

Middle to Late Paleozoic Atmospheric CO₂ Levels from Soil Carbonate and Organic Matter

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The stable carbon isotope compositions of ancient soil carbonate and coexisting soil organic matter indicate that atmospheric CO₂ levels decreased by a factor of 10 during the middle to late Paleozoic era. Proxy measurements of CO₂ were made by application of a soil carbonate CO₂ paleobarometer to a suite of paleosols that share key physical and chemical characteristics. The estimates agree with theoretical models that imply that a decrease in Paleozoic atmospheric CO₂ levels was associated with afforestation of the land surface by terrestrial plants and with global climate change leading to the extensive Permo-Carboniferous glaciation.

Fluctuations in the CO₂ content of the atmosphere may have played a critical role in determining ancient paleoclimates and ecosystem development. Theoretical models (1, 2) point to the Paleozoic era as a period of extreme fluctuation in atmospheric CO₂ levels, characterized by a 17-fold drop in CO₂ between the middle and late Paleozoic [450 to 280 million years ago (Ma)], with the lowest levels of CO₂ (about equal to modern levels) coinciding with the onset of the extensive Permo-Carboniferous glaciation. The steep decrease has been attributed to a drawdown in atmospheric CO₂ levels resulting from an increase in weathering rates, increased rates of organic carbon burial, and the rapid evolution and diversification of the terrestrial ecosystem (1, 3). Methods for proxy measurement (4) of the CO₂ content of such ancient atmospheres are sought to help evaluate the theoretical estimates. Fossil soils (paleosols) were formed in direct contact with the ancient atmosphere and may preserve evidence of changes in atmospheric compositions. In this report, we evaluate secular changes in the stable carbon isotope composition ($\delta^{13}\text{C}$) of soil-formed (pedogenic) carbonate and coexisting soil organic matter (OM) collected from a suite of well-characterized paleosols from the Late Silurian to the Early Permian periods. We use these isotopic compositions to interpret Paleozoic atmospheric CO₂ levels, using a recently developed soil carbonate CO₂ paleobarometer (5).

In order to reconstruct Paleozoic CO₂ levels with this paleobarometer, a number of specific conditions must be met: (i) Paleosols must have similar mineralogies and pedogenic histories. (ii) Stable isotope compositions must not be modified by diagenesis. (iii) The isotopic composition of soil OM must be known. (iv) Estimates of soil productivity and respiration rates must be

reasonably constrained.

We limited our study to paleosols developed in clay deposits that were confined to fluvial and deltaic fining-upward sedimentary sequences and were devoid of detrital carbonate. These paleosols have a relatively uniform mineralogy and exhibit distinctive physical characteristics, such as blocky peds, pedogenic slickensides, and sepic-plasmic fabric, formed by shrinking and swelling of smectite-rich soils in response to strongly seasonal precipitation (6). Soil factors such as porosity, permeability, and saturation state are impossible to quantify in ancient soils, but they influence CO₂ diffusion in soils and, therefore, calculated CO₂ levels (5). Limiting our study to vertic paleosols minimizes the variability of these factors in paleosols of different ages.

Pedogenic carbonates have morphologies that reflect characteristics of the flora (style of rooting) and pedogenic processes such as pedoturbation (translocation of carbonate nodules) and soil drying and cracking (circumgranular spar precipitation).

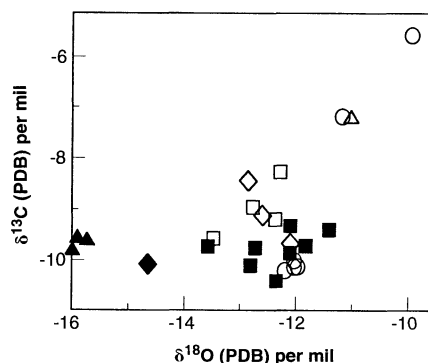


Fig. 1. Stable isotopic compositions of pedogenic carbonate in time-equivalent Late Devonian vertic paleosols from Newport, Pennsylvania (squares); Sunbury, Pennsylvania (triangles); Trout Run, Pennsylvania (circles); and Parksville, New York (diamonds). Solid symbols indicate micritic rhizoliths; open symbols indicate micrite nodules. Rhizoliths yield similar compositions in all of the paleosols and are exclusively used for CO₂ paleobarometry. PDB, Pee Dee belemnite standard.

