CO$_2$-Forced Climate and Vegetation Instability During Late Paleozoic Deglaciation


The late Paleozoic deglaciation is the vegetated Earth’s only recorded icehouse-to-greenhouse transition, yet the climate dynamics remain enigmatic. By using the stable isotopic compositions of soil-formed minerals, fossil-plant matter, and shallow-water brachiopods, we estimated the late Paleozoic deglaciation is the vegetated Earth’s only recorded icehouse-to-greenhouse transition, yet the climate dynamics remain enigmatic. By using the stable isotopic compositions of soil-formed minerals, fossil-plant matter, and shallow-water brachiopods, we estimated the

References and Notes

4. The deviation from the mass-dependent relationships is calculated by the following equations: $\Delta^{23}S = \Delta^{33}S - 1000[(1 + 1/85)\times1000^{187}S - 1]$ and $\Delta^{34}S = \Delta^{33}S - 1000[(1 + 1/85)\times1000^{187}S - 1]$. Considering the small size of the samples, our analytical accuracy, with a 2σ uncertainty, is equal to 0.12% for $\Delta^{23}S$ and varies from 0.64 to 1.63% for $\Delta^{34}S$. Only $\Delta^{23}S > 0.12\%$ and $\Delta^{34}S > 0.64\%$ are considered as diagnostic of MIF in the present study. Uncertainties (2σ) are 0.07, 0.19, and 0.52 to 1.59% for $\Delta^{23}S$, $\Delta^{34}S$, and $\Delta^{33}S$, respectively.
15. Materials and methods are available as supporting material on Science Online.
27. We acknowledge helpful discussions with S. Bekki and thank the Conseil Régional Rhônes-Alpes for partially supporting travel expenses for M.B.J.S. acknowledges the Balzan Foundation for financial support; C. Lorius and the Institut National des Sciences de l’Univers (INSU) for mass spectrometry acquisition; the French Polar Institute and M. Legrand (Institut Polaire Français Paul Emile Victor program DC17) for logistical support in Antarctica; the CNRS, under its Programme International de Coopération Scientifique; and the INSU Programme National de Chimie Atmosphérique. The NSF Office of Polar Programs provided financial support for M.H.T. We also thank J. McCabe and U. Morgenstern for helping J.S. to dig the snow pit.

Supporting Online Material

www.sciencemag.org/cgi/content/full/315/5808/84/DC1 Materials and Methods SOM Text

References

26 June 2006; accepted 15 November 2006 10.1126/science.1131754
tion, large magnitude changes in atmospheric $p$CO$_2$, and major ephemeral warmings (4, 5). As our climate system departs from the well-studied Pleistocene glacial-interglacial cycles, a deep-time perspective of $p$CO$_2$-climate-glaciation linkages is essential for a fuller understanding of what may be the Earth’s most epic deglaciation.

We present here the results of a multipronged investigation that provides evidence for significantly changing atmospheric CO$_2$ concentrations and surface temperatures during a 40-million-year period of the late Paleozoic (~305 to 265 Ma), which encompasses the deterioration of the most widespread and long-lived icehouse of the last half-billion years (6). This global warming event accompanied a permanent transition to an ice-free world, a condition that arguably lasted until the current glacial state. These results, when integrated with a newly emerging glaciation history for southern Gondwana (7–11), indicate strong linkages between $p$CO$_2$, climate, and ice-mass dynamics during the final stages of the Late Paleozoic Ice Age (end of LPIA). Integration of these climate proxy records with our newly developed tropical paleobotanical records shows repeated climate-driven ecosystem restructuring in western paleoequatorial Euramerica.

The CO$_2$ contents of ancient atmospheres can be estimated from the carbon stable isotope values ($\delta^{13}C$) of ancient soil-formed carbonates and goethites with an uncertainty of $\pm 500$ ppmv (12, 13). These minerals are the proxy of choice when $p$CO$_2$ is high ($>1000$ ppmv), whereas the method’s sensitivity decreases at lower $p$CO$_2$ (<800 ppmv) (14, 15). The precision of $p$CO$_2$ estimates reflects the variable assumptions used for each $p$CO$_2$ calculation (16), which can be further refined if the $\delta^{13}C$ of coexisting organic matter is available and if quantitative estimates of paleosol-respired CO$_2$ content and paleotemperatures can be inferred from modern analogs or independently derived geochemical proxies (15).

