

EVOLUTION OF PERMIAN ATMOSPHERIC pCO₂ AS DERIVED FROM PERMO-PENNSYLVANIAN PEDOGENIC PROXIES

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Summary

Modeling of latest Carboniferous through Permian atmospheric pCO₂ using Cerling's CO₂ paleobarometer suggests that CO₂ levels began to rise from the Late Carboniferous pCO₂ minima early in the Permian. The evolution of pCO₂ throughout the Permian was characterized by several rapid and large magnitude variations, including a second pCO₂ minima in the Early Permian. Estimated peak pCO₂ levels (~2000 to 2500 ppmv) in the Early Permian coincide temporally with numerically modeled estimates of the timing of the end of Late Paleozoic glaciation. Paleo-atmospheric pCO₂ levels in the Late Permian decreased progressively across the Permo-Triassic boundary to ultimately reach minimum values in the Early Triassic. These trends in Permian CO₂ levels were defined independently by the δ¹³C values of pedogenic carbonates from the Midland and Paradox basins indicating that the estimated evolution of pCO₂ is not a diagenetic or local artifact.

Introduction

The evolution of atmospheric pCO₂ throughout Earth's history has been of great interest to the academic community given the role pCO₂ plays in biogeochemical cycling, continental weathering, climate change, and evolutionary events. Berner (1991, 1994), through a series of geochemical models, estimated the evolution of atmospheric pCO₂ levels for the Phanerozoic. The results of his GEOCARB II model (Berner 1994) suggest that notably low CO₂ levels, comparable to present-day values (345 ppm), existed during Permo-Carboniferous glaciation. This pCO₂ minimum was followed by a rapid increase in atmospheric pCO₂ initiated sometime during the latter half of the Permian. Peak pCO₂ levels (3 to 9-fold greater than early Permian minimum values) were reached during the Middle to Late Triassic. Berner's modeled increase in pCO₂ levels during the Permian implies that the greenhouse effect was a major, if not dominant, control on Early to Middle Permian climate. However, this hypothesized evolution of Permo-Triassic atmospheric pCO₂ levels remained relatively untested in the geologic record.

In this paper, we present a newly defined record of atmospheric carbon dioxide levels for Permian estimated by applying a CO₂ paleobarometer to pedogenic carbonates in paleosols from four depositional basins in North America and Europe. Our Permian pCO₂ curve suggests that the transition from Late Paleozoic minimum values occurred very early in the Early Permian. Moreover, shorter term, high magnitude fluctuations are superimposed on the overall rise in pCO₂ during the first half of the Permian Period. Paleo-atmospheric pCO₂ levels declined progressively throughout the Late Permian reaching minimum values in the Early Triassic.

Geologic Framework and Methods

Pedogenic carbonate was collected from paleosols in four terrestrial successions: (1) the uppermost Pennsylvanian (Virgilian) through lowermost Middle Permian succession of the Eastern shelf of the Midland basin, north-central Texas, (2) the Lower Permian (Wolfcampian through Leonardian) succession of the Paradox basin, Utah, (3) the Upper Permian Val Gardena Sandstone, Italian Alps, and (4) the Upper Permian Quartermaster Formation, Palo Duro basin, Texas. The Permo-Triassic boundary occurs directly above the Val Gardena Sandstone and within the Quartermaster Formation. All three alluvial successions accumulated in low-latitude, coastal plain to piedmont settings.

Carbonate rhizoconcretions and Stage II nodules were collected from paleosols for which detailed morphologic descriptions were made (Tabor and Montañez in revision). Relative age assignment of samples was constrained by regionally correlatable sandstone markers, fusulinid biostratigraphy of intercalated marine limestones, and radiometrically dated ash layers. Carbonates were sampled from below 50 cm in the soil profile, which approximates the depth of significant diffusion of atmospheric CO₂ in modern soils. Samples were analyzed petrographically in order to identify diagenetically unaltered pedogenic carbonate. Pristine pedogenic components were microsampled using a jeweler's drill mounted to an automatic x-y-z stage fitted to a high-resolution binocular microscope. Microsamples (0.2 to 1 mg) were analyzed for δ¹³C on a Fisons Optima isotope ratio mass spectrometer at 90°C following the methods of Bemis and others (1998).

