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The land plant δ^{13}C record and plant evolution in the Late Palaeozoic

Wolfgang Peters-Kottig [a,1], Harald Strauss [a,*], Hans Kerp [b]

[a] Geologisch-Paläontologisches Institut, Westfälische Wilhelms-Universität, Corrensstr. 24, 48149 Münster, Germany
[b] Forschungsstelle für Paläobotanik, Westfälische Wilhelms-Universität, Hindenburgplatz 57, 48143 Münster, Germany

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Abstract

Based on the evaluation of 1323 carbon isotope values for Silurian to Permian terrestrial organic carbon, measured on plant fossils, cuticules, humic coals and bulk terrestrial organic matter (TOM), we conclude that the temporal trend in $\delta^{13}C_{TOM}$ records variations in the global carbon cycle, notably an increase in the fractional burial of light (terrestrial) organic matter in Late Palaeozoic sediments. $\delta^{13}C_{TOM}$ values suggest that the Late Palaeozoic pO_2 peak could have been restricted to a time frame of ~40 Ma. Carbon isotope data from four taxonomic groups reveal small differences that could be a consequence of habitat conditions. No significant differences in organic carbon isotopic composition in relation to variable climatic conditions are discernible. The carbon isotopic composition solely reflects C_3 plant metabolism.

Keywords: Palaeozoic; C-13/C-12; Organic carbon; Terrestrial; pO_2

1. Introduction

The last decade has witnessed an increasing number of studies related to early land plant evolution, its effect on the cycling of carbon and hence on the climatic history of the earth during Palaeozoic time (Gensel and Edwards, 2001; Hemsley and Poole, 2004). Scholle and Arthur (1980); cited in Robinson and Hesselbo (2004) were among the first to address that shifts in the carbon isotopic composition of marine carbonate carbon should be detectable in land plant organic matter due to the geochemical link of the marine and terrestrial realms via atmospheric carbon dioxide. Since then, the $^{13}C/^{12}C$ ratio of fossil plant remains and bulk terrestrial organic matter (TOM) has been used as a proxy for reconstructing carbon cycle dynamics, palaeoecological and palaeoclimatological conditions (Bocherens et al., 1993; Jones, 1994; Faure and Cole, 1999; Nguyen Tu et al., 2002; Gröcke, 2002; Beerling and Royer, 2002; Hesselbo et al., 2003; Berner, 2004) or as a tool for chemostratigraphic correlation (Gorter et al., 1994; Stott et al., 1996; Hansen et al., 2000; Sephton et al., 2002; Ando et al., 2002; Hasegawa, 2003; Heimhofer et al., 2003; Robinson and Hesselbo, 2004).

The aim of our present study was to investigate whether long term shifts and possibly short term variations can be found in land plant organic matter. Additionally we checked isotope variations due to gross climatic conditions and differences related to plant groups.

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* Corresponding author. Tel.: +49 251 833 3932; fax: +49 251 833 3933.

E-mail addresses: kottigw@uni-muenster.de (W. Peters-Kottig), hstrauss@uni-muenster.de (H. Strauss), kerp@uni-muenster.de (H. Kerp).

[1] Present address: August-Schlüter-Str. 35, 48249, Dülmen, Germany.

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The Late Palaeozoic was a time of profound geological changes, notably the rapid colonization of terrestrial environments by land plants since the Silurian, a change from greenhouse conditions in the Silurian–Devonian to icehouse conditions in the Permo-Carboniferous, and the final assembly of the Supercontinent Pangea in the Permian. The rise of land plants (as a new carbon sink) removed the greenhouse gas CO_2 from the atmosphere and potentially ushered in the Carboniferous-Permian glacial episode (e.g. Kump et al., 2000; Beerling and Berner, 2005). The evolutionary innovations that caused the increased storage of CO_2 did not appear prior to the Devonian, although the first significant evidence of embryophytes occupying land is from the Middle Ordovician, and the earliest occurrence of vascular plants is Middle Silurian (Gensel and Edwards, 2001; Wellman et al., 2003). These innovations include the production of lignin since the Early Devonian (Boyce et al., 2003a) and the evolution of wood since the Middle Devonian (Rowe, 2000). Wood containing the biopolymer lignin is resistant to biodegradation. Reduced decomposition contributed to increased carbon storage in terrestrial sinks.

The evolution of the carbon isotopic composition of terrestrial organic matter in context with the coeval spread of plant ecosystems is reviewed in this study.

