CO2-Forced Climate and Vegetation Instability During Late Paleozoic Deglaciation
Isabel P. Montañez, et al.
Science 315, 87 (2007);
DOI: 10.1126/science.1134207

The following resources related to this article are available online at www.sciencemag.org (this information is current as of January 5, 2007):

Updated information and services, including high-resolution figures, can be found in the online version of this article at:
http://www.sciencemag.org/cgi/content/full/315/5808/87

Supporting Online Material can be found at:
http://www.sciencemag.org/cgi/content/full/315/5808/87/DC1

This article cites 28 articles, 12 of which can be accessed for free:
http://www.sciencemag.org/cgi/content/full/315/5808/87#otherarticles

This article appears in the following subject collections:
Atmospheric Science
http://www.sciencemag.org/cgi/collection/atmos

Information about obtaining reprints of this article or about obtaining permission to reproduce this article in whole or in part can be found at:
http://www.sciencemag.org/help/about/permissions.dtl
experiments (8, 9). The Agung data are also consistent with laboratory experiments because the $\Delta^{33}$S versus $\delta^{34}$S Agung slope (Fig. 2) is the same as that of the Xe lamp experiment obtained for $\lambda > 220$ nm and very close to that of the KrF laser experiments conducted at 248 nm (8, 9).

The sulfur isotopic anomalies in volcanic samples are much smaller than those observed in Archean rocks older than 2.45 billion years (5, 6, 23, 24). In today's atmosphere, OH radicals remain the main sink of SO$_2$ emitted after a volcanic eruption, and the SO$_2^+$ + SO$_2$ reaction is a minor reaction when compared to the SO$_2$ + OH reaction. The sulfur MIF measured in volcanic sulfite recorded in snow is a diltuted signal and may actually reach the extreme values recorded in Archean rocks. To estimate the upper limit of the sulfur isotopic anomaly generated by the photodissociation process, researchers should compare the kinetics of the SO$_2$ + OH and SO$_2$ + SO$_2$ reactions. Unfortunately, the rate of SO$_2^+$ + SO$_2$ is controversial (25) and is needed for such quantification.

Sulfur mass-independent composition of volcanic sulfate is a time-dependent process, first displaying a positive $\Delta^{33}$S followed by a negative $\Delta^{33}$S at the end of the volcanic plume deposition process. This process occurs on a monthly time scale before SO$_2$ is fully oxidized in H$_2$SO$_4$, indicating a rapid process. The nonzero average $\Delta^{33}$S observed for the full duration of the event requires two conditions: First, the process creates two reservoirs of MIF with opposing signs; second, these two reservoirs must be physically separated in space and time in addition to having a difference in depositional rates. The only way to explain the oscillation of the $\Delta^{33}$S sign is to consider the fundamental role of aerosols and sedimentation in preserving the isotopic signal. Microphysical processes must be taken into account in models to reproduce sulfur MIF of stratospheric volcanic sulfate. When the relationship between aerosols and sulfur MIF is established, volcanic plume transport may be understood, allowing a precise glacial record of the climatic impact of stratospheric eruptions.

### References and Notes

4. The deviation from the mass-dependent relationships is calculated by the following equations: $\Delta^{33}S = \delta^{33}S - 1000 [(I + \delta^{34}S/1000)^{0.635} - 1]$ and $\Delta^{34}S = \delta^{34}S - 1000 [(I + \delta^{34}S/1000)^{0.635} - 1]$. Considering the small size of the samples, our analytical accuracy, with a 2σ uncertainty, is equal to 0.12% for $\Delta^{33}S$ and varies from 0.64 to 1.63% for $\Delta^{34}S$. Only $\delta^{34}S > 0.12 \%$ and $\Delta^{33}S > 0.64 \%$ are considered as diagnostic of MIF in the present study. Uncertainties (2σ) are 0.07, 0.19, and 0.53 to 1.59% for $\delta^{34}S$, $\delta^{33}S$, and $\Delta^{33}S$, respectively.
15. Materials and methods are available as supporting material on Science Online.

