

$\delta^{13}\text{C}$ depth profiles from paleosols across the Permian-Triassic boundary: Evidence for methane release

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ABSTRACT

Stable carbon isotopic analyses of organic carbon ($\delta^{13}\text{C}$) in individual paleosol profiles from Permian-Triassic sequences of Antarctica reveal systematic isotopic variations with profile depth. These variations are in many cases analogous to those in modern soils, which are functions of redox conditions, soil development, and degree and type of microbial decay. In modern soils, these isotopic depth functions develop independently from vegetation changes (C_3 versus C_4 vegetation) and can be diagnostic of soil orders. This study shows that soil-intrinsic functions can be preserved in the $\delta^{13}\text{C}$ values of paleosols as old as 260 Ma and constitute valuable data for paleoecological interpretations.

A large carbon isotopic offset of as much as 10‰ in whole paleosol profiles across the Permian-Triassic boundary indicates significant changes in the soil biogeochemistry and the soil-atmosphere system. Early Triassic paleosols are distinctive in their extremely low $\delta^{13}\text{C}$ values (to -42‰) and often show an anomalous $\delta^{13}\text{C}$ depth distribution compared to both Permian paleosols and modern soils. Highly depleted $\delta^{13}\text{C}$ values, as the ones in Early Triassic paleosols, are suggested to be associated with microbial methane oxidation (methanotrophy). This hypothesis implies increased methane concentrations in the Early Triassic soil-atmosphere system. Increased atmospheric methane was probably partly responsible for the global carbon isotopic shift documented in marine and terrestrial sediments across the Permian-Triassic boundary.

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INTRODUCTION

Soil organic matter constitutes the largest surficial pool of organic carbon on continents and has long been recognized as an important component of the global carbon cycle (Kern and Schlesinger, 1992). The depth distribution of stable and radiogenic carbon isotopes from soil organic matter reflects soil-forming processes that influence soil organic matter. Results from such studies have been used (1) to quantify rates of soil carbon turnover and storage, (2) to study climate-related vegetation changes, (3) to analyze isotopic effects of decomposition and humus formation, and (4) to classify isotopic trends with soil development (O'Brien and Stout, 1978; Stout and Rafter, 1978; Becker-Heidmann and Scharpenseel, 1990, 1992). Detailed sampling of the entire soil profile is crucial to any of these interpretations because $\delta^{13}\text{C}$ depth profiles of soil organic matter reflect systematic fractionation processes (Becker-Heidmann and Scharpenseel, 1986). With a few exceptions, analyses of paleosol organic matter for $\delta^{13}\text{C}$ depth profiles are rare in Tertiary and older paleosols (Cerling et al., 1991; Bestland and Krull, 1999). Most $\delta^{13}\text{C}$ analyses of organic matter from pre-Quaternary paleosols reported in the literature usually consist of one sample per profile. Commonly, these samples are taken in conjunction with pedogenic carbonate from Bk or Ck horizons, but it is often unclear which horizon was sampled (Kingston et al., 1994; Mora et al., 1996). As a result, $\delta^{13}\text{C}$ values display more scatter in these studies compared with the database from more densely sampled pedogenic carbonates (Quade et al., 1995; Mora et al., 1996).

Previous studies have used carbon isotopic values from organic matter mostly as an ac-

cessory tool to assess diagenetic effects of associated carbonates or as an additional variable in modeling past atmospheric $p\text{CO}_2$ or evaluating vegetation changes (Cerling et al., 1989; Quade et al., 1995; Mora et al., 1996). Thus, paleosol $\delta^{13}\text{C}$ variation with soil depth in the absence of C_3/C_4 vegetation changes remains little explored. As our results show, pedogenic $\delta^{13}\text{C}$ trends similar to those of modern soils can be preserved and recognized in paleosols and can be important indicators of biogeochemical processes in terrestrial paleoenvironments.

METHODS

Stratigraphic sections bracketing the Permian-Triassic boundary were measured in the Allan Hills and at Graphite Peak, Antarctica (Fig. 1; Retallack et al., 1995, 1996a; Krull, 1998). Each paleosol type (in the sense of Retallack, 1988) was characterized in detail from field observations, petrographic analyses, and bulk-rock geochemical analyses (Table 1). Field observations included identification of color according to the Munsell color chart, reaction with dilute HCl acid, and degree of development of paleosols, based on criterion of Retallack (1988). Thin sections of representative profiles were counted for 500 points using a Swift automatic point counter for grain-size analysis and for analysis of constituent minerals with accuracy of $\sim 2\%$. Fresh rock samples from paleosols were collected from outcrops for analysis of major and trace elements and for $\delta^{13}\text{C}$ analysis. For $\delta^{13}\text{C}$ analysis of the long stratigraphic sections, we refrained from analyzing coals to ensure adequate comparison among pedotypes and to avoid isotopic artifacts due to the very different mode of formation of Histosols. Instead, deeply rooted underclays, which are less susceptible to waterlogging and accumulation of organic mat-

ter, were sampled. For $\delta^{13}\text{C}$ analysis of individual paleosol profiles, coals were included.

Chemical analyses for major elements (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , and P_2O_5) were obtained by inductively coupled plasma-fusion spectroscopy and loss on ignition from 4 h at 1000 °C. Standard deviations were 0.23 wt% (SiO_2), <0.01 wt% (TiO_2), 0.13 wt% (Al_2O_3), 0.12 wt% (Fe_2O_3), 0.005 wt% (MnO), 0.03 wt% (MgO), 0.16 wt% (CaO), 0.02 wt% (Na_2O), 0.16 wt% (K_2O), and 0.004 wt% (P_2O_5). Analysis for ferrous iron was from ammonium sulfate titration (standard deviation was 0.15 wt%). Analyses of barium and strontium were by X-ray fluorescence. All geochemical analyses were done by Bondar Clegg Inc., Vancouver, British Columbia.

In preparation for isotopic analysis, samples were powdered and sieved through a 0.210 mm screen, then treated for 1 h with hot 2 N HCl to remove all carbonates and other acid-soluble minerals. Acid-insoluble residues were washed until neutral and oven-dried for at least 12 h. The dried and weighed residues were loaded into 9 mm quartz tubes with 1 g CuO , 50 mg Ag foil, and 1 g elemental Cu each, following the procedure of Boutton (1991). The tubes were evacuated, sealed, and combusted at 860 °C for 6 h and then slowly cooled to 25 °C over 20 h. CO_2 was collected by cryogenic distillation and total organic carbon (TOC) content was determined by measuring the volume of CO_2 and converting it to total amount of carbon (Boutton, 1991). The $\delta^{13}\text{C}$ analysis was done using the Finnigan Delta-E triple collector isotope ratio mass spectrometer at the Illinois State Geological Survey. Standard deviation from replicates averaged 0.32‰. Isotope results are reported in the conventional notation as per mil deviation from the Pee Dee belemnite standard (Craig, 1957).

CHRONOSTRATIGRAPHIC FRAMEWORK

Permian–Triassic strata investigated here belong to the Victoria Group and consist of cyclothem of clastic alluvial sediments, coal measures, and paleosols, similar to other well-studied Gondwanan sequences (Retallack et al., 1996b). Two localities, Graphite Peak in the central Transantarctic Mountains and Allan Hills in southern Victoria Land, were selected for detailed stratigraphic, geochemical, and carbon isotopic studies of paleosols (Fig. 2, A and B).

Permian strata in both localities are composed of fining-upward sequences of sand-

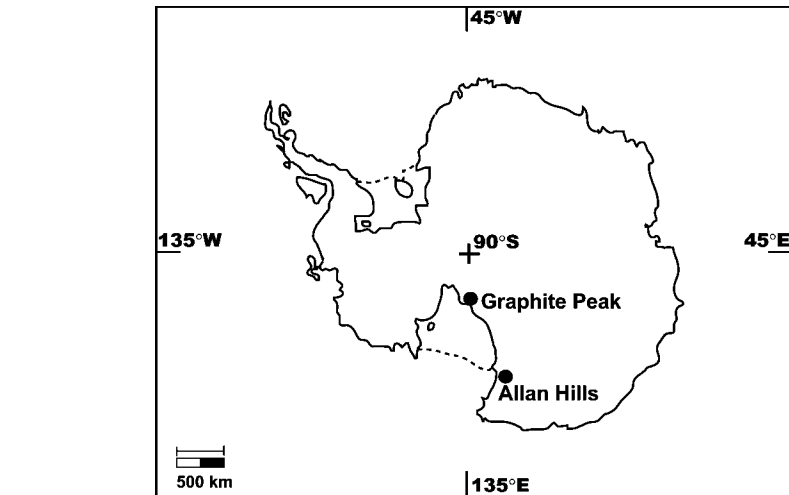


Figure 1. Locality map of Graphite Peak and Allan Hills in Antarctica.

TABLE 1. LATE PERMIAN AND EARLY TRIASSIC PALEOSOLS OF ANTARCTICA

U.S. Taxonomy*	Diagnosis	Former ecotype	Time to form
Histosol	Thick clean coal (0), on clay or silt, deeply penetrating <i>Vertebraria</i> roots.	Seasonally drained, swampy depressions	20–50 k.y.
Entisol	Gray-green cherty siltstone with simple (unchambered) root traces.	Streamside swales of flood plains	5–100 yr
Gleyed Inceptisol	Gray-green silty or sandy surface (A) over large berthierine nodules (Bg).	Seasonally wet flood plain	1–2 k.y.
Ultisol	Gray silty fissured surface (A) over thick clayey subsurface (Bt).	Higher parts of flood plain	40–60 k.y.
Alfisol	Gray-green surface (A) over red (10R) clayey subsurface (Bt).	Well-drained flood plain or terrace	40–50 yr
Gleyed Entisol	Dark gray shaly surface (A) over green-gray subsurface.	Streamside swales and flood plain depressions	5–100 yr

*Soil Survey Staff (1997).

stone, siltstone, underclay, and coal. Coaly Histosols are the most abundant paleosol types in these sequences, next to weakly to moderately developed Inceptisols. Early Triassic paleosols lack coaly Histosols and paleosol types consist of Inceptisols, Entisols, and a few Alfisols (Retallack and Krull, 1999).