2. Samples and methods

Here we examine the $\delta^{13}C_{TOM}$ values of 1323 Late Silurian to Late Permian samples from terrestrial successions collected from >200 localities from a variety of sedimentary basins. 617 of these isotope data have been taken from the literature (Maass et al., 1975; Redding et al., 1980; Botz and Müller, 1981; Maynard, 1981; Hatch et al., 1984; Schwarzkopf and Schoell, 1985; Wenger et al., 1988; Kotarba, 1990; Jones, 1994; Gorter et al., 1994; Morante et al., 1994; Faure et al., 1995; Mora et al., 1996; Yapp and Poths, 1996; Lecuyer and Paris, 1997; Ader et al., 1998; Krull, 1998; Elick, 1999; Faure and Cole, 1999; Mastalerz et al., 1999; Hansen et al., 2000; Montañez et al., 2000; Ghosh et al., 2001; Korte et al., 2001; Beerling, 2002; Beerling et al., 2002; Boyce et al., 2003a; Kotarba and Clayton, 2003; Tabor et al., 2004). The great majority of samples originate from foreland basins in the vicinity of the Variscan orogen or from intramontane basins in the remnants of the Caledonian and Variscan mountain belts. Additionally, many measurements represent plant remains from diverse terrestrial successions of Gondwana. It is well known that age assignments of Palaeozoic terrestrial sediments are extremely problematic compared to the marine realm and that the Palaeozoic fossil record continues to remain fragmentary. Bearing this in mind we have chosen a compromise between number of samples and age uncertainties. Samples/localities with a maximum error of stratigraphic age determination of ±10 Ma were considered for this study. Fig. 1 illustrates that the error of age determination for the majority of samples is well below 10 Ma (mean error of age for all samples is ±1.4 Ma). We used the Stratigraphic Table of Germany (Menning and German Stratigraphic Commission, 2002) as the basis for assigning numerical ages due to its detailed age calibration and a wide variety of local, regional and global reference scales for stratigraphic correlation between different successions. System boundaries are defined as follows: Silurian–Devonian 417.5 Ma, Devonian–Carboniferous 358 Ma, Carboniferous–Permian 296 Ma, Permian–Triassic 251 Ma.

A total of 706 samples were collected from a variety of terrestrial (mainly fluvial-limnic) successions spanning the time frame from the early Wenlockian (Silurian) to the Permian-Triassic boundary. Four different kinds of fossil plant material (humic coal, cuticles and coalified tissue from compression fossils, bulk organic matter) were processed using standard chemical preparation techniques (e.g., Strauss et al., 1992). Coal samples and coalified tissue picked from compressional fossils were pulverized and immersed in 20% HCl in order to remove carbonate minerals. Cuticles and small pieces of coalified tissue could be handpicked from kerogen concentrates after repeated treatment of whole rock samples with 48% HF and 20% HCl. All residues were carefully rinsed in deionized water several times until neutrality was reached and dried at 40 °C. Bulk rock samples containing finely dispersed organic matter were pulverized, decarbonated with HCl, rinsed and dried.

Measurements of the carbon isotope ratios of coals, cuticles and coalified tissue were performed using a coupled Carlo–Erba elemental analyzer Thermo Quest Finnigan DELTA^{plus} isotope ratio mass spectrometer. Bulk rock samples were further processed using the sealed tube combustion method (Strauss et al., 1992). Pulverized and decarbonated sample material was sealed in a quartz glass tube under vacuum together with CuO and combusted at 850 °C over 5 h. Liberated CO_2 was cryogenically purified, sealed in 6 mm pyrex tubes and introduced offline into the mass spectrometer. Replicate measurements yielded a precision of 0.3‰ (2σ). Isotopic compositions were measured against internal standards and are reported in the standard δ-notation as per mil (‰) deviation from VPDB.