Generally, we observed two morphologically and isotopically distinct pedogenic carbonate phases (7): spherical micrite nodules and micritic root traces (rhizoliths); rhizoliths resemble root sheaths formed around geologically young plant roots (8).

Studies of modern soils indicate that the $\delta^{13}\text{C}$ values of shallow (upper 20 to 30 cm) soil carbonate increase upward along a steep gradient in response to mixing with ^{13}C -enriched atmospheric CO₂ and will thus tend to overestimate CO₂ levels (5). The $\delta^{13}\text{C}$ values tend to approach a constant value at depth; these carbonates yield consistent minimum estimates of atmospheric CO₂ levels. In all the paleosols that we studied, nodules had more positive $\delta^{13}\text{C}$ values than did rhizoliths (Figs. 1 and 2), reflecting their formation at, and common translocation to, higher levels in the soil. Rhizoliths have consistent $\delta^{13}\text{C}$ values in geographically separated, time-equivalent paleosols (Fig. 2), which suggests that rhizoliths best preserve pedogenic isotopic compositions (9) that are useful for CO₂ paleobarometry.

Modification of pedogenic isotope compositions during diagenesis has been viewed as a major obstacle to isotopic paleobarometers. Pedogenic carbonate can be identified by petrographic and chemical examination (10). As shown in Fig. 2, $\delta^{13}\text{C}$ values of the pedogenic carbonate we studied were not substantially altered during burial diagenesis, even if oxygen isotope compositions were substantially shifted; similar results have been reported for younger paleosols (5). Alteration of oxygen isotope compositions without concomitant alter-

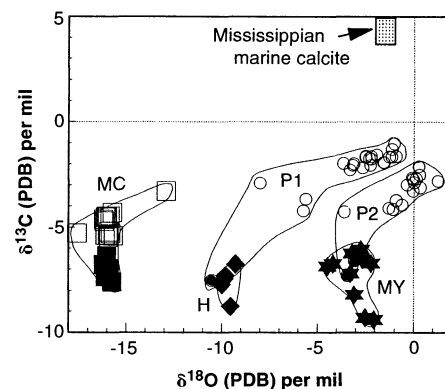


Fig. 2. Stable isotopic compositions of pedogenic carbonate from Late Mississippian vertic paleosols. Solid and open symbols are as defined in Fig. 1. PDB standard. Paleosol abbreviations and approximate depth of burial are: MC, Mauch Chunk Fm., 7 to 8 km; H, Hinton Fm., 4 km; MY, Maccrady Fm., 4.5 km; and P1 and P2, Pennington Fm., 1 to 3 km. The $\delta^{13}\text{C}$ values of rhizoliths in these paleosols are unaffected by varying degrees of burial diagenesis; extreme isotopic shifts in Pennington Fm. nodules are due to early post-pedogenic dolomitization of the pedogenic calcite.

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ation of the carbon isotopes is possible if recrystallization proceeds in the presence of small amounts of water or if diagenetic fluids are poor in dissolved carbon.

The isotopic composition of atmospheric CO₂ is regulated on a long-term basis by equilibrium with marine inorganic carbon. A number of studies report an increase in the $\delta^{13}\text{C}$ of marine inorganic carbon (marine carbonate rocks) from 0 per mil in the Late Silurian to 6 per mil in the Early Permian (11); the $\delta^{13}\text{C}$ of atmospheric CO₂ is thus predicted to parallel this trend, with values ~ 7 per mil more negative (12). Although terrestrial plants use atmospheric CO₂ during photosynthesis, there is no agreement on whether $\delta^{13}\text{C}$ values of terrestrial OM show this secular variation (13).