Atmospheric CO₂ Paleobarometer

Cerling (1991) introduced a CO₂ paleobarometer based on geochemical modeling and field observations of modern carbonate-bearing soils, which indicate that a relationship exists between the δ¹³C composition of pedogenic carbonate and atmospheric CO₂. The CO₂ paleobarometer equation, cast in terms of the isotopic composition of atmospheric CO₂ is:

$$\begin{aligned} & \delta^{13}\text{C}_s - 1.0044\delta^{13}\text{C}_o - 4.4 \\ &= S(z) \frac{\delta^{13}\text{C}_a - \delta^{13}\text{C}_s}{\delta^{13}\text{C}_a - \delta^{13}\text{C}_s} \end{aligned}$$

where S(z) is CO₂ contributed by soil respiration, and δ¹³C_s, δ¹³C_o, and δ¹³C_a are the isotopic composition of soil CO₂, soil-respired CO₂, and the atmosphere, respectively. The isotopic composition of soil CO₂ (δ¹³C_s) is calculated from the measured δ¹³C value of pedogenic carbonate using the temperature dependent fractionation factor of Romanek and others (1992). The remaining input variables (S(z), temperature and δ¹³C_o, and δ¹³C_a) must be assumed or estimated from proxy records.

The concentration of soil-respired CO₂ (S(z)) is a function of soil respiration rate, porosity and depth in the soil, and reaches a nearly constant value below 50 cm depth (Cerling and Quade 1993), typical of depths from which the studied

pedogenic carbonates were collected. A constant S(z) value of 5000 ppmv is assumed for the modeling given that S(z) in modern soils, analogous to those used in this study, ranges between 4000 and 7000 ppmv in the zone of carbonate accumulation (Ekar *et al.* in press). However, calculated pCO₂ is directly proportional to S(z) and is thus a major source of uncertainty in the method. Given the low paleolatitude and low paleoelevation (<1000 m) of the studied terrestrial successions we assume a constant temperature of 25°C.

For our modeling, the $\delta^{13}\text{C}$ composition of soil-respired CO₂ ($\delta^{13}\text{C}_o$) and atmospheric CO₂ ($\delta^{13}\text{C}_a$) are calculated from the proxy record of marine carbonate $\delta^{13}\text{C}$ values (Veizer *et al.* 2000). In order to calculate the paleo-atmospheric $\delta^{13}\text{C}$ composition, we assume a carbon isotope enrichment factor between atmospheric CO₂ and surface ocean marine calcite of ~8‰ at 25°C based on the isotopic composition of pre-industrial carbon dioxide trapped in glacial ice (Friedli *et al.* 1986) and contemporaneous surface ocean carbonates (Shackleton *et al.* 1983). In turn, we assume that the fractionation in $\delta^{13}\text{C}$ compositions of atmospheric CO₂ and soil organic matter (a proxy for the $\delta^{13}\text{C}$ composition of soil-respired CO₂ ($\delta^{13}\text{C}_o$)) is 18‰ based on the range of modern C₃ ecosystem fractionations (Buchmann *et al.* 1998).

The $\delta^{13}\text{C}$ composition of the latest Pennsylvanian through Early Permian atmosphere likely varied between -3 to -5‰, and the $\delta^{13}\text{C}$ composition of contemporaneous soil organic matter likely varied between -21 and 23‰. These values are suggested by applying the aforementioned fractionation factors

for carbon cycling between surface ocean waters, the atmosphere and C₃ land plants to Veizer and others' (2000) marine carbonate secular $\delta^{13}\text{C}$ curve for the equivalent time period ($\delta^{13}\text{C}_{\text{carbonate}}$ values of +3 to +4.5‰). Furthermore, the marine carbonate secular $\delta^{13}\text{C}$ isotope curve suggests that seawater, and by inference paleo-atmospheric $\delta^{13}\text{C}$ compositions fluctuated within these aforementioned ranges during latest Carboniferous through Permian time.

As an independent check on the calculated $\delta^{13}\text{C}_o$ and $\delta^{13}\text{C}_a$ values derived from the marine carbonate proxy record, we analyzed the $\delta^{13}\text{C}$ composition of soil organic matter, charcoal, and reptilian tooth enameloid (Table 1) from the terrestrial succession of the Midland basin, north-central Texas. The $\delta^{13}\text{C}$ composition of bulk organic matter extracted from the matrix of carbonate-bearing, Lower Permian paleosols ranges between -20.0 and -22.8‰. The $\delta^{13}\text{C}$ values of well-preserved charcoals, which are interbedded with the paleosols, are identical supporting the use of soil matrix organic matter $\delta^{13}\text{C}$ values as a proxy for the $\delta^{13}\text{C}$ composition of soil-respired CO₂. Moreover, the stratigraphic distribution of $\delta^{13}\text{C}_{\text{org}}$ values show a nonlinear temporal trend with the most positive values occurring in mid-Leonardian Waggoner Ranch paleosols. Significantly, the range in measured $\delta^{13}\text{C}_{\text{organic}}$ values and their temporal variation compare well with that estimated for soil organic matter derived from Veizer and others' (2000) marine carbonate $\delta^{13}\text{C}$ secular curve. This strongly supports the use of the marine carbonate proxy record for deriving the input parameters $\delta^{13}\text{C}_o$ and $\delta^{13}\text{C}_a$ for our pCO₂ models.