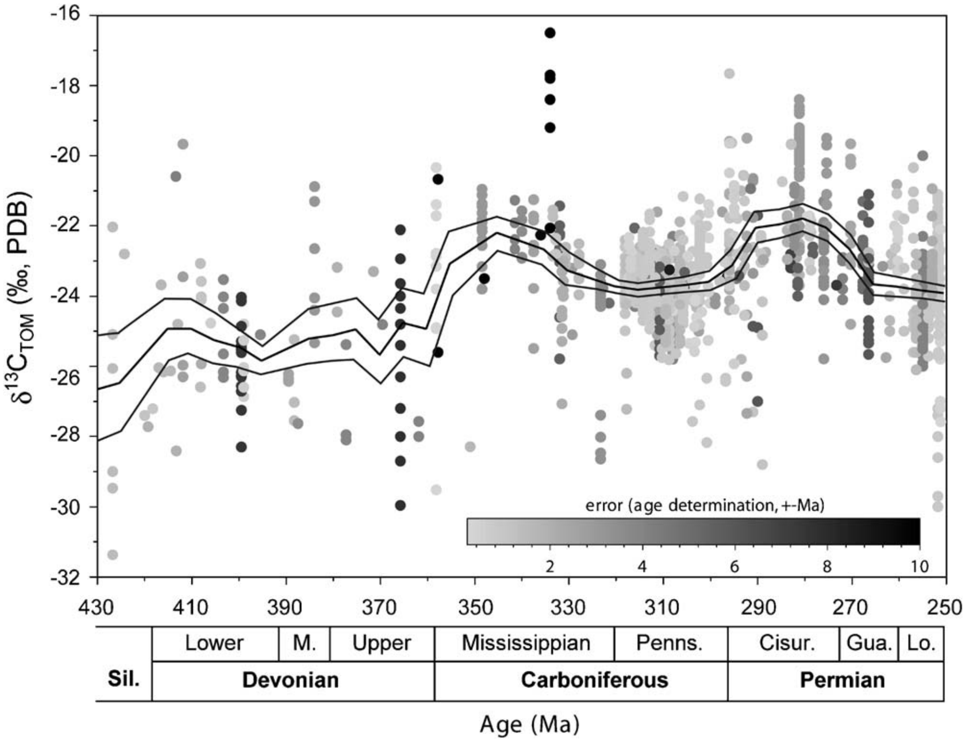

Fig. 1. Terrestrial organic carbon isotope record for the Late Palaeozoic. Gray shading of data points illustrates error of stratigraphic age determination. The center solid line is the moving average based on 20 Ma window and 5 Ma forward step. 95% confidence interval is shown by the two outer solid lines.

2.1. The effect of diagenesis and sample treatment on carbon isotope values

The optimal way to address variations in $\delta^{13}C_{TOM}$ related to plant evolution and/or changes in climate would be through detailed molecular analysis via GC-MS/IRMS (e.g., Poole et al., 2004). The problem inherent in this approach is artifacts caused by laborious processing of the sample material. Additionally, only selected organic compounds (such as long-chain *n*-alkanes) survive the advanced degree of sediment diagenesis and thermal degradation which characterize many Palaeozoic sediments.

We have chosen an alternative approach by analyzing the bulk isotopic composition of different types of organic matter (coal, cuticles, coalified tissue from compression fossils, bulk organic matter). An essentially random selection of a large number of samples from different sources substantially decreases the likelihood of misinterpretations based on extreme individual results from a certain typed habitat. Hence, we feel that the obtained conclusions are valid.

It is widely known that during early diagenesis plant organic matter is subject to chemical variation with each moiety having its own $\delta^{13}C$ signature which can affect the average isotopic composition of plant remains (Hedges et al., 1985; Benner et al., 1987; Hayes, 2001; Van Bergen and Poole, 2002). Late diagenetic and metamorphic processes are known to potentially alter the isotopic composition of fossil organic matter (Hoefs and Frey, 1976; Monin et al., 1981). Recent studies suggest a rather complex and sometimes contradictory relationship between the chemical modification of original organic compounds during early diagenesis and concurrent alteration of $\delta^{13}C_{TOM}$. The actual amount and direction of isotopic shifts due to modification and destruction of organic moieties is apparently more complicated than initially envisaged (Tyson, 1995). A number of studies have been conducted which attempt to simulate natural alteration processes by laboratory experiments that apply chemical and thermal catalysis of "modern" or subfossil plant material. Schleser et al. (1999) found that the $\delta^{13}C$ of wood samples heated in a sealed tube filled with water initially decreased and subsequently increased. Maximum isotopic change after several months of heating at 180 °C was 1‰. Lehmann et al. (2002) conducted a series of oxic and anoxic incubation experiments of lacustrine particulate organic carbon and recorded a decrease in $\delta^{13}C$ value by 1.6‰. In a study by Fernandez et al. (2003), changes in the $\delta^{13}C$ value of solids at successive stages of biodegradation showed enrichment in ^{13}C followed by decrease and final increase.

Researchers investigated the effects of artificial coalification under controlled laboratory conditions as a simulation of thermal alteration. Experimental laboratory burns of C_3 and C_4 vegetation conducted by Turekian et al. (1998) revealed a minor enrichment in ^{13}C for temperatures up to ~230 °C. Jones and Chaloner (1991) also recorded a slight increase in $\delta^{13}C$ (0.5‰) in wood at temperatures of up to 150 °C. This was followed by a decrease in $\delta^{13}C$ values of 1‰ at temperatures of up to 600 °C. Similar results were found by Czimczik et al. (2002) and Poole et al. (2004) who also noted initial increases in $\delta^{13}C$ values followed by decrease of up to 1.4‰ and 2‰ at higher temperatures (~500 °C).