The Permian–Triassic boundary in similar Gondwanan sequences has been established by correlating high-precision $^{206}\text{Pb}/^{238}\text{U}$ radiometric dates of detrital zircons in marine sequences of China (Claoué-Long et al., 1991) with radiometric dates on tuffs in coal measures of New South Wales (Veevers et al., 1994). These data, together with the $\delta^{13}\text{C}$ excursion in terrestrial deposits in Australia, identify the boundary at the lithological change from coal measures to sandstone and siltstone (Retallack, 1995; Morante, 1996). In Australian basins the negative $\delta^{13}\text{C}$ excursion occurs at or near the base of the palynological *Protohaploxypinus microcorpus* zone, which coincides with the cessation of Late Permian

coal measures and the onset of the Early Triassic coal gap (Morante, 1996; Retallack et al., 1996b). Thus, the boundary in terrestrial sections is placed between the last Late Permian coal seam, containing *Glossopteris* leaves and *Vertebraria* roots, and sandy-silty deposits yielding the seed fern *Dicroidium callipteroides* (Retallack, 1995).

Graphite Peak

At Graphite Peak (Fig. 2A) the paleontologically established Permian–Triassic boundary is between the last *Glossopteris*-bearing coal of the Late Permian Buckley Formation and strata that yield the earliest Triassic reptiles *Lystrosaurus*, *Thrinaxodon*, and *Prolacerta* of the Fremouw Formation (Hammer, 1989, 1990). Fossil remnants of *Lystrosaurus* (at 291 m), *Dicroidium zuberii* (at 369 m), and *Dicroidium odontopteroides* (at 558 m) indicate early Scythian, late Scythian, and Anisian ages, respectively. Small amounts of shocked

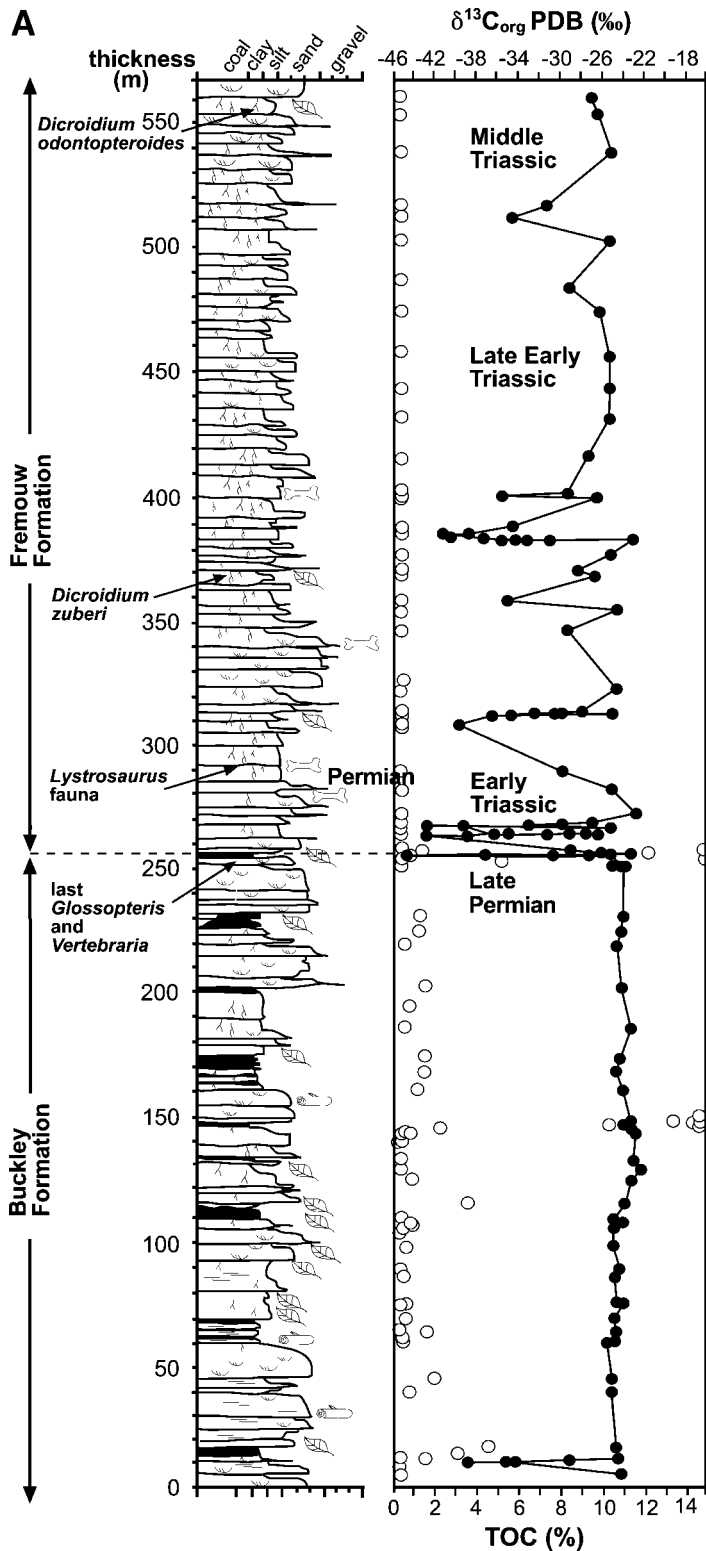


Figure 2. Stratigraphic sections of Graphite Peak (A) and Allan Hills (B) showing changes in paleosols, $\delta^{13}\text{C}$ (solid circles; PDB—Peedee belemnite), and total organic carbon (TOC—open circles) values. Note that for the long stratigraphic sections, we did not analyze coals to ensure adequate comparison among Permian and Triassic pedotypes. Instead, we sampled deeply rooted underclays, which are comparable to gleyed Inceptisols.

quartz have been reported from a claystone breccia immediately above the last coal at 256 m, and a faint iridium enrichment occurs at the base of the last coal (Retallack et al., 1998). A pronounced shift toward more negative $\delta^{13}\text{C}$ values occurs within the last coal seam of the Late Permian Buckley Formation at 256 m (Fig. 2A), and low isotopic values continue into the overlying Early Triassic Fremouw Formation (average is -31.4‰). This shift toward negative $\delta^{13}\text{C}$ values in the terminal Permian, the persistently low isotopic values, and the lower TOC values in the Early Triassic, are consistent with results from other isotopic studies (e.g., Magaritz et al., 1992; Morante, 1996) and suggest that this excursion at the Buckley-Fremouw contact marks the Permian-Triassic boundary.

An earlier negative excursion occurs at the base of the Graphite Peak section. These low values may record an earlier Late Permian negative isotopic event, as reported in marine and terrestrial sections by Baud et al. (1989), Magaritz et al. (1992), Grotzinger and Knoll (1995), and MacLeod et al. (1997). This negative excursion may correlate with a Late Permian (end Guadalupian) marine extinction event (Stanley and Yang, 1994) and a Late Permian (but not latest Permian) extinction event in the terrestrial Karoo basin, South Africa (King, 1991).

Allan Hills

In the Allan Hills (Fig. 2B), the Weller Coal Measures include mid-Permian, but not latest Permian, fossil plants and pollen (Kyle, 1977; Kyle and Schopf, 1982). The overlying Feather Conglomerate in the Allan Hills has yielded no fossils of established biostratigraphic utility, but in other parts of Victoria Land, late Early Triassic to early Middle Triassic (Spathian to early Anisian) palynomorphs were found in the upper part of the Feather Conglomerate (Kyle, 1977). In the Allan Hills, the lowermost Lashly Formation has fossil plants of Middle to Late Triassic (Anisian–Ladinian) ages (Retallack and Alonso-Zarza, 1998).

The $\delta^{13}\text{C}$ values of the mid-Permian Weller Coal Measures Formation remain at an average value of -23.5‰ until 17 m above the last mid-Permian coal seam (Fig. 2B). In the lower Feather Conglomerate, $\delta^{13}\text{C}$ values increase (average is -17.2‰); maximum values reach -16.6‰ . By comparison, stratigraphically higher in the Feather Conglomerate, $\delta^{13}\text{C}$ values are lower, but range widely, from -46.2‰ to -17.2‰ . A critical hiatus is thought to be present at the base or within the Feather Conglomerate, obscuring the Perm-

ian-Triassic boundary. Such stratigraphic incompleteness has long been recognized in the Allan Hills (Collinson et al., 1994) and hinders exact placement of the boundary. The basal Lashly Formation in the Allan Hills is Middle Triassic (Retallack and Alonso-Zarza, 1998) and $\delta^{13}\text{C}$ values are about 6.5‰ lower compared with data from the Permian Weller Coal Measures (-29.8‰).

PEDOGENESIS AND DIAGENESIS OF ORGANIC MATTER

Carbon isotopes of organic matter generally resist fractionation during burial diagenesis (Hayes et al., 1983). At conditions below greenschist facies (<350 °C) and at H/C ratios >0.2, diagenetic alteration of organic carbon isotopes is negligible (Hayes et al., 1983). Diagenetically affected high-rank kerogen is also indicated by a dry ash-free carbon content (DAF) >92% (McKirdy and Powell, 1974).

Both localities of this study were affected to different degrees by regional and local metamorphism from Jurassic dolerite intrusions (Coates et al., 1990). The H/C values for Allan Hills coals average 0.44 (Schopf and Long, 1966) and 0.46 for Graphite Peak (Coates et al., 1990) and are thus above the isotopically critical values. The DAF carbon contents for both localities are below the critical value, being 84% for the Allan Hills and 67% for Graphite Peak (Schopf and Long, 1966; Coates et al., 1990). In addition, authigenic mineral assemblages in the Allan Hills and the central Transantarctic Mountains include zeolites (Ballance, 1977), which have an upper stability limit of 300 °C and 3 kbar, well below isotopically critical conditions of greenschist facies.

In addition, to ensure that our isotopic data are not the result of contamination or thermally driven loss of hydrocarbons during diagenesis, we compared TOC contents against $\delta^{13}\text{C}$ values of each formation (Fig. 3, A and B). No significant statistical correlation between TOC and $\delta^{13}\text{C}$ values was recognizable; R^2 values are consistently below 0.1. From these data, we conclude that our $\delta^{13}\text{C}$ values can be interpreted as an original isotopic signature.