To reconstruct atmospheric CO$_2$ during the end of the LPIA, we measured the $\delta^{13}C$ values of soil-formed calcites ($\delta^{13}C_{\text{carb}}$) collected from mature, well-drained profiles from the Eastern Shelf of the Midland Basin; the Pedregosa, Anadarko, and Paradox Basins; and the Grand Canyon Embayment of western paleoequatorial Euramerica (fig. S1 and table S1) (17). We considered measured paleosol $\delta^{13}C_{\text{carb}}$ values to be a robust proxy of soil-water CO$_2$ during formation, given the lack of evidence for mineral recrystallization and overgrowth and their overall shallow and low-temperature burial histories (18). Furthermore, we consider the $\delta^{13}C$ of well-preserved fossil plant matter ($\delta^{13}C_{\text{org}}$) to be a faithful proxy of the C isotope composition of soil-respired CO$_2$ and, in turn, of atmospheric CO$_2$ (19, 20). Compression and permineralized fossil plants, cuticles, coal, and charcoal were collected from mudstone deposits of abandoned

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**Fig. 1.** Temporal distribution of carbonate (A) and fossil plant (B) $\delta^{13}C$ values used to construct best estimate of Permo-Carboniferous atmospheric $p$CO$_2$ (C). Individual points in (A) and (B) are the average of analyses from suites of contemporaneous paleosols (from 5 to 18) and associated plant localities (from 3 to 21); c and p encompasses all compression and permineralized plant matter, coals, and charcoals. Vertical bars are ±2 SE around the mean. PDB, Pee Dee belemnite. (B) Solid curve is three-point weighted running average through samples from the Eastern Shelf, Midland Basin. Gray band is $\delta^{13}C_{\text{org}}$ of Permo-Carboniferous coals from three correlated successions in North China Platform (22). Overlapping $\delta^{13}C_{\text{org}}$ trends but different $\delta^{13}C_{\text{org}}$ values are interpreted to reflect overall wetter conditions for the North China Platform relative to western paleoequatorial Euramerica in the Permian. Data and $p$CO$_2$ presented on an age model (51) developed for the terrestrial composite section by linearly interpolating between known biostratigraphic boundaries. (C) Best estimate of paleo-$p$CO$_2$ (black curve) from Monte Carlo simulation of chronostratigraphically well-constrained sample populations; uncertainty in $p$CO$_2$ estimates (gray curves) reflects variability in $\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$, interpreted to record inter- and intrasabinal variations in soil conditions, vegetation, and climate. Vertical bars are published goethite-based CO$_2$ estimates from the same set of paleosols (25).
fluvial channels and floodplains, which are stratigraphically intercalated (on a sub-10-m resolution) with carbonate-bearing paleosols (table S2). The use of measured \( \delta^{13}C_{org} \) rather than contemporaneous marine carbonates as a proxy of atmospheric \( \delta^{13}C \) reflects a growing appreciation of local-scale C cycling effects on the \( \delta^{13}C \) values of epicontinental marine carbonates (21). The terrestrial \( \delta^{13}C_{carb} \) and \( \delta^{13}C_{org} \) time series have an average sampling interval of <1 million years (My) and define long-term trends that exhibit systematic variability (Fig. 1, A and B). That the long-term \( \delta^{13}C_{org} \) trend records first-order variations in atmospheric \( \delta^{13}C \) is supported by its similarity to time-equivalent \( \delta^{13}C_{org} \) records of Permo-Carboniferous coals from the North China Platform (22) and by a narrow range, throughout the study area, in the ratio of intracellular, \( \delta^{13}C_{carb} \) and atmospheric, \( \delta^{13}C_{org} \), partial pressures of CO\(_2\) in paleoflora \([0.46 to 0.57 \pm 0.3 (2 \text{ SE})]\), which were estimated by using measured \( \delta^{13}C_{org} \) values of fossil plants and \( \delta^{13}C_{org} \) values of contemporaneous marine brachiopods (17). These factors indicate that changes in geomorphic or environmental conditions in the study area were secondary to atmospheric \( \delta^{13}C \) in influencing measured fossil-plant \( \delta^{13}C_{org} \) values.

Ranges of paleosol-respired CO\(_2\) content were inferred from the morphologies of suites of contemporaneous paleosols (23) by comparison with modern analogs, addressing a major source of uncertainty in previous applications of the CO\(_2\) paleobarometer (table S3) (14, 15). Paleotemperatures were inferred from the oxygen and hydrogen isotopic compositions of pedogenic phyllosilicates and Fe oxides obtained from the same set of paleosols (18, 24). The best estimate of paleoatmospheric pCO\(_2\) was defined by using Monte Carlo simulation involving 1000 randomly drawn samples for each variable for each time-location combination (17). Monte Carlo simulations use random sampling techniques to stochastically solve physical process problems, in this case quantitatively estimating paleo-pCO\(_2\) and the associated uncertainty by integrating across all of the inferred and measured input variables.