Table 1. $\delta^{13}\text{C}$ values of bulk organic matter, charcoal and tooth enamel (Diadectes and Dimetrodon reptiles) from Early Permian paleosols, Eastern shelf of the Midland basin, north-central Texas

<u>Formation/Group</u>	<u>Stratigraphic Age</u>	<u>Soil Organic Matter $\delta^{13}\text{C} \pm 1\sigma$</u> (n)	<u>Charcoal $\delta^{13}\text{C} \pm 1\sigma$</u> (n)	<u>Diadectes $\delta^{13}\text{C} \pm 1\sigma$</u> (n)	<u>Dimetrodon $\delta^{13}\text{C} \pm 1\sigma$</u> (n)
Upper Clear Fork	Leonardian	-22.6 \pm 0.4 (3)			
Middle Clear Fork	Leonardian	-22.8 \pm 1.5 (9)			
Lower Clear Fork	Leonardian	-22.6 \pm 1.2 (6)	-22.6 (1)		
Waggoner Ranch	Leonardian	-20.0 \pm 0.7 (7)	-20.4 \pm 1.0 (4)		
Petrolia	Leonardian			-10.0 (1)	-7.1 \pm 1.1 (2)
Archer City	Wolfcampian	-21.7 \pm 0.5 (2)			

Lastly, the $\delta^{13}\text{C}$ composition of tooth enamel from herbivorous and carnivorous Permian reptiles offers an independent check on values for $\delta^{13}\text{C}_o$ and $\delta^{13}\text{C}_a$ derived from the marine carbonate proxy record. The $\delta^{13}\text{C}$ composition of mammal tooth enamel reflects the $\delta^{13}\text{C}$ composition of their diet (Cerling and Sharp, 1996), and is much less susceptible to the effects of diagenetic alteration than paleosol organic matter (Koch 1998). Although the structure of reptile teeth (enameloid) is different than that of mammals, their teeth share the same mineralogy and tight structure and thus likely exhibit similar systematics. The $\delta^{13}\text{C}$ value (-10.0‰) of one sample of tooth enameloid from Diadectes, considered to be the earliest herbivorous reptile, is ~10 to 12‰ enriched over

(Table 1). The fractionation between modern mammal tooth enamel and soil organic matter ($\delta^{13}\text{C}_{\text{tooth}} - \delta^{13}\text{C}_{\text{organic matter}}$) is ~13‰ (Koch 1998).

The slightly smaller fractionation between herbivore tooth enameloid and soil organic matter in Lower Permian paleosols than expected with mammals reflects the uncertainty in the fractionation between reptilian tooth enameloid and organic matter, and the lack of $\delta^{13}\text{C}$ data for soil organic matter contemporaneous with the analyzed reptile teeth. Thus, the observed 12‰ enrichment lends additional support to our interpretation that the measured $\delta^{13}\text{C}$ values of soil organic matter and charcoals record original depositional compositions. Moreover, the $\delta^{13}\text{C}$ composition of Permian atmospheric CO₂ (-3.5‰) estimated from the herbivore teeth $\delta^{13}\text{C}$ values falls within the range derived from the marine carbonate $\delta^{13}\text{C}$ proxy curve. Two samples of tooth enameloid from Dimetrodon, a Permian carnivorous reptile, have $\delta^{13}\text{C}$ values of -8.2 and -6.0‰

soil organic matter and charcoal in slightly older (Archer City Formation) and younger (Waggoner Ranch Formation) deposits

(avg. of -7.1‰ ; Table 1). These $\delta^{13}\text{C}$ values are enriched by 2 to 4‰ over the $\delta^{13}\text{C}$ composition of herbivore tooth enameloid. This observed enrichment approximates that which would be expected between the tooth enamel of a carnivore and that of the herbivore it devoured (~ 2 to 3‰). Thus, the $\delta^{13}\text{C}$ values of a few reptile teeth further support our use of the marine carbonate proxy record for deriving the input parameters $\delta^{13}\text{C}_o$ and $\delta^{13}\text{C}_a$ for our pCO_2 models.

Permian Paleo- pCO_2

The results of our pCO_2 calculations are shown in Figure 1. A 3 point weighted average of our best estimate of CO_2 concentrations throughout the Permian is plotted as a function of time. Notably, the effect of changes in the $\delta^{13}\text{C}$ composition of the Permian atmosphere are factored out of the modeled pCO_2 curve given our use of Veizer and others' (2000) marine carbonate $\delta^{13}\text{C}$ proxy record to derive various input parameters. Note also that each data point shown on Figure 1 is the average of 5 to 17 pedogenic carbonate values from 2 to 9 paleosols within a stratigraphic formation or member.