With respect to a possible alteration of the original isotopic composition of plant remains from the Palaeozoic it is utterly impossible to differentiate between taphonomic/early diagenetic effects and late diagenetic alteration resulting mainly from thermal degradation. Strauss and Peters-Kottig (2003) have attempted to identify a possible influence of late diagenetic thermal alteration through vitrinite reflectance measurements. No significant correlation of $\delta^{13}C_{TOM}$ to mean vitrinite reflectance values was detected. This observation is in agreement with other studies suggesting that a systematic increase in $\delta^{13}C$ values does probably not occur at temperatures below ~250 °C or possibly even ~350 °C (Schwarzkopf and Schoell, 1985; Whiticar, 1996; Watanabe et al., 1997). To summarize all these studies, diagenesis causes an isotope change of less than 2‰, commonly less than 1‰. Hence, no clear systematic variation in $\delta^{13}C$ values as a consequence of post-depositional, diagenetic alteration is discernible.

We conducted a very simple laboratory experiment in order to examine the effect of further oxidation on the $\delta^{13}C$ value of fossil organic C. To do so, we modified a standard maceration technique used by palaeobotanists to isolate plant cuticles from the sediment (e.g., Kerp, 1990). A random batch of 35 pulverized samples representing different kinds of organic matter (see Table 1) was heated (80 °C) with Schulze's reagent, an extremely oxidative agent (65% nitric acid containing few crystals of potassium chlorate). Subsequently, the samples were repeatedly rinsed with deionized water, dried and analyzed for their carbon isotopic composition. This experiment admittedly renders a rather simplistic simulation of diagenesis. However, it also provides an opportunity to check whether the standard chemical treatment of fossil organic carbon (maceration) prior to isotope analysis alters the isotopic composition in a systematic way when compared to $\delta^{13}C_{TOM}$ results of unprocessed samples (Table 1 and Fig. 2). The experimental data reveals that strong chemical treatment does not alter the carbon isotopic composition of consolidated organic matter. We interpret this as a qualitative measure of resistance to diagenesis.

Table 1
Influence of chemical processing on $\delta^{13}C$ of terrestrial organic matter of different quality

Sample	R_m (%)[a]	Organic matter type	$\delta^{13}C_{TOM}$ (‰) untreated	$\delta^{13}C_{TOM}$ (‰) maceration treatment
0001b	0.60	Cuticles	−24.6	−24.8
0071	n.d.	Coal	−22.2	−22.4
0074	0.70	Coal	−24.8	−24.5
0075	0.62	Coal	−24.1	−23.9
0082	0.70	Coal	−24.1	−24.2
0083	0.40	Coal	−21.4	−21.7
0085	0.55	Coal	−22.6	−22.9
0091	0.57	Coal	−22.8	−22.4
0093	0.54	Coal	−23.1	−23.2
0094	0.54	Coalified tissue	−23.8	−23.6
109	1.00	Coal	−23.2	−23.0
0161	n.d.	Cuticles	−23.6	−23.3
0201	n.d.	Coalified tissue	−23.7	−23.3
0204	n.d.	Coalified tissue	−24.9	−24.6
0214	2.00	Coalified tissue	−23.6	−23.4
0218	1.90	Coalified tissue	−23.2	−23.0
0236	3.14	Coalified tissue	−24.4	−24.4
0237	3.20	Coalified tissue	−25.3	−25.3
0246	0.70	Coalified tissue	−23.9	−23.5
0256	n.d.	Coal	−24.0	−23.6
0258b	n.d.	Coalified tissue	−23.6	−23.4
0270	n.d.	Coal	−23.0	−22.8
0278	0.80	Coal	−23.0	−22.9
0280	0.70	Coal	−22.5	−22.2
0281	0.70	Coalified tissue	−23.0	−22.7
0283	0.70	Coalified tissue	−23.9	−23.4
0284	0.70	Coal	−23.9	−23.7
0287	0.90	Coal	−27.2	−27.2
0310	0.69	Coal	−23.6	−23.5
0440	n.d.	Coal	−21.7	−21.7
0565	n.d.	Cuticles	−22.9	−22.9
0671	1.30	Coalified tissue	−23.4	−23.3

[a] R_m is mean random vitrinite reflectance of the host rock (e.g., Taylor et al., 1998).