Organic material is scarce in the oxidized, red-bed vertic paleosols we examined; however, we were able to concentrate sufficient bulk organic carbon for isotopic analysis (14). Our results (Table 1) indicate that the $\delta^{13}\text{C}$ value for bulk OM increased from -27.4 per mil in Late Silurian paleosols to -23.5 per mil in Early Permian paleosols. We interpret these values to be representative of original soil OM for several reasons. (i) The $\delta^{13}\text{C}$ of organic material composing coals and kerogens is, in general, unaffected by diagenesis (15). Some change may occur in the $\delta^{13}\text{C}$ of bulk soil OM during decomposition of labile organic compounds in plant tissue and soil litter (16), but these changes generally occur at a rate that is several orders of magnitude faster than that of soil carbonate precipitation (10^1 versus 10^2 to 10^3 years). Thus we can assume that the relatively inert compounds composing the paleosol OM we measured reflect the time-averaged composition of soil OM during pedogenic carbonate precipitation. (ii) The paleosols are not associated with marine or lacustrine deposits, which indicates that terrestrial plant and animal remains most likely make up the organic fraction in the paleosols. Concentration of organic material near or within rhizoliths suggests that plant material dominates (17).

As shown in Fig. 3, the isotopic fractionation between atmospheric CO₂ and soil OM ($\delta^{13}\text{C}_{\text{atmos}} - \text{OM} = \delta^{13}\text{C}_{\text{atmos}} - \delta^{13}\text{C}_{\text{OM}}$) remained relatively constant (~ 21 to 22.5 per mil) through the middle to late Paleozoic, despite the 6 per mil change inferred for $\delta^{13}\text{C}$ of atmospheric CO₂ over this time period. Thus, the bulk soil organic carbon directly tracked secular changes in the isotopic composition of atmospheric CO₂. In contrast, the isotopic fractionation between pedogenic carbonate and soil organic carbon ($\delta^{13}\text{C}_{\text{calcite}} - \text{OM}$) is quite variable, ranging from ~ 21 per mil in Late Silurian to ~ 14 per mil in

Table 1. Isotopic data for Paleozoic paleosols and calculated levels of atmospheric CO₂. Isotope ratios are reported in delta notation, where $\delta^{13}\text{C} = [({}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}})/({}^{13}\text{C}/{}^{12}\text{C}_{\text{standard}}) - 1]1000$ per mil relative to the PDB standard. Average $\delta^{13}\text{C}$ of pedogenic calcite includes rhizolith compositions only, $\pm 1\sigma$; n is number of samples. Atmospheric CO₂ was calculated from the soil carbonate barometer (5) with the use of measured $\delta^{13}\text{C}$ pedogenic calcite (average value to -1σ) and soil OM; $\delta^{13}\text{C}$ atmospheric CO₂ was determined from marine inorganic carbon (see text); and soil CO₂ = 3000 to 7000 parts per million determined by volume (ppm V) which is typical of semi-arid, tropical to temperate soils (5). Uncertainties (± 0.5 per mil) in average $\delta^{13}\text{C}(\text{OM})$ are not accounted for in the CO₂ calculations; changes of this magnitude would increase or decrease calculated CO₂ by $\sim 15\%$.