$\delta^{13}\text{C}$ AND SOIL ORGANIC MATTER IN MODERN SOILS

Organic carbon dynamics in modern soils need to be considered in order to evaluate ancient $\delta^{13}\text{C}$ and TOC depth trends in paleosols. During humus formation in soils, a large fraction of organic matter is lost due to decom-

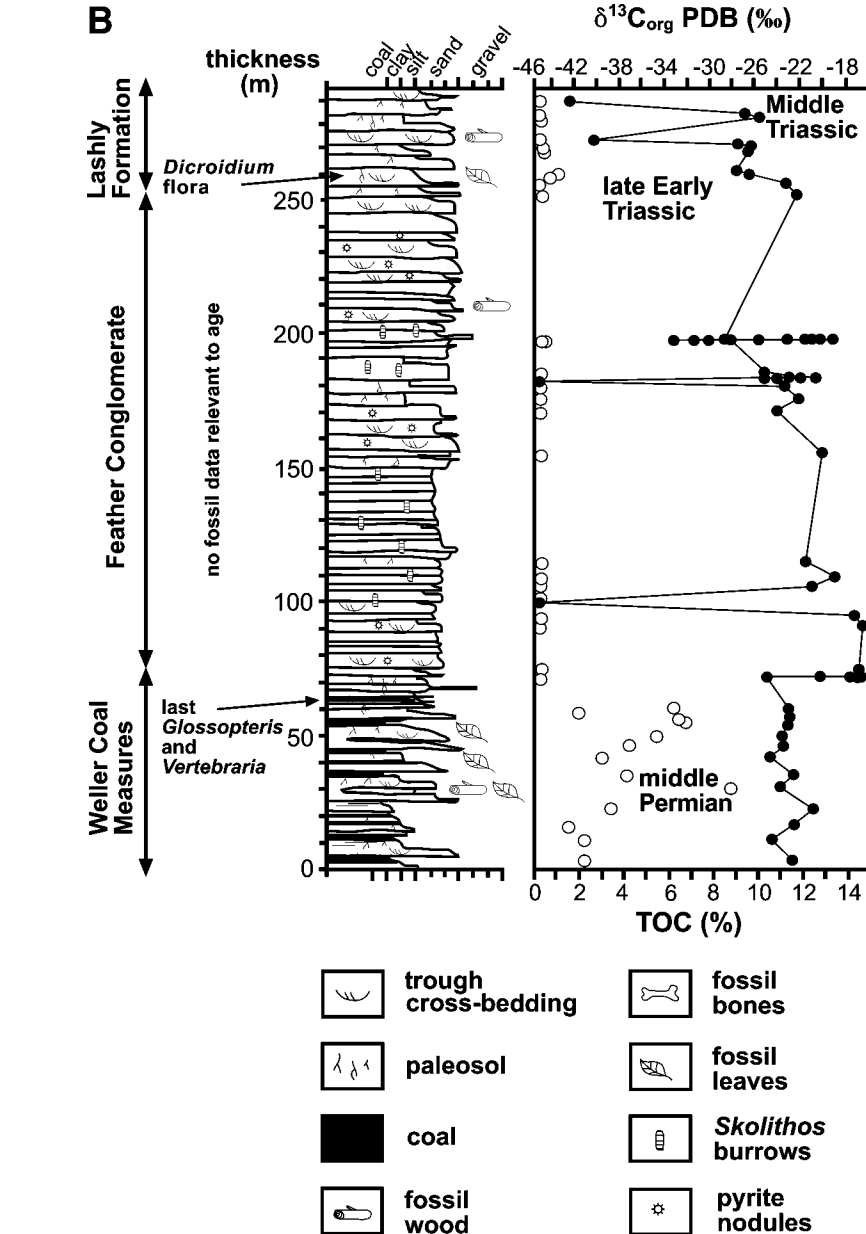


Figure 2. (Continued).

position processes, and only the resistant and refractory organic constituents are incorporated in the long-term organic carbon pool (Balascent and Mariotti, 1996). The TOC content in modern nonpeaty soils decreases abruptly from the litter and O horizon (10%–40%) to the A horizon (1%–5%) and B horizon (~1%) and approaches a constant value in the C horizon (<1%) (Stevenson, 1969; Huang et al., 1996). Exceptions are Histosols (soils developed from peat, containing >50% by weight organic matter), where decomposition of organic matter has been impeded and much of the original carbon content is preserved (Stevenson, 1969).

In modern soils systematic $\delta^{13}\text{C}$ depth trends have been suggested to be governed either by vegetation change of C_3 versus C_4 plants or by different rooting depths under a mixed C_3 and C_4 vegetation (Kelly et al., 1991). However, isotopic data from soils developed under pure C_3 or C_4 vegetation also show systematic fractionation trends in $\delta^{13}\text{C}$ values with depth (Stout and Rafter, 1978; Nadelhoffer and Fry, 1988; Becker-Heidmann and Scharpenseel, 1986). Thus, $\delta^{13}\text{C}$ depth distributions are not necessarily a function of vegetation change, but are significantly controlled by decompositional processes. These include selective preservation of more resis-

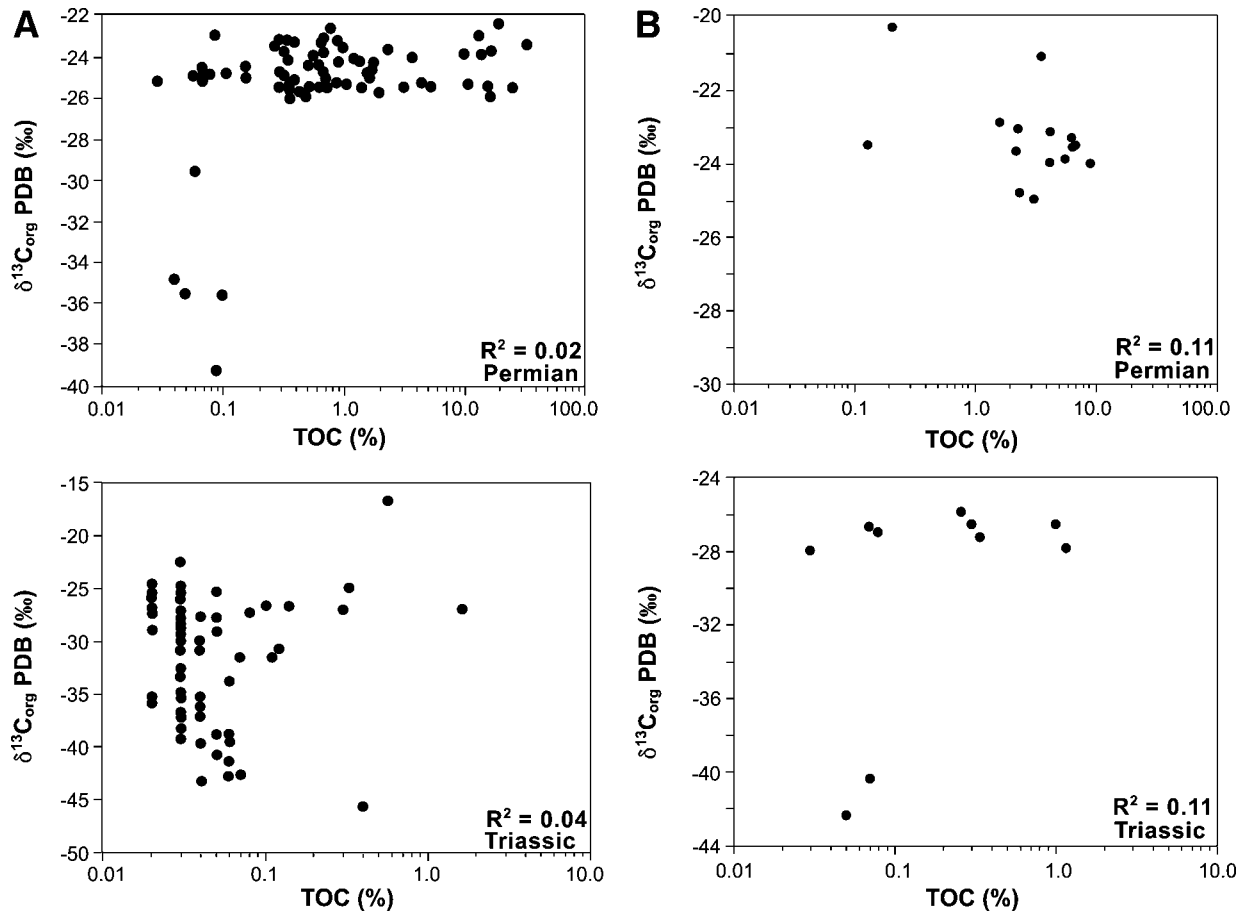


Figure 3. Cross plots of carbon isotopic values ($\delta^{13}\text{C}$ ‰; PDB—Peedee belemnite) and total organic carbon contents (TOC%) for (A) the Permian Buckley Formation and Triassic Fremouw Formation (Graphite Peak), and (B) the Permian Buckley Formation and Triassic Lashly Formation (Allan Hills).

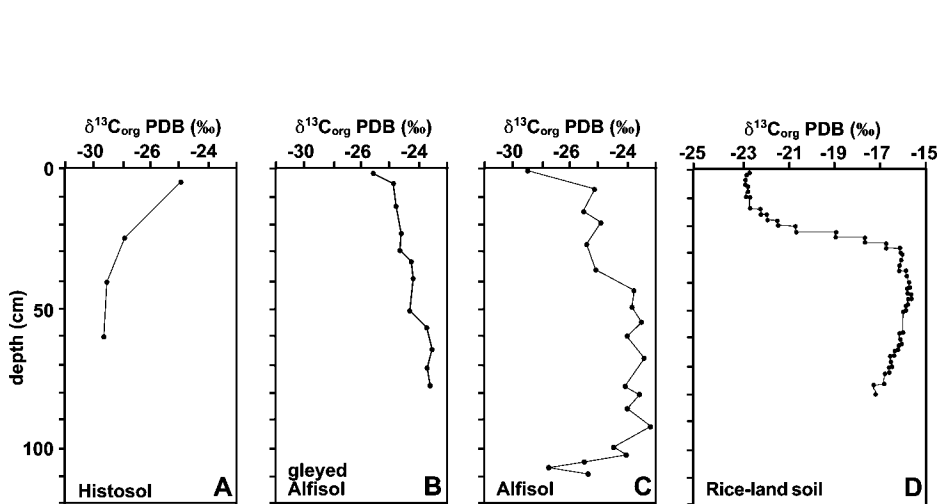


Figure 4. Examples of typical $\delta^{13}\text{C}$ (PDB—Peedee belemnite) depth profiles from modern soils. (A) A modern Histosol from New Zealand (modified from Stout and Rafter, 1978). (B) A modern gleyed Alfisol from northern Germany (modified from Becker-Heidmann et al., 1996). (C) A modern well-drained Alfisol from northern Germany (modified from Becker-Heidmann and Scharpenseel, 1986). (D) A modern rice-land soil at Los Banos, Philippines (modified from Neue et al., 1990).

tant macromolecules, microbial fractionation of organic matter, and addition of microbial biomass to the carbon pool. In addition, high clay content may enhance selective adsorption of the heavier isotope (Becker-Heidmann and Scharpenseel, 1986, 1992; Wedin et al., 1995; Balesdent and Mariotti, 1996; Huang et al., 1996). Isotopic depth trends in modern soils that are independent of vegetation changes can be divided into three distinct categories: (1) a $\delta^{13}\text{C}$ depth trend toward slightly lower values, (2) a uniform $\delta^{13}\text{C}$ depth trend, or (3) a $\delta^{13}\text{C}$ depth trend toward higher values.