We acknowledge useful discussion with S. Bekki and thank the Conseil Régional Rhône-Alpes for partially supporting travel expenses for M.B.S. acknowledges the Balzan Foundation for financial support; C. Lorus and the Institut National des Sciences de l’Univers (INSU) for mass spectrometry acquisition; the French Polar Institute and M. Legrand (Institut Pélée Fransais Paul Emile Victor program D17) 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. Morgenster for helping J.S. to dig the snow pit.

Supporting Online Material

www.sciencemag.org/cgi/content/full/315/5808/84/DCl

Materials and Methods

SOM Text

Fig. S1

Tables S1 and S2

References

26 June 2006; accepted 15 November 2006
10.1126/science.1131754

**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 atmospheric partial pressure of carbon dioxide (pCO$_2$) and tropical marine surface temperatures during this climate transition. Comparison to southern Gondwanan glacial records documents covariance between inferred shifts in pCO$_2$ temperature, and ice volume consistent with greenhouse gas forcing of climate. Major restructurings of paleotropical flora in western Euramerica occurred in step with climate and pCO$_2$ shifts, illustrating the biotic impact associated with past CO$_2$-forced turnover to a permanent ice-free world.

A decade of studying Pleistocene ice cores has unequivocally documented a strong coupling of atmospheric partial pressure of CO$_2$ (pCO$_2$) and surface temperatures with changing global ice volume (7, 8). Although the precise mechanistic link between atmospheric greenhouse gases and climate is debated, there remains little doubt that high concentrations of atmospheric CO$_2$ have strongly amplified Earth's past climates. Anthropogenic CO$_2$ emissions have increased atmospheric CO$_2$ to concentrations higher than at any time in at least the past 650,000 years and could increase it to more than 2000 parts per million by volume (ppmv) as accessible fossil fuel reservoirs are exhausted (3). The last time such concentrations were seen on Earth was at the onset of our modern icehouse (~40 to 34 million years ago (Ma)), a transition from ice-free to glacial conditions characterized by repeated C cycle perturbations.

---

*Department of Geology, University of California, Davis, CA 95616, USA. ^Department of Geological Sciences, Southern Methodist University, Dallas, TX 75275, USA. *Department of Civil and Environmental Engineering, University of California, Davis, CA 95616, USA. ^Department of Paleobiology, Smithsonian Museum of Natural History, Washington, DC 20560, USA. ^Department of Geosciences, 214 Bessell Hall, University of California, Davis, CA 95616, USA. ^Department of Geology, State University of New York, College at Potsdam, Potsdam, NY 13676, USA.

*To whom correspondence should be addressed. E-mail: montanez@geology.ucdavis.edu

†Present address: Department of Geology, State University of New York, College at Potsdam, Potsdam, NY 13676, USA.
tion, large magnitude changes in atmospheric \( pCO_2 \), and major ephemeral warmings (4, 5). As our climate system departs from the well-studied Pleistocene glacial-interglacial cycles, a deep-time perspective of \( pCO_2 \)-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 \( CO_2 \) 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 glacial history for southern Gondwana (7–11), indicate strong linkages between \( pCO_2 \), 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 \( \pm500 \) ppmv (12, 13). These minerals are the proxy of choice when \( pCO_2 \) is high (\( \geq1000 \) ppmv), whereas the method’s sensitivity decreases at lower \( pCO_2 \) (<800 ppmv) (14, 15). The precision of \( pCO_2 \) estimates reflects the variable assumptions used for each \( pCO_2 \) 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 (\( \delta^{13}C_{carb} \)) 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 consider measured paleosol \( \delta^{13}C_{carb} \) 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 welldeserved fossil plant matter (\( \delta^{13}C_{org} \)) 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