A subset of samples used in this study has been previously investigated by Strauss and Peters-Kottig (2003). These authors showed that no systematic difference in average isotopic composition exists between the four types of organic matter identified:

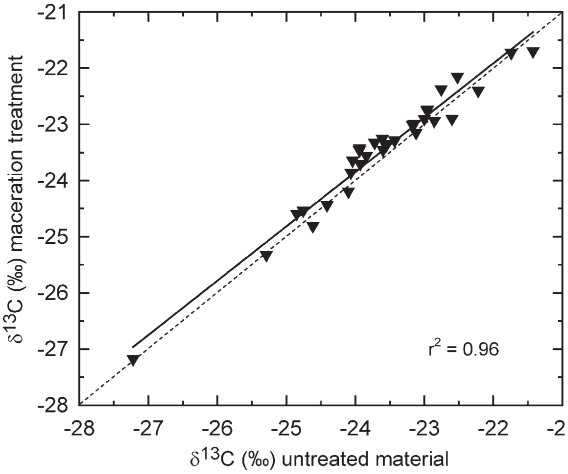

Fig. 2. Effect of chemical maceration treatment on δ^{13}C.

plant fossils, cuticules, humic coal and bulk organic matter. Also, no effect of rock lithology was found. Additionally, as shown in this study (Fig. 3) the $\delta^{13}C_{TOM}$ values of organic carbon from compression fossils are generally well correlated with results for bulk organic carbon from the same specimen. This observation was also reported by Arens and Jahren (2000). It can be summarized that different forms of diagenetic alteration did not affect the primary isotopic signal in a systematic and, moreover, a significant way.

2.2. The Palaeozoic record of $\delta^{13}C_{TOM}$

Palaeozoic TOM generally reflects a range in organic carbon δ^{13}C that is quite comparable to modern C_3-plants which clusters between −34‰ and −20‰ (mean −27.1 ± 2‰; O'Leary, 1988). Today, plants that use the C_3-type photosynthetic pathway include more than 95% of the plant species on earth. A set of $\delta^{13}C_{TOM}$ values of Permo-Carboniferous age depicted in Fig. 1 appear to be substantially different. These cannot easily be accounted for by a C_3-plant physiology but instead lie in the range of δ^{13}C values for modern C_4 or CAM plants (i. e. $\delta^{13}C_{TOM}$ higher than −20‰). To date it is assumed that C_4 plants, which prefer drier and warmer habitats probably appeared sometimes during the Oligocene against the background of declining atmospheric pCO$_2$ and drier environmental conditions, and, that they did not become ubiquitous prior to the Late Miocene (Sage, 2004). Still, it should be noted that the biochemical steps involved in Carbon Concentrating Mechanisms (CCM) were possibly widespread in flowering plants long before this pathway was fully expressed (Raven, 2002; Keeley and Rundel, 2003). Due to carbon isotope measurements on various materials, some authors have postulated that C_4 or CAM plants might have been present already in the Cretaceous (Bocherens et al., 1993; Kuypers et al., 1999).

Several factors render a search for early C_4/CAM plants in the fossil record difficult. Typical anatomical features older than Pleistocene have only been found in Miocene and Pliocene plants so far (Nambudiri et al., 1978; Thomasson et al., 1988). In general, the preservation potential of C_4 and CAM plants is very reduced in the fossil record, because terrestrial organic matter is preferably preserved under humid/wet conditions (Kerp, 1996) whereas C_4 and CAM plants favor drier habitats or even microsite aridity (Keeley and Rundel, 2003). Nevertheless, Palaeozoic plants with a Carbon Concentrating Mechanism (CAM, C_4 or intermediate) should be detectable through expected less negative $\delta^{13}C_{TOM}$ values (possibly > −10‰). But, to date, no such extreme values have been measured.

In summary we consider one of the following situations characteristic for the Palaeozoic. (1) C_4/CAM pathways or intermediate evolutionary innovations didn't exist yet. (2) The biochemical inventory was present but did not become manifest in the bulk isotopic composition of plant tissue. (3) Plants with a Carbon Concentrating Mechanism predominantly or even exclusively occupied drier habitats in extrabasinal hinterland areas where organic matter preservation is rather unlikely. Single positive isotope data most probably represent extreme habitat conditions or possibly singular short lived isotopic events in the global carbon cycle that have not been detected in other records to date.