Modeled CO\(_2\) concentrations (Fig. 1C and table S4) define a long-term rise from an average of present atmospheric levels (PAL = 280 ppmv) in the earliest Permian to values of up to 3500 ppmv by the late Early Permian. A substantial decline in pCO\(_2\) into the early Middle Permian is corroborated by independently derived goethite-based estimates of Permian pCO\(_2\) (25). A short-lived (~2 My) drop in pCO\(_2\) to near PAL, defined by contemporaneous paleosols, punctuates the Early Permian rise. Modeled pCO\(_2\) suggests that PAL values were limited to the earliest Permian after latest Carboniferous levels of up to 1000 ppmv, in accord with pCO\(_2\) inferred from marine carbonate \( \delta^{13}C \) (26) and with Southern Gondwanan sedimentologic and geochemical evidence for latest Carboniferous warming (9, 27). Our record refines the structure of well-established pCO\(_2\) reconstructions, which indicate sustained PAL values throughout much of the Permo-Carboniferous (15, 28, 29). The higher-frequency oscillations revealed by this study would be below the temporal resolution (5 to 20 My time-averaging) of those long-term CO\(_2\) records.

In order to evaluate the nature of the CO\(_2\)-climate relationship, we developed a time-equivalent record of paleotropical sea-surface temperatures (SSTs) by using \( \delta^{18}O \) values from a global compilation of well-preserved latest Carboniferous through Middle Permian tropical shallow-water brachiopods (table S5) (30); brachiopods have diagenetically resistant, low-Mg calcitic shells that incorporate oxygen isotopes in equilibrium with seawater (31). The residual brachiopod \( \delta^{18}O \) record (Fig. 2A) displays clear isotopic fluctuations, with intervals of maximum values corresponding to Permian glacial maxima or marked coolings in Antarctica and/or Australia (10, 11) and, to the degree afforded by geochronologic dates, with the younger periods of inferred glacial maxima in the Karoo Basin (8, 32), southern Argentina (9), and Tasmania (33). Intervals of minimum \( \delta^{18}O_{carb} \) values correspond with independently inferred periods of marked warming and sealevel rise (7–9, 34) (Fig. 2C).

Inferring secular paleotemperatures from \( \delta^{18}O_{carb} \) requires careful consideration of the compound effects on values of continental ice
volume, local hydrography, and SST, as well as any vital effects and postdepositional alteration (31, 35). The eustatic component in the Permo-Carboniferous brachiopod δ18O record due to ice volume variability likely accounts for far less than 2 per mil (‰) of the observed δ18O variation given reconstructed amplitudes (10 to <100 m) of Permo-Carboniferous glacio-eustasy (10) and an O isotope composition of seawater (δ18Osw)–sea level relationship of 0.1‰ per 10 m of sea level change (36). The residual secular δ18Ocarb signal is interpreted to record changes in temperature, salinity, and pH. Local hydrographic variations in tropical epicontinental seas would have dampened the magnitude of δ18Ocarb shifts, given hypothesized heightened freshwater discharge to continental shelves (decreased salinity and lowered δ18Osw) during late Paleozoic periods of maximum glaciation, and increased evaporation (increased salinity and δ18Osw) during drier, highly seasonal glacial minima (36). Moreover, paleo-SSTs under elevated pCO2 may be underestimated by up to 2°C, given that lowered seawater pH would have shifted δ18Ocarb to less negative values (38, 39).

The amplitudes of the reconstructed SST shifts (40) indicate substantial changes in the mean state of tropical climate during the end of the LPIA, with glacial tropical oceans at least 4° to 7°C cooler than those of intervening glacial minima (Fig. 2B). Inferred periods of elevated tropical SSTs and pCO2 coincide with independently recognized intervals of warmer temperate conditions in high-latitude southern Gondwana (Fig. 2C) indicated by the accumulation of nonglacial sediments, including extensive kaolin and bauxite deposits in Australia during peak (Artinskian) warming and pCO2 (7) and increased faunal diversity in Australia and South America (7, 11, 41). The covariance among inferred shifts in paleotropical SSTs, pCO2, and variations in high-latitude Gondwanan glaciation and climate implies a strong CO2-climate-glaciation linkage during the Permian. Although our coupled records suggest atmospheric CO2 may have played a direct role in forcing Early to Middle Permian climate and ice mass stability, a determination of phase relationships between these parameters is precluded by the uncertainties in the age models. The inferred variations in tropical SSTs between periods of glacial maxima and minima, however, are consistent with the range predicted by Permain climate simulations for a change in radiative CO2 forcing from 1 to 8 PAL (42).