Our best estimate of the evolution of latest Carboniferous through Permian pCO_2 (Fig. 1) defines several large magnitude and apparently rapid fluctuations in pCO_2 . Minimum pCO_2 levels occur in the latest Carboniferous and earliest Permian, corroborating previous estimates of pCO_2 for this time interval (Mora *et al.* 1996). These minimum values are similar to present-day atmospheric CO_2 levels (345 ppmv). CO_2 levels rise rapidly in the Early Permian to initial peak values of ~ 2000 to 2500 ppmv in the Sakmarian (upper Wolfcampian), and then drop rapidly in the latest Wolfcampian (~ 285 to 290 Ma) to a second period of minimum CO_2 contents. Significantly, both pCO_2 minima are defined by several paleosol groups from 2 depositional basins (Midland and Paradox basins). Subsequent to the youngest pCO_2 minima, CO_2 levels rise to peak values of ~ 2500 to 3000 ppmv in the Middle to earliest Late Permian. Ultimately, pCO_2 levels drop progressively across the Permo-Triassic boundary (~ 251.4 Ma), reaching minimum values in the Early Triassic (Ekart *et al.* in press). The fact that the latest Pennsylvanian through Early Permian portion of the pCO_2 evolution curve is defined independently by the $\delta^{13}\text{C}$ values of pedogenic carbonates from two depositional basins (Midland and Paradox basins) indicates that the estimated changes in pCO_2 are not a diagenetic or local artifact.

Temporal estimates of maximum deglaciation in the Permian range from early to middle Sakmarian time (Gibbs *et al.*, 1997), early Late Permian time (Crowell, 1994; Veevers and Powell, 1987), to latest Permian time (Epshteyn, 1981). However, recent climate models of Gibbs and others (1997) suggest that maximum deglaciation most likely occurred during the Sakmarian. We find it intriguing that the best estimate of timing of the initial peak in pCO_2 levels is latest Wolfcampian (Sakmarian) time. This suggests that rapidly increasing CO_2 levels in the Early Permian may have been a major factor in terminating Late Paleozoic glaciation. The subsequent fall in pCO_2 levels may record increased continental weathering associated with deglaciation as well as uplift of Himalayan-scale, Alleghanian, Ouachita and Hercynian mountains in the

Early Permian. What processes brought on the rapid return to peak pCO_2 levels in the Middle to earliest Late Permian remains to be investigated. Significantly, the Permo-Triassic boundary occurs on the falling limb of the pCO_2 curve, which reaches minimum levels in the Early Triassic.

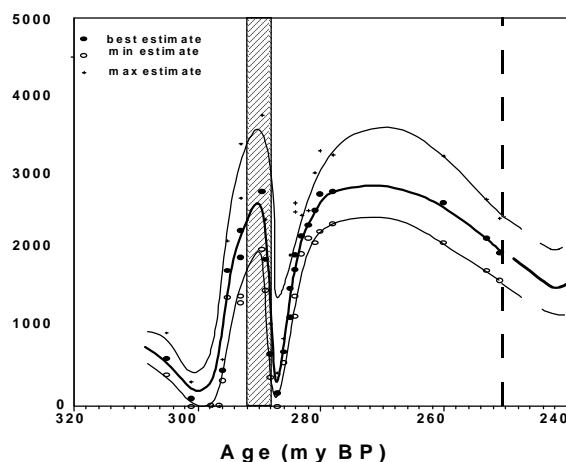


Figure 1. Modeled pCO_2 for latest Carboniferous through Permian time. Time scale reflects ages of $301 \text{ Ma} \pm 2 \text{ m.y.}$ for Carboniferous-Permian boundary (Rasbury *et al.* 1998) and $<251.4 \text{ Ma} \pm 0.4 \text{ m.y.}$ for the Permo-Triassic boundary (Bowring *et al.* 1998). Heavy curve is best estimate of pCO_2 evolution. Curves delineated by lighter lines are the upper and lower uncertainty estimates based on calculating a pCO_2 value one standard deviation above and below the average $\delta^{13}\text{C}$ values used to define the 'best estimate of pCO_2 '. The vertical, diagonal-line bar delineates the Sakmarian Stage.

Conclusions

Modeling of latest Carboniferous through Permian atmospheric pCO_2 using Cerling's CO_2 paleobarometer suggests that the rise in CO_2 levels following the Carboniferous pCO_2 minima occurred earlier in the Permian than previously suggested (Berner 1994). In addition, the evolution of Permian pCO_2 was characterized by several rapid and large magnitude variations. Paleo-atmospheric pCO_2 levels in the Late Permian decreased progressively across the Permo-Triassic boundary to ultimately reach minimum values in the Early Triassic. These trends in Permian CO_2 levels were defined independently by the $\delta^{13}\text{C}$ values of pedogenic carbonates from different basins lending credence to the validity of our estimated evolution of Permian pCO_2 .

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