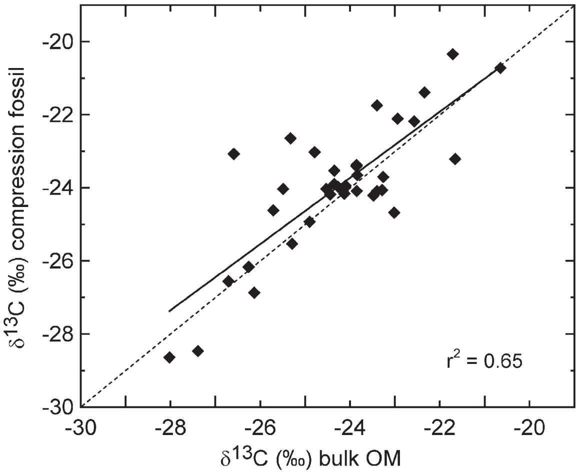

Fig. 3. δ^{13}C of organic matter from compression fossils (cuticles and coalified tissue) and bulk organic matter from the same rock specimen.

The overall average composition of $\delta^{13}C_{TOM}$ for the Silurian–Devonian samples is −25.3‰ and for the Permo-Carboniferous samples −23.4‰. Smoothing of the data with a moving average (Fig. 1) documents a temporal trend from $\delta^{13}C_{TOM}$ values of about −25‰ to −26‰ during the Silurian and Devonian to more ^{13}C enriched values of −22‰ to −23‰ in the Permo-Carboniferous. There are two longer phases in the Pennsylvanian and to the end of the Permian that display more negative values near −24‰. The difference between the $\delta^{13}C$ values for recent C_3 plants and the isotopically heavier fossil material is related to the observation that during the Late Palaeozoic, $\delta^{13}C$ of atmospheric CO_2 exhibited values several per mil less negative than at present (Mora et al., 1996; Beerling et al., 2002). Because plants reflect the carbon isotopic composition of the atmosphere (Farquhar et al., 1989) the underlying reason for the enrichment of ^{13}C in the carbon cycle in the Late Palaeozoic is an incremental growth of the isotopically light sedimentary organic carbon pool due to carbon burial. Terrestrial organic matter is isotopically light due to its biological origin. The increase in organic carbon burial has been attributed to the increasing carbon storage in land plant organic matter and, subsequently, coal (e.g., Berner and Raiswell, 1983; Berner, 2003). This long term trend of increasing $\delta^{13}C$ values has also been detected in the marine realm, both for organic and carbonate carbon (Hayes et al., 1999; Veizer et al., 1999).

2.3. Silurian–Devonian $\delta^{13}C$ values

A close inspection of the dataset for Silurian and Devonian $\delta^{13}C_{TOM}$ values (Fig. 1) reveals the relative scarcity of measurements in the older part of the record. A total of 103 measurements for the Silurian–Devonian indicate the apparent difficulty to obtain a sufficient number of well-dated samples that could be identified as originating from terrestrial sediments. The oldest material has been collected from terrestrial-lacustrine settings from Silurian inliers along the southern margin of the Midland Valley of Scotland (Charles Wellman, pers. comm., 2000). Due to the absence of recognizable plant remains, this material was processed as bulk rock samples (circles in Fig. 4). We cannot rule out the possibility that the organic matter did not originate from true vascular plants, but terrestrial plant microfossils have been found in these sediments (Wellman and Richardson, 1993). Some very limited HI–OI data (Hydrogen-Index, Oxygen-Index) from Rock-Eval-Pyrolysis conducted on subsamples of this material point to Type-III kerogen, which originated from land plants, as the main carbon source.

The temporal distribution of organic matter types shows that cuticles and coalified tissue are common in the sample set compared to bulk OM, whereas coal is scarcely represented in the Devonian (Fig. 4). Thus, we assume that the isotopic composition of Silurian–Devonian TOM mainly reflects $\delta^{13}C$ of land plants. However, OM contributions from non-vascular land plants of equivocal systematic position cannot be ruled out, particularly when they tend to be isotopically indistinguishable from vascular plants (for example *Spongiophyton*; Jahren et al., 2003; Fletcher et al., 2004). Fossil remains of the common, yet enigmatic Devonian organism *Prototaxites* which produces a wide variety of carbon isotope values that are mostly heavier than $\delta^{13}C$ of contemporaneous vascular plants (Boyce et al., 2003b) is also a possible carbon source. $\delta^{13}C$ values of fossil remains from seven identified Devonian taxa in our dataset suggest a C_3-type photosynthetic pathway (see Appendix). Part of the data scatter seen in the oldest part of the record might be a consequence of the presence of unknown evolutionary innovations in the land plants.