Age (Ma)	Formation	$\delta^{13}\text{C}$ soil calcite (n)	$\delta^{13}\text{C}$ soil OM (n)	$\delta^{13}\text{C}$ atmos.	Atmospheric CO ₂ (ppm V)
410 to 415	Bloomsburg	-5.3 ± 1.2 (9)	-27.4 (5)	-7	3200 to 5200
	Catskill				
366 to 368	Sherman Creek Member	-9.0 ± 0.1 (5)	-27.2 (6)	-5	950 to 2050
363 to 366	Duncannon Member	-9.8 ± 0.3 (12)			700 to 1275
350 to 353	Maccrady	-7.6 ± 1.2 (9)	-23.8 (3)	-2.5	450 to 500
332 to 345	Mauch Chunk	-7.0 ± 0.5 (5)			600 to 1000
332 to 335	Hinton	-7.6 ± 0.8 (5)			450 to 650
332 to 335	Pennington	-7.0 ± 0.5 (3)			600 to 1000
300 to 310	Conemaugh	-7.2 ± 0.6 (8)	-23.6 (1)	-1	450 to 800
280 to 292	Dunkard	-8.7 ± 0.4 (5)	-23.5 (3)	-1	150 to 200

Early Permian paleosols. Fractionations in the range 14 to 16 per mil are observed in modern Holocene soils that have low to moderate respiration rates and are dominated by C₃ vegetation (5); values in this range indicate the absence of a substantial input of atmospheric CO₂. Much larger fractionations are most plausibly interpreted as indicating substantially higher atmospheric levels of CO₂ in the mid-Paleozoic.

Silurian paleosols pose a special problem for application of the soil carbonate paleobarometer. The primitive vascular plants that colonized these soils (18) were small and lacked true roots, and plant cover may have been sparse as compared with more robust Devonian and Carboniferous ecosystems. Thus, the mean production depth for CO₂ in these soils may have been shallow

(<5 cm) and rates of soil respiration were likely low. Consequently, soil CO₂ (and carbonate) in Late Silurian paleosols may be substantially influenced by isotopically heavy atmospheric CO₂; we estimate that atmospheric CO₂ contributed 35 to 40% of the soil CO₂ in paleosols from the Late Silurian Bloomsburg Formation (Fm.) (19). These factors would tend to result in overestimation of Silurian atmospheric CO₂; however, their effect may have been mediated if early vascular plants preferred moister soils (such as lowland or near-channel environments) (18), because the decreased porosity and permeability of a wetter soil would effectively increase soil CO₂ content; or if OM was incorporated into deeper lev-

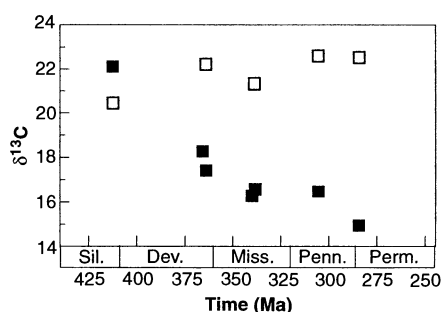


Fig. 3. Carbon isotope fractionations between atmospheric CO₂ and bulk OM (open symbols) or pedogenic carbonate (solid symbols) in Paleozoic paleosols. Constant fractionations between atmosphere and soil OM suggest that the OM is tracking secular changes in atmospheric CO₂. Variable fractionations between pedogenic calcite and soil OM suggest declining levels of atmospheric CO₂ from the middle to late Paleozoic. Sil., Silurian; Dev., Devonian; Miss., Mississippian; Penn., Pennsylvanian; and Perm., Permian.

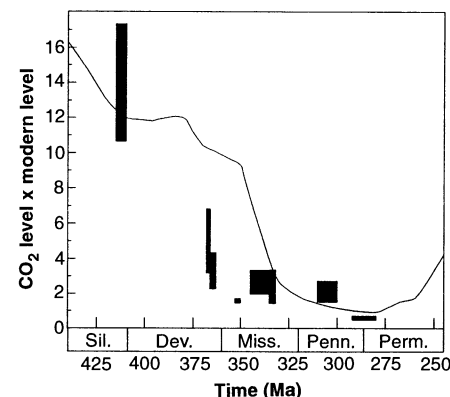


Fig. 4. Estimates of Paleozoic atmospheric CO₂ calculated from pedogenic carbonate and soil organic carbon compositions in Paleozoic vertic paleosols (solid bars) compared to estimates from theoretical long-term carbon mass balance calculations (1) (line). The steepest period of decline coincides with a period of rapid evolution and diversification of the terrestrial ecosystem. Modern CO₂ level = 300 ppm V.

els of Silurian soils as a result of pedoturbation, effectively increasing the average depth of soil CO₂ production.