Slight decreases in $\delta^{13}\text{C}$ values with soil depth are common for soils that are constantly waterlogged, such as peat-producing Histosols (Fig. 4A) (Stout and Rafter, 1978). The anaerobic conditions apparently produce the small variations in $\delta^{13}\text{C}$ values with depth and cause little microbial fractionation of original organic matter (Stout and Rafter, 1978; Deines, 1980; Stout et al., 1981). The occasional slight decrease in $\delta^{13}\text{C}$ values with depth in the order of 2‰–3‰ in peaty soils may arise

from preservation of isotopically more negative lignin compared with hemicellulose or cellulose (Deines, 1980; Benner et al., 1987; Boutton, 1996).

A uniform depth trend is characteristic for relatively young and poorly drained soils that undergo more fluctuating, less waterlogged conditions than Histosols (Stout and Rafter, 1978) (Fig. 4B). In these soils, the uniform $\delta^{13}\text{C}$ depth profiles are mainly the result of little time for soil formation and therefore limited decompositional fractionation, which is further impeded by partial waterlogging.

Pronounced $\delta^{13}\text{C}$ increases of as much as 5‰ with soil depth are the norm in mature, well-drained modern soils (Fig. 4C; Stout et al., 1981; Becker-Heidmann and Scharpenseel, 1986; Balesdent and Mariotti, 1996). Increases of as much as 7‰ are exceptional and have been found only in riceland soils, where carbon turnover rates are high and methanogenesis is pronounced (Fig. 4D; Neue et al., 1990). In soils other than rice-land soils, this systematic $\delta^{13}\text{C}$ increase from the A to the B horizon is attributed to a combination of biological and physical factors (Nadelhoffer and Fry, 1988; Becker-Heidmann and Scharpenseel, 1990; Balesdent and Mariotti, 1996). Aerobic conditions within the soil favor selective loss of $^{12}\text{CO}_2$ accompanying microbial degradation and fractionation, particularly in the subsurface horizon around the nutrient-rich rhizosphere and in the presence of clays (Martin and Haider, 1986). The abundant clays in the subsurface are also known to selectively bind ^{13}C (Mortland, 1986; Becker-Heidmann and Scharpenseel, 1986).

In many modern soils, a 1‰–3‰ return to more negative values in the lower B and C horizons has been observed. This $\delta^{13}\text{C}$ trend is mostly a function of the translocation of soluble, relatively young, and undecomposed organic substances down the profile (Becker-Heidmann and Scharpenseel, 1992; Balesdent and Mariotti, 1996).

$\delta^{13}\text{C}$ DEPTH DISTRIBUTION IN PALEOSOLS

Studies of depth distribution of stable carbon isotopes from paleosol organic matter must consider the possibility of vegetation changes. Fossil evidence for C_4 plants before the Tertiary is equivocal and it is considered unlikely that C_4 plants thrived at the high paleolatitudes of Antarctica with insufficient year-round illumination, low temperatures, and high precipitation (Retallack and Dilcher, 1988; Ehleringer et al., 1991). Therefore, microbial fractionation and clay content are con-

sidered the most important fractionation processes in Permian and Triassic paleosols.

In addition, interpretation of isotopic depth trends from paleosols has to consider possible isotopic changes shortly after burial. In non-peaty paleosols, TOC contents typically do not exceed 1 wt% and are often below 0.1%; however, a trend toward decreasing carbon content with depth analogous to modern soils is usually preserved (Krull, 1998; Bestland and Krull, 1999). Decomposition of organic matter after soil burial may influence $\delta^{13}\text{C}$ values (Balesdent and Mariotti, 1996). During this process, fractionation by anaerobic bacteria, increased contributions of bacterial cells at the expense of soil humus, and new formation of organic macromolecules is possible (Gong and Hollander, 1997; Harvey and Macko, 1997; Lichtfouse et al., 1998). Taking into account these potential postburial changes, several Permian and Triassic paleosol types are described and discussed with respect to their individual $\delta^{13}\text{C}$ depth trends. A summary of the studied Permian and Triassic paleosols is given in Table 1.

Late Permian Coaly Histosol

Histosols are organic-rich soils with thick peaty horizons that typically form in low-lying, swampy, and boggy areas with a shallow groundwater table. Permian Histosols contain abundant chambered roots of *Vertebraria*, fragments of the plant *Glossopteris*, and a thick coaly O horizon (Fig. 5; Table 1).

The $\delta^{13}\text{C}$ distribution in the type Permian Histosol (at 250 m, Fig. 2A) is relatively uniform (2.2‰ total variation); the average value is -24.8‰ , typical for C_3 vegetation. From the O horizon to the A and Bw horizons, the $\delta^{13}\text{C}$ values increase from -25.5‰ to -23.7‰ . The TOC contents decline with depth, from 25.6% to 0.3%.

These trends in $\delta^{13}\text{C}$ and TOC are similar to modern peaty soils. The relatively uniform isotopic values are most likely associated with a permanently high water table where decomposition by anaerobic bacteria is slow. Consequently, organic matter undergoes only minor compositional changes, preserving much of its original $\delta^{13}\text{C}$ value (Stout et al., 1975;

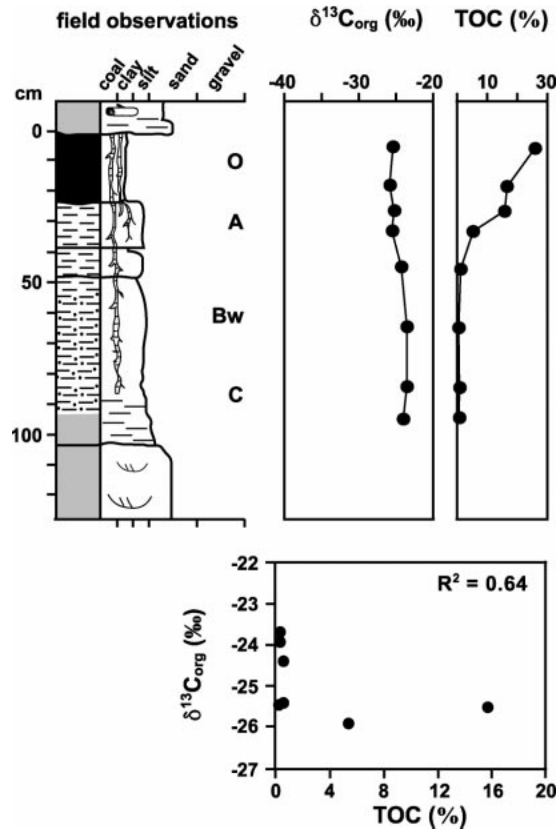


Figure 5. Carbon isotopic depth profile of a Permian Histosol, showing a typical uniform distribution of $\delta^{13}\text{C}$ values (PDB—Pee Dee belemnite) and decreasing total organic carbon (TOC) content with depth.

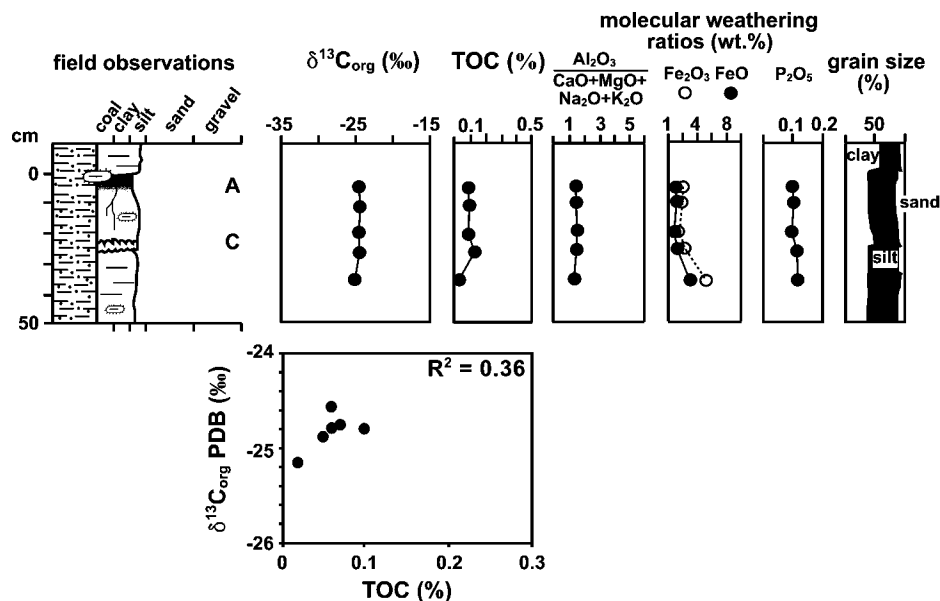


Figure 6. Carbon isotopic depth profile and bulk-rock geochemical data from a gleyed Permian Entisol, showing small $\delta^{13}\text{C}$ variation with depth. Gleying and low weathering rates are indicated by low ratios of $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ and alumina/bases, respectively. PDB—Pee Dee belemnite. TOC—total organic carbon.

