate icehouse period in the late Paleozoic. The dynamic glaciation history of this icehouse period (the late Paleozoic ice age – LPIA) came to a close by the end of the early Permian with turnover to permanent greenhouse conditions. Thus, improved constraints on how atmospheric  $p\text{CO}_2$  evolved during the LPIA and its subsequent demise is crucial for better understanding the role of greenhouse gas forcing on Earth system processes during this time. The new and age-recalibrated  $p\text{CO}_2$  reconstruction presented here for a 40 Myr interval (~ 313 to 273 Ma) of the late Paleozoic substantially refines existing Permian CO<sub>2</sub> estimates and provides perhaps the highest temporal resolution protracted  $p\text{CO}_2$  record prior to the Cenozoic. The multiproxy record confirms the previously hypothesized CO<sub>2</sub>–glaciation linkage, including documenting the coincidence of a 10 Myr period of minimum  $p\text{CO}_2$  with inferred maximum ice extent during the earliest Permian. A long-term decline in  $p\text{CO}_2$  through the late Carboniferous period of glaciation, culminating in the earliest Permian CO<sub>2</sub> nadir, lends support for a previously modeled progressive decrease in the CO<sub>2</sub> threshold for continental ice sheets through the LPIA.

Our new  $p\text{CO}_2$  record provides the first stomatal-based evidence for elevated (up to 700 ppm) atmospheric CO<sub>2</sub> concentrations during short-term (10<sup>4</sup>-year) interglacials. Together with new O<sub>2</sub>/CO<sub>2</sub> estimates of similar temporal resolution to  $p\text{CO}_2$ , the new atmospheric trends indicate a close temporal relationship to repeated ecosystem restructuring in the terrestrial and marine realms. In terrestrial ecosystems, the appearance and/or rise to dominance of plants with physiological and anatomical mechanisms for coping with CO<sub>2</sub> starvation and marked aridity correspond to drops in CO<sub>2</sub> below 400 ppm (as low as ~ 180 ppm), and O<sub>2</sub>/CO<sub>2</sub> ratios nearly doubled those of late Paleozoic background values. Similarly, decreasing rates of macroevolution and diversity

in the low-latitude oceans corresponded to falling CO<sub>2</sub> to below 400 ppm. These CO<sub>2</sub>–ecosystem relationships lead us to hypothesize that 400 ppm was an important threshold for ecosystem resilience during the late Paleozoic.

Modeling of steady-state  $p\text{CO}_2$  during the late Paleozoic using an intermediate-complexity climate–carbon cycle model (GEOCLIM) and comparison to the new multiproxy CO<sub>2</sub> record provides new insight into the relative influences of uplift of the Central Pangean Mountains, intensifying aridification, and increasing mafic to granite ratio of outcropping rocks on the global efficiency of CO<sub>2</sub> consumption and secular change in steady-state  $p\text{CO}_2$  through the late Paleozoic. The simulations confirm that, for the Carboniferous, enhanced weatherability and CO<sub>2</sub> consumption provided by the influence of uplift on surface hydrology and erosion could have lowered atmospheric  $p\text{CO}_2$  well below the threshold for ice sheet initiation. Increasing the availability of mafic rocks for weathering drives CO<sub>2</sub> levels toward Snowball Earth conditions in the Carboniferous. Conversely, a substantial increase (up to a 4-fold increase) in the surface outcropping of mafic rocks over those modeled for the Carboniferous is needed to maintain the 10 Myr CO<sub>2</sub> nadir in the earliest Permian and is compatible with maximum exhumation of the Hercynian orogenic belt at this time, as well as with a rapid decline in proxy-based seawater <sup>87</sup>Sr/<sup>86</sup>Sr. Although these findings support the hypothesis of atmospheric  $p\text{CO}_2$  response to uplift of the CPM as the primary driver for Carboniferous initiation of the LPIA (Goddéris et al., 2017), they argue for a major reorganization of the predominant surface factors influencing weatherability in the tropics across the Carboniferous–Permian in order for  $p\text{CO}_2$  values to have fallen to well below 300 ppm. The demise of the LPIA was greenhouse gas forced, reflecting the increasing importance of magmatic degassing and likely decreased weathering efficiency driven by intensifying aridification, denudation of the CPM, and the loss of the wetland forests throughout tropical Euramerica.

**Data availability.** Underlying primary data are deposited in the Dryad Digital Repository (Richey et al., 2020) and can be accessed at <https://doi.org/10.25338/B8S90Q>.

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**Author contributions.** JDR and IPM designed the study. JDR collected the data, wrote the article, and drafted the figures; IPM and YG carried out the GEOCLIM modeling, wrote relevant parts of the article, and drafted Fig. 5. All co-authors provided comments on the article.

**Competing interests.** The authors declare that they have no conflict of interest.

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