Our results (Table 1) imply that atmospheric CO₂ declined by a factor of 10 from the Late Silurian to the Early Permian, closely following (Fig. 4) a decline predicted by theoretical carbon mass balance models (1). The largest decrease, between the Late Silurian and Late Devonian, coincides with a period of rapid evolution and diversification of the terrestrial ecosystem (18). Estimates of atmospheric CO₂ levels from geographically separated, time-equivalent paleosols are consistent, suggesting that a coherent record of changing atmospheric chemistry is preserved in the ancient soil record.

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9. We note the isotopic distinction between nodules and rhizoliths in >20 different Paleozoic red-bed vertic paleosols; the relation appears to be a general one for paleosols of vertic affinity. Pedogenic carbonate formed in soils subject to a different set of physical processes may not show this distinction.
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14. We concentrated bulk OM to 0.5 to 3 weight % by floating crushed paleosol samples in distilled water. Material that floated was composed predominantly of illite, calcite, and OM; Fe-oxides and silt-sized silicates preferentially settled. The float was washed in 10% HCl, thoroughly rinsed and dried, mixed with CuO, and combusted at 1050°C for 15 min to produce CO₂. The CO₂ was purified cryogenically before isotope ratio analysis. Eighteen of 30 paleosol samples thus prepared generated sufficient CO₂ to analyze with reproducibility of ± 0.2 per mil. Standard deviation about the mean for a given time period was about ± 0.5 per mil.
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17. We analyzed five samples from a 30- to 50-cm organic-rich lens within a Silurian red-bed, paleosol-bearing succession [described by P. K. Strother, *J. Paleontol.* **62**, 967 (1988)] that had qualitatively different proportions of plant-derived (*Nematolithus*) and animal-derived (cuticular fragments) OM. Only the sample most dominated by animal-derived OM differed by >0.4 per mil from a sample of plant-derived OM, which suggests that admixed animal OM will not substantially alter the $\delta^{13}\text{C}$ of bulk OM in a soil.
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Initial Results of Radio Occultation Observations of Earth's Atmosphere Using the Global Positioning System

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Recent radio occultation measurements using Global Positioning System satellite transmitters and an orbiting receiver have provided a globally distributed set of high-resolution atmospheric profiles, suggesting that the technique may make a significant contribution to global change and weather prediction programs. Biases in occultation temperatures relative to radiosonde and model data are about 1 kelvin or less in the tropics and are generally less than 0.5 kelvin at higher latitudes. Data quality is sufficient to quantify significant model errors in remote regions. Temperature profiles also reveal either an equatorial Rossby-gravity or an inertia-gravity wave. Such waves provide a fundamental source of momentum for the stratospheric circulation.

Radio occultation is a technique for sounding the structure of atmospheres from space with high accuracy and vertical resolution. Since the mid-1960s, it has been used by planetary spacecraft to measure vertical

density, pressure, and temperature structure in the atmospheres of Venus, Mars, and the outer planets (1–4). With the completion of the constellation of 24 orbiting radio transmitters known as the Global Positioning System (GPS), the sensitivity and coverage necessary to improve upon existing data sets for the Earth's atmosphere in a simple, cost-effective manner are now available. Here we present initial temperature and water vapor profile data derived from measurements made in April and May 1995 during the prototype GPS occultation mission, GPS-MET, launched in April 1995 (5). These profiles are compared with radiosonde (balloon) data and atmospheric anal-

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