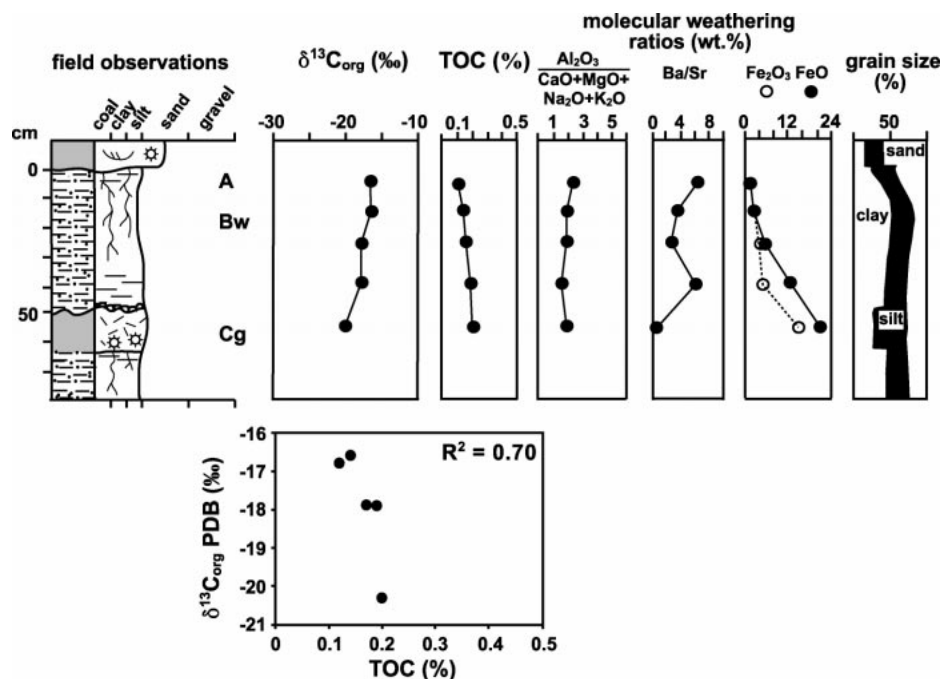


Figure 7. Carbon isotopic depth profile and bulk-rock geochemical data from a gleyed Triassic Inceptisol, showing decreasing values with depth. The relatively high $\delta^{13}\text{C}$ values may indicate the presence of CAM (Crassulacean acid metabolism) plants. PDB—Pee Dee belemnite. TOC—total organic carbon.

Nadelhoffer and Fry, 1988). The slight increase from the O to the Bw horizon is interpreted as a result of temporarily better drained conditions (Fig. 5). Periods of better drainage

would favor faster degradation by aerobic bacteria and consequentially would result in greater fractionation and enrichment in $\delta^{13}\text{C}$. Better drained conditions are also indicated by

deeply rooted *Vertebraria* roots, representing better aerated conditions that predated significant peat accumulation.

The significant TOC decrease with depth here is typical in modern soils due to decompositional processes and is expected to be preserved in paleosols as well (Stevenson, 1986). It is interesting that the $\delta^{13}\text{C}$ values do not follow this trend. The strong decline in TOC content and the uniformity of $\delta^{13}\text{C}$ values, as seen in the depth profile and cross-plot in Figure 5, suggest that $\delta^{13}\text{C}$ distributions with paleosol depth are not primarily controlled by TOC content.

Late Permian Entisols

Entisols are very weakly developed soils, typically developed on flood plains beneath plant communities early in ecological succession (Buol et al., 1989; Soil Survey Staff, 1997).

The type Permian Entisol (at 75 m, Fig. 2A) contains fossil plants of the horsetails *Phyllothea* and *Paracalamites* and is composed of thinly bedded, gray-green, chlorite-bearing tuffaceous siltstones (Krull, 1998) (Fig. 6; Table 1). Ratios of alumina to other base cations ($\text{Al}_2\text{O}_3/\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$) and $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ are low (Fig. 6). Carbon isotopic values average -24.8‰ and display minimal variation down the profile (0.6‰). The TOC content increases down the profile from 0.08% in the uppermost A horizon to 0.11% in the upper C horizon; there is no apparent correlation ($R^2 = 0.36$) between $\delta^{13}\text{C}$ and TOC values.

As in modern soils, greenish or grayish colors are indicative of the presence of reduced iron and suggest anaerobic conditions down the profile from temporary waterlogging (gleization) (Buol et al., 1989; Moore et al., 1992). Weathering and oxidation in gleyed soils is not pronounced, as indicated by low ratios of alumina/base cations and $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$. The uniform $\delta^{13}\text{C}$ values of this paleosol are typical for gleyed, weakly developed soils (Becker-Heidmann et al., 1996). Anaerobic conditions favor preservation of organic matter, which explains the slightly higher TOC contents with depth.

Triassic Inceptisol

Inceptisols are moderately developed soils that have modest clay accumulations in the B horizon (Birkeland, 1984; Buol et al., 1989). The degree of weathering, indicated by the ratio of alumina to base cations, is generally low (Birkeland, 1984). The type fossil Inceptisol

(at 70 m, Fig. 2B) is characterized by large chamosite (iron chlorite) nodules in the Cg horizon and abundant reduced iron species (Fe^{II+}) with depth (Fig. 7 and Table 1). The $\delta^{13}\text{C}$ values steadily decrease from the A to the Cg horizon, from -16.8‰ to -20.3‰ . The TOC content increases slightly down the profile. An apparent correlation between $\delta^{13}\text{C}$ and TOC is shown by an R^2 value of 0.7 (Fig. 7). However, this correlation is not thought to be meaningful, considering the scale of variation in TOC (0.07%) compared to the much larger variation of $\delta^{13}\text{C}$ values (3.5%).

As in the previous Entisol, poorly aerated soil conditions may have resulted from water-logging, which impeded weathering and decomposition of organic matter. Nonetheless, increased $\delta^{13}\text{C}$ values with depth indicate fractionation by bacterial decomposition and perhaps seasonally better drained conditions. Bacterial decomposition alone does not suffice to explain the relatively high isotopic values that average -19‰ . These values are too high for C₃ plants (modern average is -27‰) and too low to account for a flora dominated by C₄ plants with isotopic values ranging from -17‰ to -9‰ (average is -13‰) (Deines, 1980; Boutton, 1996). Although the observed value of -19‰ can be interpreted as a mix of C₃ and C₄ plants (Sikes, 1994), it is unlikely that C₄ plants existed at that time or at such high paleolatitudes. By comparison, CAM (Crassulacean acid metabolism) plants have $\delta^{13}\text{C}$ values intermediate between C₃ and C₄ plants (the range is -28‰ to -10‰) and could account for these values (Boutton, 1996).

Triassic Ultisol

Ultisols are well-developed, deeply weathered soils that commonly form below forest vegetation. These soils are characterized by a clay-enriched (Bt) horizon, strong weathering profiles, and base-depleted clays (Buol et al., 1989). The type fossil Ultisol (at 195 m, Fig. 2B) has abundant, thick, and deeply reaching root traces (Fig. 8; Table 1). Values for ratios of alumina/bases and Ba/Sr are relatively high. Clay accumulation is pronounced in the sub-surface horizon, as estimated from field observation and grain-size analysis (Fig. 8).

The type Ultisol paleosol profile has $\delta^{13}\text{C}$ values that average -25.8‰ . The $\delta^{13}\text{C}$ values increase markedly from -28‰ in the A horizon to -20‰ in the upper Bt and -19.4‰ in the lower Bt horizon. This isotopic trend corresponds with an increase in clay content and a decrease in organic carbon content. From the B to the C horizon, $\delta^{13}\text{C}$ values de-

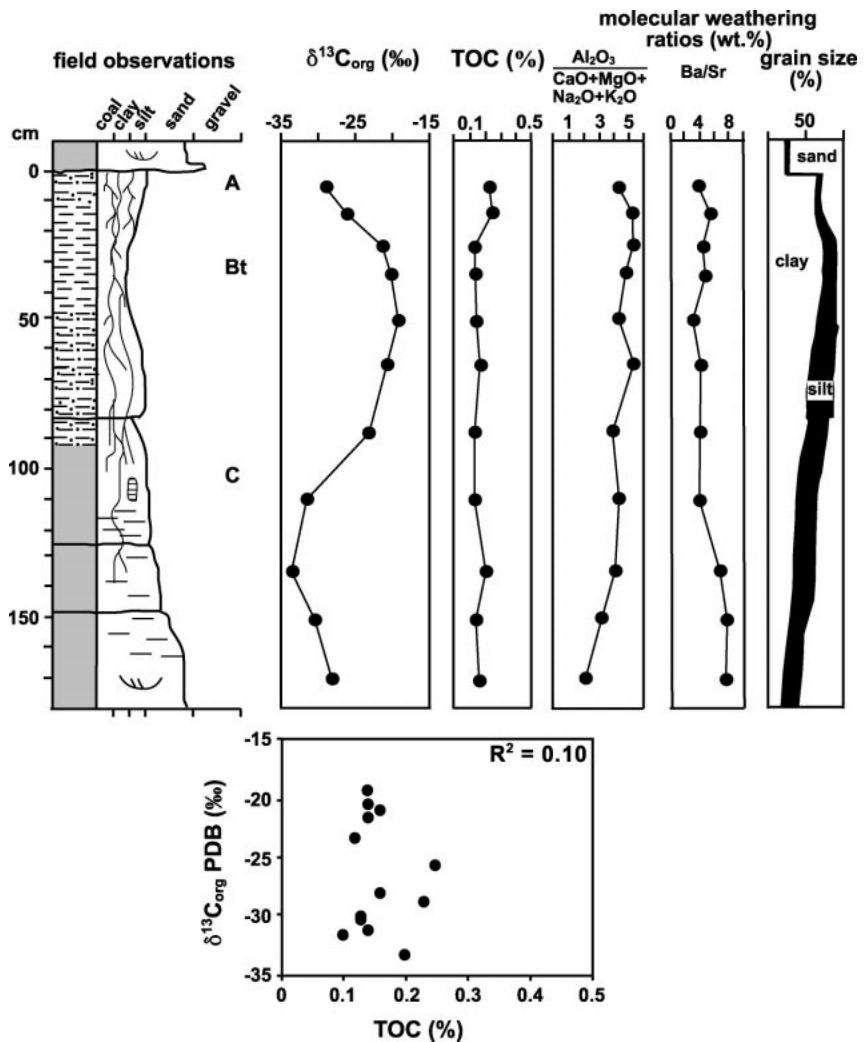


Figure 8. Carbon isotopic depth profile and bulk-rock geochemical data from a Triassic Ultisol, showing pronounced and systematic isotopic variation with depth. The $\delta^{13}\text{C}$ trend shows the classic isotopic curve of modern well-developed soils with ^{13}C -enrichment in the Bt horizon. The return to more negative $\delta^{13}\text{C}$ values in the C horizon is most likely due to translocation of relatively undecomposed carbon down the profile, analogous to translocation processes in modern soils. PDB—Peedee belemnite. TOC—total organic carbon.

crease from -21‰ to -33‰ and TOC values continue to decline. The overall isotopic variation within this profile is $>10\text{‰}$. There is no significant correlation ($R^2 = 0.1$) between $\delta^{13}\text{C}$ values and TOC content (Fig. 8).