Permo-Carboniferous plant assemblages from western paleoequatorial Euramerica archive a mechanistic vegetational response to late Paleozoic pCO2 and climate change. Reconstructed plant communities from the same terrestrial successions that host the pedogenic mineral-bearing paleosols document major dominance-diversity changes corresponding one-for-one to inferred changes in paleotropical climate, pCO2, and glacial extent (Fig. 3 and table S6). Four tropical biomes appear in succession, composed of increasingly xeromorphic species, representing progressively more seasonally moisture-stressed environments. These biomes are floristically distinct, sharing only a few opportunistic ferns and sphenopsids (43). Typical latest Carboniferous flora, rich in marattialean ferns, medullosan pteridosperms, sphenopsids, and sigillarian lycopsids, was replaced essentially instantaneously by one rich in conifers [Walchia and Ernestiodendron; compare with Brachyphyllum (44), callipterids (Rhachiphyllum), cycadophytes (Russellites), and other seed plants [Cordaites, Sphenopteridium (45)]]. This floristic shift is synchronous with an abrupt continental climate transition from everwet to semi-arid conditions (Fig. 3A), characterized by increased temperatures (18, 24) and seasonal moisture availability inferred from paleosol morphologies (23).

Conifers and callipterids diversified in seasonally dry habitats during the initial Early Permian (Sakmarian) rise in CO2 and the warm period of glacial minima, spatially replacing the tree fern–rich and the pteridosperm–rich wetland floras (Fig. 3). Tree fern–rich floras reappeared during wetter, cooler conditions of the mid-
Perrinian (Artinskian) glaciation, stratigraphically intercalated but not mixed, with conifer-carpilliferan floras. These two glacial floras show limited species overlap and oscillated at the 10^2- to 10^4-year scale, reflecting short-lived pluvials (46). Dramatic floristic changes also occurred during the cold period at the close of the Early Perrinian (Kungurian), with the migration into lowland basins of unique seed-plant assemblages not observed again until the Late Perrinian (conifers) and the Mesozoic (cyads) (47). These temporally successive floras tracked climatic conditions and contained progressively more evolutionarily advanced lineages. This suggests that evolutionary innovation, the appearance of new plant body plans, occurred in extrabasinal areas and was revealed by climate-driven floral migration into lowland basins.

The history of latest Carboniferous to Middle Permian climate provides a unique deep-time perspective on the precarious balance between icehouse and greenhouse states during major climate transitions, which are coupled to changing atmospheric CO2 content. Maximum expansion of Gondwanan continental ice sheets occurred during earliest Permian time (10) under the lowest paleoatmospheric CO2 levels and paleotropical SSTs. Widespread Early Permian (mid-Sakmarian) collapse of ice sheets (8, 10) coincided with the onset of rising atmospheric CO2 levels, after which time tropical SSTs and pCO2 rose. Subsequent glacial influence was restricted to eastern Australia (6), with resurgent ice masses occurring during three more episodes (11) of lowered atmospheric pCO2 before the permanent transition to an ice-free world (260 Ma).

Our study indicates that ice buildup in Australia during subsequent cold periods, however, was progressively less widespread, with the two youngest glacially generally confined to local valleys or mountain ice caps along the polar margin of Australian Gondwana. Notably, SSTs and pCO2 did not return to earliest Permian levels during these post-Sakmarian glacial periods.

Our reconstructed pCO2, paleotemperatures, and inferred glacial history depict an Early Permian atmosphere that systematically increased from PAL to levels similar to those predicted to exist if fossil fuels are exhausted. Although global-scale deglaciation was unrelated to rising Early Permian atmospheric CO2, transient periods of icehouse stability and glacial resurgence returned during short-lived intervals of low pCO2, perhaps until a CO2 threshold and greenhouse stability precluded the reestablishment of glacial conditions [compare with (48)]. This late Paleozoic climate behavior mimics, in reverse, the magnitude and temporal scale of atmospheric CO2 changes and ephemeral warmings that foreshadowed the transition into our present glacial state (4, 5), further documenting the degree of climate variability, carbon cycle perturbation, and tropical ecosystem restructuring that has been associated with past CO2-forced climate transitions.