These Early Devonian land plants grew in, at least temporarily humid, lowland environments. They had not yet evolved all morphological and physiological departures from the ancestral aquatic conditions of plants that were essential to invade the drier hinterland: the evolution of a root system (Raven and Edwards, 2001) and of advanced reproductive adaptations (seeds) (Hilton, 1998). Except for *Bitelaria* of which no vascular system is known, all are pteridophytes, either belonging to the Rhyniophytes (*Renalia hueberi*), to the Zosterophyllophytes (*Crenaticaulis verruculosus*), or to the Trimerophytes (*Pertica varia*) (Taylor and Taylor, 1993). Most taxa were small, varying from a few centimetres to a few decimetres in height. They were all leafless and had rather thick cuticles. In our study, only one specimen provided kerogen concentrates containing cuticular OM. *P. varia* is the most robust plant known from the Lower Devonian, reaching a height of up to 3 m (Gensel and Andrews, 1984). *Leclercqia complexa* is a Middle Devonian herbaceous lycopsid. The Late Devonian fern-like *Rhacophyton* and the progymnosperm *Tetraxylopteris*, were both small trees and also bound to rather humid conditions, at least during the stage of reproduction. A further potential source of the scatter observed in the $\delta^{13}C$ values at any time in the record is probably due to intraspecific and interspecific variation, or variable habitat conditions

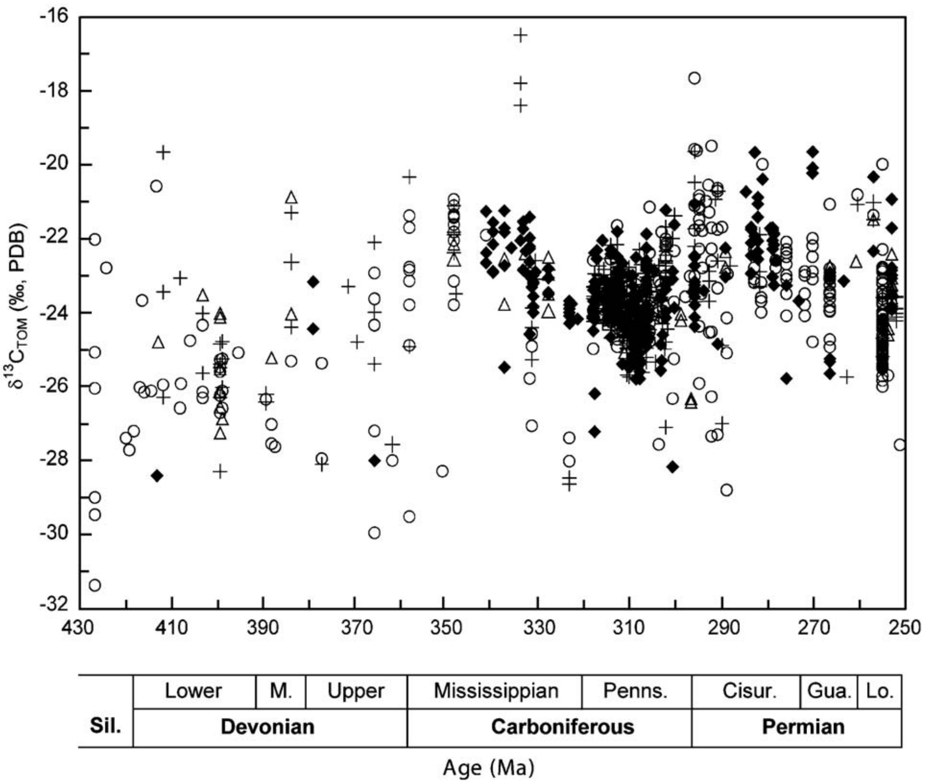

Fig. 4. Distribution of carbon isotope results for coals (diamonds), cuticles (open triangles), coalified tissue (crosses) and bulk OM (open circles). For $\delta^{13}C$ data that have been taken from the literature, the organic matter types that were originally analyzed are often unknown ($n = 378$). These data are not included in Fig. 4.

such as seasonal variation. All the effects are known to potentially shift the $^{13}C/^{12}C$ ratio by up to several per mil (see, e.g., the compilation in Arens et al., 2000). In addition, dating errors could have mixed samples of different ages.

2.4. Permo-Carboniferous $\delta^{13}C$ values

In contrast to the Devonian, the Carboniferous to Permian terrestrial organic carbon isotope record is much better constrained and displays a structured moving average curve (Fig. 1). The $\delta^{13}C$ values (starting around −23‰ in the Mississippian) are generally higher compared to the Silurian–Devonian record. The latter has been previously documented in the contemporaneous record from marine carbonates. Similarly, the decrease to negative values towards the end of the Permian is known already from marine inorganic carbonate carbon isotope data (Veizer et al., 1999). Mean $\delta^{13}C_{TOM}$ values exhibit high values during the Early Mississippian (near −22‰) followed by a phase of relatively ^{13}C depleted TOM in the Late Mississippian and Pennsylvanian (near −24‰). During the Permian, the mean $\delta^{13}C_{TOM}$ increases to values near −22‰, before declining to values of −24‰ near the Permian-Triassic boundary.