Overall base depletion, high Ba/Sr ratios, and clay enrichment in the B horizon support the interpretation of this paleosol as a well-weathered Ultisol (Buol et al., 1989). The pronounced $\delta^{13}\text{C}$ trend toward higher values down the profile is comparable to $\delta^{13}\text{C}$ trends of well-developed, well-drained modern soils (Becker-Heidmann and Scharpenseel, 1990, 1992). Such an isotopic trend is interpreted as a combination of adsorption of the heavier isotope on clays and microbial fractionation

during decomposition (Balesdent and Mariotti, 1996). More negative values in the lowermost part of the paleosol may represent translocation of relatively unfractionated soil organic matter, analogous to modern soils (Becker-Heidmann and Scharpenseel, 1986, 1992).

Permian-Triassic Boundary Paleosols

The Permian-Triassic boundary at Graphite Peak has been previously identified paleontologically and has been confirmed in this study by both changes in paleosol types across the boundary and $\delta^{13}\text{C}$ chemostratigraphy (Retallack and Krull, 1999; Krull, 1998). The

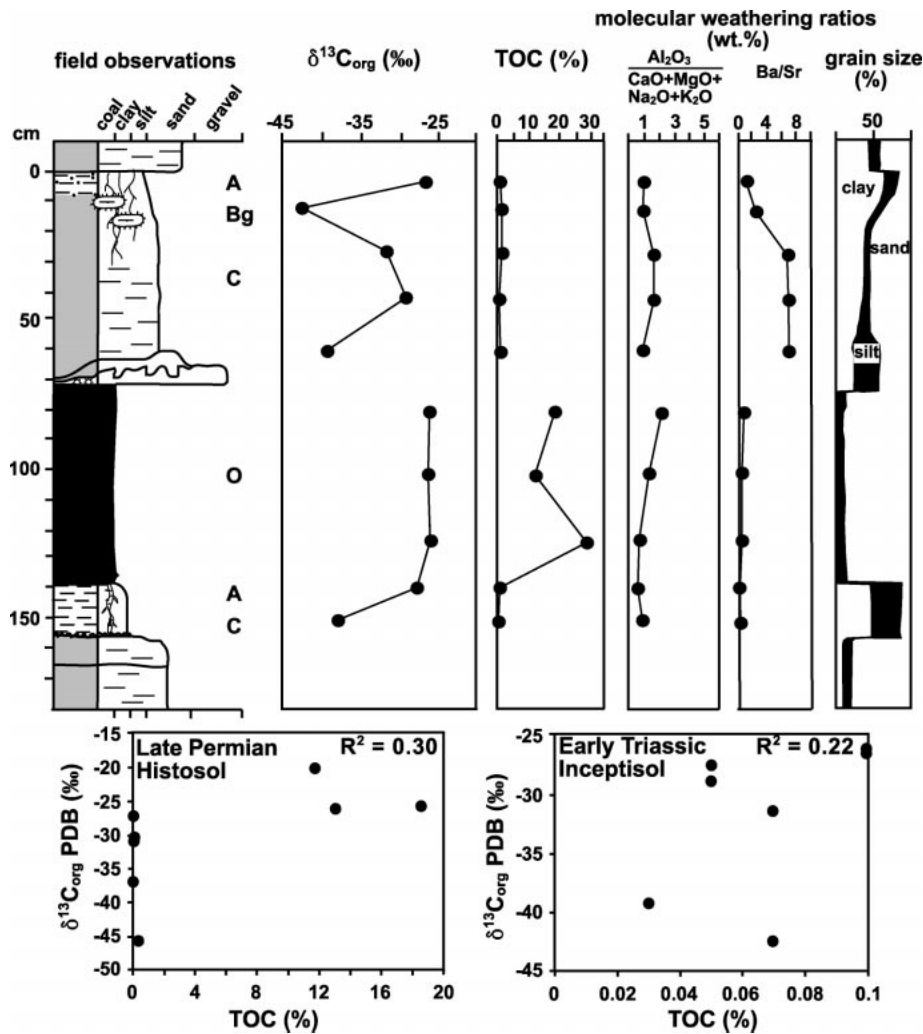


Figure 9. Carbon isotopic depth profiles and bulk-rock geochemical data from the Permian-Triassic boundary section, showing the last Late Permian Histosol, overlain by an Early Triassic Inceptisol. Unique in this profile is the rather large negative shift in the C horizon, already indicating changing organic carbon dynamics. The Early Triassic Inceptisol is characterized by strong ^{13}C depletion in the B horizon, unlike most $\delta^{13}\text{C}$ profiles in modern soils. PDB—Pee Dee belemnite. TOC—total organic carbon.

boundary sequence at Graphite Peak consists of a Late Permian coaly Histosol, directly overlain by an Early Triassic Inceptisol (at 256 m, Fig. 2A). No coaly Histosols are found in the Early Triassic, in agreement with the global coal gap of the Early Triassic (Retallack et al., 1996b). Similarly, the iron- and chlorite-rich Inceptisols, which are diagnostic of Early Triassic paleosol types, are absent in Permian strata (Retallack and Krull, 1999; Krull, 1998). The following description and discussion of carbon isotopic depth profiles from the boundary sequence illustrate the rapidly changing carbon dynamics from the Late Permian to the Early Triassic.

The last Late Permian paleosol is a fossil Histosol (Fig. 9). Little $\delta^{13}\text{C}$ variation (0.4‰)

occurs within the coaly O horizon. From the A to the C horizon $\delta^{13}\text{C}$ values decrease to -37.1‰ . This decrease of 10‰ is remarkable for Histosols, which typically have much less pronounced isotopic depth profiles (Stout et al., 1975). Such low $\delta^{13}\text{C}$ values are outside the range known for C_3 plants (Deines, 1980). This paleosol is further characterized by markedly declining TOC values from the O (20.8%) to the A (0.08%) and C horizons (0.04%), and generally low values of weathering ratios of alumina/bases and Ba/Sr. No significant correlation ($R^2 = 0.3$) was observed between $\delta^{13}\text{C}$ values and TOC content (Fig. 9).

The strong isotopic variation and the very low $\delta^{13}\text{C}$ values are unusual for modern and

fossil Histosols and contrast with the dominantly anaerobic conditions in Histosols that generally impede strong fractionation. Low ratios of alumina/bases and Ba/Sr indicate that weathering and leaching were not substantial in this paleosol. Overall, this paleosol displays a $\delta^{13}\text{C}$ depth profile that is not only uncharacteristic for Histosols, but also does not correspond with any documented $\delta^{13}\text{C}$ depth profile of modern soils.

The Early Triassic paleosol that directly overlies the Histosol has been classified as a fossil Inceptisol (Table 1; Fig. 9). This paleosol is characterized by a grayish-greenish A horizon and a gleyed B (Bg) horizon with iron-chlorite rich nodules. Carbon isotopic values are highly variable and have exceptionally low $\delta^{13}\text{C}$ values. An abrupt $\delta^{13}\text{C}$ decrease occurs from the A horizon (-26.5‰) to the iron- and chlorite-rich Bg horizon (-42.5‰). In the Bw horizon $\delta^{13}\text{C}$ values return to higher values of on average -30.2‰ and decrease again in the C horizon to -39.2‰ . The TOC contents are low throughout the profile but show a steady decrease from 0.1% in the A horizon to 0.07% in the B and 0.03% in the C horizons. No significant correlation ($R^2 = 0.2$) was observed between $\delta^{13}\text{C}$ values and TOC content (Fig. 9).

Insufficient drainage and a fluctuating water table are indicated by abundant minerals containing Fe^{II+} in nodules of the Bg horizon and low weathering ratios of alumina/bases. Under these gleyed conditions a relatively homogeneous $\delta^{13}\text{C}$ trend would be expected. By comparison, the observed $\delta^{13}\text{C}$ profile displays a large spread of $>10\text{‰}$. Only well-developed modern soils show pronounced isotopic variation with ^{13}C enrichment with depth. However, the depth trend in this Early Triassic Inceptisol is associated with lower $\delta^{13}\text{C}$ (^{13}C depleted) values in the B horizon instead of the expected ^{13}C enrichment. Furthermore, these low values of -42‰ in the Bg and C horizons clearly exceed the isotopic range that is commonly known for C_3 plants. These isotopic features have not been observed in modern soils; thus no modern analogues have been documented that could explain this $\delta^{13}\text{C}$ trend.

Other Early Triassic Paleosols

The distinct isotopic characteristics present in this Early Triassic Inceptisol of (1) large intraprofile variation of $\delta^{13}\text{C}$ values, (2) very low $\delta^{13}\text{C}$ values in the subsurface (B horizon), and (3) anomalously low $\delta^{13}\text{C}$ values to -40‰ , are found in other Early Triassic paleosol types as well (Table 1). For example, the isotopic depth profile in the Early Triassic

type Alfisol (at 380 m, Fig. 2A) is characterized by very low $\delta^{13}\text{C}$ values (average -36.5‰) and high variability of $>10\text{‰}$ (Fig. 10). From the A horizon to the Bt horizon, values decrease from -38.7‰ to an average of -40‰ . In the C horizon, $\delta^{13}\text{C}$ values increase to -30.6‰ . A weak correlation between $\delta^{13}\text{C}$ values and TOC content is suggested by $R^2 = 0.6$. Although, it is questionable whether a variation of 0.02% in TOC values can be considered significant (Fig. 10).