![Fig. 1. Temporal distribution of carbonate (A) and fossil plant (B) \( \delta^{13}C \) values used to construct best estimate of Permo-Carboniferous atmospheric \( pCO_2 \) (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 \( \pm2 \) 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 \( \delta^{13}C_{org} \) of Permo-Carboniferous coals from three correlated successions in North China Platform (22). Overlapping \( \delta^{13}C_{org} \) trends but different \( \delta^{13}C_{org} \) values are interpreted to reflect overall wetter conditions for the North China Platform relative to western paleoequatorial Euramerica in the Permian. Data and \( pCO_2 \) presented on an age model (51) developed for the terrestrial composite section by linearly interpolating between known biostratigraphic boundaries. (C) Best estimate of paleo-\( pCO_2 \) (black curve) from Monte Carlo simulation of chronostratigraphically well-constrained sample populations; uncertainty in \( pCO_2 \) estimates (gray curves) reflects variability in \( \delta^{13}C_{carb} \) and \( \delta^{13}C_{org} \) interpreted to record inter- and intrabasinal 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 δ13Corg rather than penecontemporaneous marine carbonates as a proxy of atmospheric δ13C reflects a growing appreciation of local-scale C cycling effects on the δ13C values of epicontinental marine carbonates (21). The terrestrial δ13C_carb and δ13Corg 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 δ13C_carb trend records first-order variations in atmospheric δ13C is supported by its similarity to time-equivalent δ13Corg 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, ρi, and atmospheric, pa, partial pressures of CO2 in paleoflora [0.46 to 0.57 ± 0.3 (2 SE)], which were estimated by using measured δ13Corg values of fossil plants and δ13C_carb values of contemporaneous marine brachiopods (17). These factors indicate that changes in geomorphic or environmental conditions in the study area were secondary to atmospheric δ13C in influencing measured fossil-plant δ13Corg values.

Ranges of paleosol-respired CO2 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 CO2 paleobarometer (table S3) (14, 15). Paleosol temperatures 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 pCO2 was defined by using Monte Carlo simulation involving 1000 randomly drawn samples for each variable for each time-location combination (17). Monte Carlo simulation uses random sampling techniques to stochastically solve physical process problems, in this case quantitatively estimating paleo-pCO2 and the associated uncertainty by integrating across all of the inferred and measured input variables.

Modeled CO2 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 pCO2 into the early Middle Permian is corroborated by independently derived goethite-based estimates of Permian pCO2 (25). A short-lived (~2 My) drop in pCO2 to near PAL, defined by contemporaneous paleosols, punctuates the Early Permian rise. Modeled pCO2 suggests that PAL values were limited to the earliest Permian after latest Carboniferous levels of up to 1000 ppmv, in accord with pCO2 inferred from marine carbonate δ13C (26) and with southern Gondwanan sedimentologic and geochemical evidence for latest Carboniferous warming (9, 27). Our record refines the structure of well-established pCO2 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 CO2 records.

In order to evaluate the nature of the CO2-climate relationship, we developed a time-equivalent record of paleotropical sea-surface temperatures (SSTs) by using δ18O values from a global compilation of well-preserved latest Carboniferous through Middle Permian tropical shallow-water brachiopods (table S5) (30); brachiopods have diagnostically resistant, low-Mg calcitic shells that incorporate oxygen isotopes in equilibrium with seawater (31). The residual brachiopod δ18O 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 δ18O_carb values correspond with independently inferred periods of marked warming and sea-level rise (7–9, 34) (Fig. 2C).

Inferring secular paleotemperatures from δ18O_carb requires careful consideration of the compound effects on values of continental ice
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 temperature 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 Permian climate simulations for a change in radiative CO₂ forcing from 1 to 8 PAL (42).

Permno-Carboniferous plant assemblages from western paleoequatorial Euramerica archive a mechanistic vegetation 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 seasonally moisture-stressed environments. These biomes are floristically distinct, sharing only a few opportunistic ferns and sphenopsids (43). Typical latest Carboniferous flora, rich in marattian ferns, medullosan pteridosperms, sphenopsids, and sigillarian lycopsids, was replaced essentially instantaneously by one rich in conifers (Walchia and Ernestiodendron; compare with Brachyphyllum (44), callipterids (Rhaciphyllum), 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 florals (Fig. 3). Tree fern–rich florals reappeared during wetter, cooler conditions of the mid-Early
Permian (Artinskian) glaciation, stratigraphically intercalated but not mixed, with conifer-caliperiid floras. These two glacial floras show limited species overlap and oscillated at the 102- to 103-year scale, reflecting short-lived pluvials (46). Dramatic floristic changes also occurred during the cold period at the close of the Early Permian (Kungurian), with the migration into lowland basins of unique seed-plant assemblages not observed again until the Late Permian (conifers) and the Mesozoic (cycads) (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 (150 Ma) 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 glaciers generally confined to local valleys or mountain ice caps along the polar margin of Australian Gondwan. 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 unrelenting under 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.