The Early Triassic type Entisol (at 260 m, Fig. 2A) is another example of these distinct Early Triassic $\delta^{13}\text{C}$ depth trends. In this paleosol, $\delta^{13}\text{C}$ values average -36.4‰ and show large intraprofile variations ($>10\text{‰}$) (Fig. 11). Isotopic values decrease from -35.3‰ in the A horizon to -39.0‰ in the Bw horizon. In the C horizon, $\delta^{13}\text{C}$ values increase to -28.0‰ . No significant correlation was observed between $\delta^{13}\text{C}$ values and TOC content ($R^2 = 0.3$) (Fig. 11).

ISOTOPIC ENIGMA

Large Isotopic Variation

Several paleosols investigated in this study show isotopic depth variations that are $>10\text{‰}$. In modern soils, isotopic variations seldom exceed 5‰ (Becker-Heidmann et al., 1996), except in rice-paddy soils (Fig. 4D; Neue et al., 1990) or when associated with a C_3/C_4 vegetation change. Such vegetation changes are known to impart large and abrupt isotopic depth trends on soils (Ambrose and Sikes, 1991; Kelly et al., 1991; Pessenda et al., 1996), but C_4 -like photosynthesis is undocumented for the late Paleozoic–early Mesozoic. Considering the unlikelihood of contribution from C_4 plants, most intraprofile variations are believed to be governed by factors other than vegetation change.

Many of the isotopic depth profiles presented here preserve gradual changes with depth, analogous to modern soils, but with a greater isotopic spread. It is interesting that Permian Histosols and weakly developed Permian Inceptisols do not display major shifts in $\delta^{13}\text{C}$ values with depth, but better developed paleosols do.

The more pronounced isotopic depth trends in paleosols compared with modern soils suggest that either soil fractionation processes were different then or that postburial fractionation processes had affected the original isotopic values. Possible causes for such large $\delta^{13}\text{C}$ variations are examined in the following discussion of the type fossil Ultisol (Fig. 8). This paleosol has a trend similar to that of

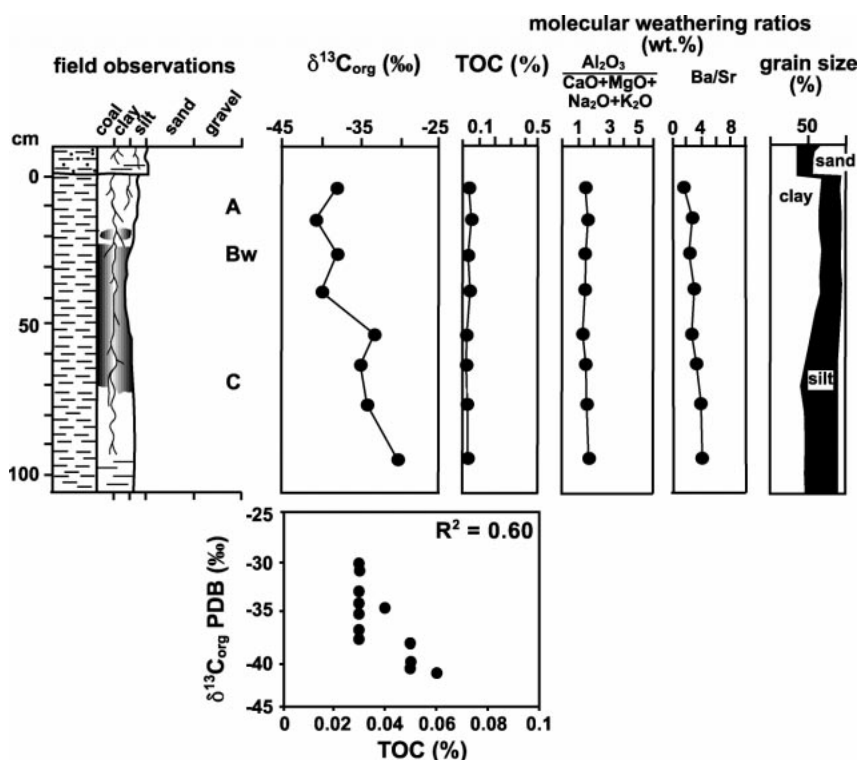


Figure 10. Carbon isotopic depth profile and bulk-rock geochemical data from an Early Triassic Alfisol, showing strong ^{13}C depletion in the B horizon. The distinctly negative $\delta^{13}\text{C}$ values and the reversed isotopic depth trend (of more negative values in the B horizon) point to significant diffusion of methane into the profile and fixation by methane-oxidizing bacteria. PDB—Pee Dee belemnite. TOC—total organic carbon.

modern well-developed soils, with increasing $\delta^{13}\text{C}$ values from the A to the B horizon and return to lower values in the C horizon. However, the large intraprofile $\delta^{13}\text{C}$ variation here is very different from the common $\delta^{13}\text{C}$ variation observed in modern soils.

The most negative $\delta^{13}\text{C}$ values in this paleosol occur in the A horizon (-28.9‰) and C horizon (-33.3‰) and the highest values are found in the lower Bt horizon (-19.3‰). The large increase of $\delta^{13}\text{C}$ values in the B horizon might be due to postburial fractionation. Postburial microbial decomposition within the B horizon may have resulted in increasingly degraded organic matter with high $\delta^{13}\text{C}$ values. With continued degradation, organic carbon in buried soils tends to become increasingly enriched in bacterial cells (necromass) which, due to their high resistance to further degradation, are selectively preserved, especially in the presence of clays (Lichtfouse et al., 1995a, 1995b; Gong and Hollander, 1997; Harvey and Macko, 1997; Hedges and Oades, 1997). The observed $\delta^{13}\text{C}$ trend suggests that B horizons that were subject to significant fractionation processes during pedogenesis are particularly susceptible to further postburial

fractionation. This is consistent with the observation that paleosols with little pedogenic modification, such as Histosols or weakly developed Permian Entisols, have small isotopic variations.

^{13}C -Enriched Values

The $\delta^{13}\text{C}$ values higher than typical for C_3 plants occur in several paleosols of the Feather Conglomerate of Middle Triassic age (Figs. 2 and 7). These gleyed Inceptisols probably formed under partially waterlogged conditions. The relict bedding suggests only weak colonization by plants (Table 1). The $\delta^{13}\text{C}$ values with depth are fairly uniform and average -17.9‰ . This isotopic value is well outside the average of pure C_3 (-27‰) and pure C_4 (-13‰) plants, but within the range of CAM plants (Deines, 1980).

The ^{13}C enrichment in this paleosol could be produced by the colonization of aquatic CAM plants, such as *Isoetes*. Evidence that the CAM photosynthetic pathway was well established during the late Mesozoic has been documented isotopically and paleobotanically from fossil plants of the latest Cretaceous

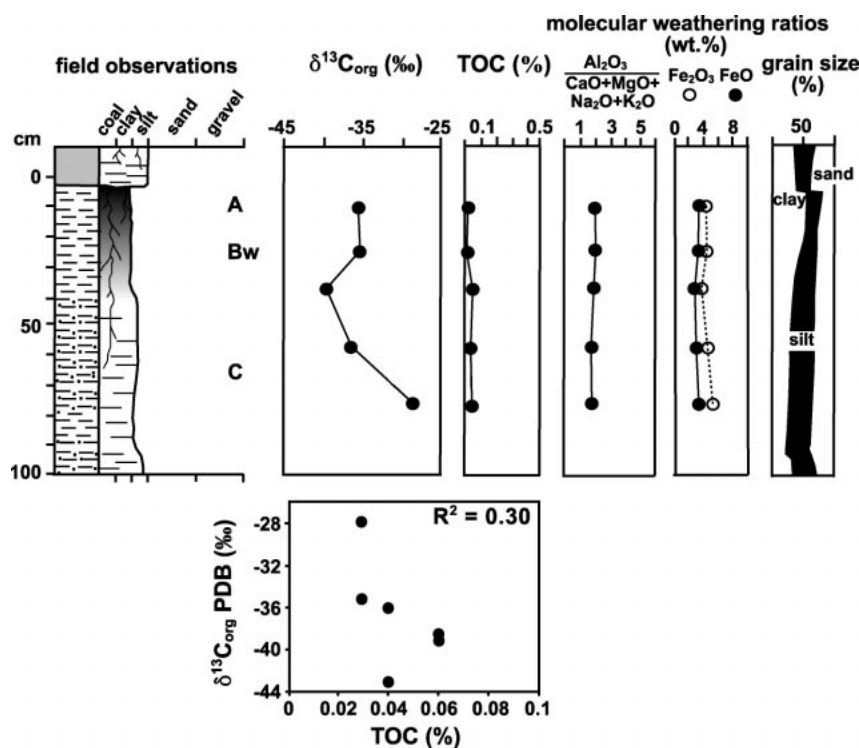


Figure 11. Carbon isotopic depth profile and bulk-rock geochemical data from an Early Triassic Entisol, displaying the anomalous isotopic depth trend and very negative values common to other Early Triassic paleosols of this study. PDB—Peedee belemnite. TOC—total organic carbon.

(Bocherens et al., 1993). Living aquatic plants such as the primitive spore-bearing *Isoetes*, as well as some monocots (Poaceae) and dicots (Crassulaceae and Plantaginaceae) are known to use the CAM photosynthetic pathway (Keeley, 1990). Fossil species of *Isoetes* and allied plants have been reported from numerous localities in Early Triassic paleosols of Australia, South Africa, Argentina, and India (Retalack, 1997).

¹³C-Depleted Values

Early Triassic paleosols show anomalously large isotopic variation with extremely depleted values, usually in the subsurface horizons. Isotopic values as low as -35‰ have been observed in leaves of tropical rainforests (Jackson et al., 1993). This occurs when CO_2 is assimilated from ¹³C-depleted soil respiration. Biochemical fractions such as lipids can be depleted in $\delta^{13}\text{C}$ by as much as 8‰ (average depletion is 5‰) relative to the whole plant (Deines, 1980). Individual lipid compounds (biomarkers) may be depleted by 9‰ or more relative to bulk soil carbon (Lichtfouse et al., 1995b; Huang et al., 1996). Biomarkers of bacterial origin (hopanoids) with

$\delta^{13}\text{C}$ values lower than -40‰ have been reported from Eocene lake sediments and have been associated with methane recycling by methanotrophic bacteria (Hayes et al., 1987; Freeman et al., 1990). Unfortunately, compound-specific isotopic analysis of biomarkers does not provide conclusive evidence for predominance of certain bacterial populations in former sedimentary organic matter. Damsté and Schouten (1997) demonstrated that in most of these biomarker studies, bulk $\delta^{13}\text{C}$ values are not significantly influenced by the presence of isotopically depleted biomarkers. Instead, the bulk $\delta^{13}\text{C}$ values of these studies show values typical of C_3 plants, suggesting that the contribution of individual bacterial compounds to the bulk isotopic signature is small. Therefore, only in cases where the $\delta^{13}\text{C}$ values of bulk organic matter show significant depletion can it be concluded that a large fraction of the organic matter is derived from methanotrophic processes (Perry Burhan et al., 1995; Holland, 1997).

Global occurrence of such highly depleted carbon isotopic values in Earth's history is rare. The only other time in Earth's history when $\delta^{13}\text{C}$ values as low as the ones in these Early Triassic paleosols are detected globally

was during a brief interval of the Precambrian (Hayes et al., 1983; Hayes, 1994; Holland, 1997). Pronounced excursions with $\delta^{13}\text{C}$ values as low as -60‰ occurred worldwide at the Archean-Proterozoic transition, ca. 2.75–2.5 Ga. These low $\delta^{13}\text{C}$ excursions during the Archean-Proterozoic transition are interpreted as marking the onset of widespread methanotrophy (methane oxidation). Methanogenesis is thought to have been ubiquitously present during the Archean. However, prior to onset of methanotrophy, the isotopic signature of methanogenic fractionation could not be effectively recorded due to the lack of conversion from gaseous to solid matter (Hayes, 1994). Thus, the evolution of methanotrophic bacteria allowed for oxidation of methane and incorporation of the ¹³C-depleted carbon from methanogenesis in the geologic organic carbon isotopic record (Hayes, 1994).

Today, methanotrophic bacteria are abundant in a variety of ecosystems, occurring wherever oxygen and methane occur in close proximity such as in soils, oxic and anoxic sediments, freshwater and marine systems, and plant tissues (King, 1992; Hanson and Hanson, 1996). Most methanotrophs are aerobic or facultative anaerobic bacteria that oxidize atmospheric methane within oxic-anoxic interfaces. Due to their ubiquity, they play an important role in uptake of atmospheric methane and in the biosphere-climatic feedback system (Priemé and Christensen, 1997; Saari et al., 1997). Methanotrophic bacteria are particularly abundant in mid-latitude forest soils. Here, the source of methane is not from below-ground methanogenesis, but from diffusion of atmospheric methane into the soil, where it is oxidized in the subsurface. At sufficiently high methane concentrations, fractionation against the heavier ¹³C isotope can be as much as 20‰ (Coleman et al., 1981; Alperin et al., 1988; Tyler et al., 1994). Thus, the residual methane compared with the source methane is ¹³C enriched, whereas the respired CO_2 and bacterial cells of methanotrophs become extremely depleted in ¹³C, down to $\delta^{13}\text{C}$ values of -60‰ (Borowski et al., 1997; Boschker et al., 1998; Jahnke et al., 1999). Although widespread in modern soils, methanotrophy is not dominant enough to significantly alter the $\delta^{13}\text{C}$ signature of bulk soil organic matter. Consequently, to preserve a methanotrophic signature in Early Triassic paleosol organic matter, two processes are necessary. First, atmospheric methane levels must have been high enough to sustain a large population of methanotrophic bacteria. Second, postburial decomposition degraded much of the soil organic matter and preserved the more

refractory bacterial organic matter, such that its contribution dominates the bulk $\delta^{13}\text{C}$ record.

IMPLICATIONS FOR THE PERMIAN–TRIASSIC BOUNDARY

The negative $\delta^{13}\text{C}$ shift from the Late Permian to the Early Triassic has been interpreted as a chemostratigraphic marker of the Permian–Triassic boundary (Erwin, 1993; Morante, 1996). In our Antarctic sections $\delta^{13}\text{C}$ values decrease on average 7‰ from Late Permian to Early Triassic paleosols (Fig. 12). Comparably large isotopic shifts have also been reported from terrestrial sediments from Australia and South Africa (Morante, 1996; MacLeod et al., 1997). Due to continuous carbon exchange between the atmosphere–hydrosphere–biosphere system, such low values have been interpreted as evidence of a ^{13}C -depleted Early Triassic atmosphere (Erwin, 1993).

An atmospheric isotopic shift of this magnitude is most likely explained by an increased flux of ^{13}C -depleted methane (Erwin, 1993). Its preservation in the organic carbon isotopic record was probably achieved by bacterial methane oxidation. Previous hypotheses of large methane releases across the Permian–Triassic boundary involved destabilization of clathrates, possibly associated with a meteorite impact, or methane release from continental shelf deposits during the Late Permian regression (Erwin, 1993; Bowring et al., 1998).

The duration of the isotopic shift across the Permian–Triassic boundary, which is necessary to model the volume of carbon involved, is more difficult to estimate. Earlier studies based on paleontological evidence estimate the excursion to have lasted 1–3 m.y. (Holser et al., 1989; Magaritz, 1989), suggesting an isotopic recovery lag throughout the Scythian, analogous to the recovery lag in the fossil record (Erwin, 1993). More recent studies based on sedimentation rates (Wang et al., 1994) and U/Pb zircon geochronology in China (Bowring et al., 1998) estimate a much shorter duration of the isotopic excursion, lasting only 50–150 k.y. The estimates by Bowring et al. (1998) proved to be controversial, as follow-up studies produced different results, suggesting a significantly longer duration (Mundil et al., 1999). Thus, estimates of the duration of the Permian–Triassic boundary are equivocal and await further documentation.

The Permian–Triassic $\delta^{13}\text{C}$ shift is comparable to a similar isotopic event in the late Paleocene, for which a catastrophic, short-term methane release has been hypothesized

(Dickens et al., 1997; Bains et al., 1999; Katz et al., 1999). For an estimated duration of 10 k.y. and an isotopic shift of 2‰–3‰, the amount of methane necessary is $\sim 1.4\text{--}2.8 \times 10^{18}$ g. If the methane was derived from clathrates, this amount would correspond to $\sim 14\%$ of the present-day reservoir (using estimates of Kvenvolden, 1993).

In the case of the Permian–Triassic boundary, a more sustained or repeated methane flux would be required, even when using the conservative estimates by Bowring et al. (1998). Evidence for a prolonged (but possibly highly variable) methane release is supported by the unusual $\delta^{13}\text{C}$ depth distribution in Early Triassic paleosols (^{13}C depletion in the subsurface horizon and very low values). A short-term (hundreds to thousands of years) methane release would result in rapid oxidation to ^{13}C -depleted CO_2 due to the brief residence time of methane (10 yr; Khalil and Rasmussen, 1990). Therefore, a short-term (tens of thousands of years) release would not produce the evidence for increased methanotrophy as seen in several paleosols (Fig. 2A). Instead, the preservation of these anomalous depth trends and occurrence in numerous paleosols throughout the Early Triassic suggests that methane release must have been pronounced enough to support increased methanotrophic activity over a long period of time, and must have occurred as multiple events, because paleosol profiles with normal values occur between the ^{13}C -depleted events (Fig. 2A).

An explanation for such a long-term release of methane has to involve an efficient trigger mechanism as well as a positive feedback system. The marine regression during the Changxingian stage would have substantially lowered hydrostatic pressure in shelf environments and could have led to initial clathrate destabilization and methane release. This would have led to the first pulse of ^{13}C -depleted methane and the onset of an increase in greenhouse gases (CH_4 and CO_2). Additional greenhouse gases such as CO_2 and H_2O from the eruption of the Siberian Traps during the latest Changxingian stage (250 ± 0.2 Ma) may have furthered paleoclimatic warming (Erwin, 1993; Renne et al., 1995; Bowring et al., 1998). In response to this warming trend, clathrates in the polar regions could have become increasingly unstable, resulting in a second pulse of ^{13}C -depleted methane (Krull, 1999; Krull et al., 2000). This additional release of methane and CO_2 would further add to greenhouse warming and generate a positive feedback cycle of clathrate destabilization and global warming. This continued, but prob-

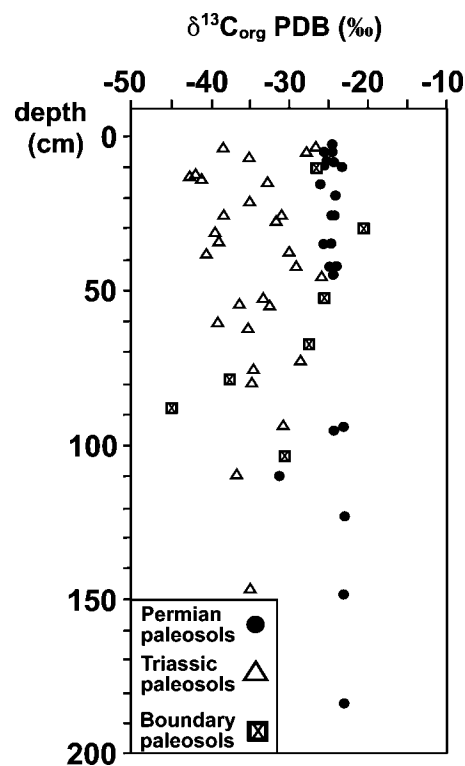


Figure 12. Isotopic depth profiles of paleosols from Graphite Peak, showing an average offset of $\sim 7\text{‰}$ in $\delta^{13}\text{C}$ values between Permian and Triassic paleosols. PDB—Pee-dee belemnite.

ably highly variable, supply of methane to the Early Triassic atmosphere probably accounts for the low $\delta^{13}\text{C}$ values of paleosol organic matter observed in this study.

CONCLUSIONS

From our study of $\delta^{13}\text{C}$ trends of paleosol organic matter across the Permian–Triassic boundary, the following conclusions can be drawn.

1. Organic carbon isotopic values from Permian and Triassic paleosol depth profiles can preserve an original pedogenic signature analogous to modern soils.
2. Paleosols associated with severe perturbations of the global carbon cycle (as in the Early Triassic) yield isotopic depth profiles of greater $\delta^{13}\text{C}$ variation, more extreme values, and depth trends without modern analogs.
3. The extreme negative isotopic values and the ^{13}C depletion in the B horizon of Early Triassic paleosols are interpreted as a result of methanotrophic activity during a prolonged methane release during the Early Triassic.

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