The increase of $\delta^{13}C_{TOM}$ in the early stages of the Carboniferous parallels one of the largest $\delta^{13}C_{carb}$ excursions in the Phanerozoic, a trend which is interpreted as reflecting enhanced accumulation and burial of organic matter in deep-sea, deltaic-shelf, and other depositional environments (Saltzman et al., 2004). ^{13}C enrichment in the surficial carbon pools mirrors this onset of vast C_{org} burial, particularly in tropical wetland areas of the Euramerican Coal Province (Calder and Gibling, 1994). It is probable that the initial Carboniferous increase of $\delta^{13}C_{TOM}$ values is a consequence of an evolutionary achievement of higher land plants. During the end-Famennian, the coastal lowland vegetation communities with potential for peat accumulation had reached a worldwide distribution from sub-polar to equatorial regions (Streel et al., 2000). In addition, plant groups with a high lignin content which served as a protection against decomposition had gained an increased dominance by the end of the Devonian (Robinson, 1990).

The most prominent feature in our record is the subsequent long lasting phase of decreased $\delta^{13}C_{TOM}$ values during the late Mississippian and the Pennsylvanian, which is recorded by several hundred of well characterized samples. Decreasing $\delta^{13}C$ values during this time interval are in marked contrast to the marine carbonate carbon record. Popp et al. (1986) first pointed out a shift to heavier $\delta^{13}C$ values of marine carbonate carbon near the Mississippian–Pennsylvanian boundary that has since been recorded in various sections with some interoceanic variability in the magnitude of the shift (Bruckschen et al., 1999; Veizer et al., 1999; Mii et al., 2001; Grossman et al., 2002). Because the decrease of $\delta^{13}C_{TOM}$ values during the Late Carboniferous does not parallel the carbonate carbon isotope record in these sections, it likely points to a physiological response to the abundance of atmospheric oxygen that will be reviewed in the following section: photorespiration.

In C_3 photosynthesis Rubisco is the primary enzyme for fixing CO_2. However, it can also act as oxygenase when sufficient O_2 is available, because both carbon dioxide and oxygen compete for reaction at the active site of Rubisco (Lorimer, 1981; Raven, 1991). One metabolic consequence of increased photorespiration due to enhanced O_2 is an increase in carbon isotopic fractionation that has been observed in laboratory experiments (Berry et al., 1972; Berner et al., 2000). Geochemical models suggest that atmospheric oxygen content has fluctuated between ~0.5 and ~2 PAL (Present Atmospheric Level) during the Phanerozoic (Lasaga and Ohmoto, 2002). It possibly reached an all time high in the late Palaeozoic (Berner et al., 2003) as a result of (1) high oxygen production by the emerging terrestrial flora and (2) enhanced burial of organic carbon, effectively inhibiting O_2 consumption during oxidative weathering of OM. Although there is considerable disagreement on the upper threshold value of pO_2 with respect to regulatory feedback mechanisms that limits pO_2 (e.g., forest fires; Lenton and Watson, 2000; Wildman et al., 2004), independent evidence from the Palaeozoic faunal record (Graham et al., 1995; Dudley, 1998) suggests that the Pennsylvanian to Early Permian was a time of increased oxygen levels in the atmosphere. Phenotypic response to enhanced O_2 levels is particularly evident from contemporaneous gigantism within a variety of Late Palaeozoic arthropod taxa, which adapted to the evolutionary options inherent in increased respiratory capacity. The timing and particularly the duration of the Late Palaeozoic O_2 peak are somewhat ill-defined from geochemical modeling due to broad margins of error inherent in the methods. Furthermore, a study of isotopic fractionation as qualitative measure of atmospheric oxygen level conducted by Beerling et al. (2002) suffered from a rather small data pool.

Modeling indicates that the Late Palaeozoic O_2 peak might have lasted for roughly a hundred million years (Berner et al., 2003). Our carbon isotope data suggest that the O_2 peak could have been restricted merely to the Late Mississippian and the Pennsylvanian— a time frame of ~40 Ma with comparatively negative carbon isotope values. Alternatively, it is possible that the O_2 peak lasted until the End-Permian, but its effect on carbon isotopes in plants was covered by the effect of maximum C_{org} burial and concomitant rise in $\delta^{13}C$ somewhere around 280 to 290 Ma (Berner, 2003). The latter process might have had a larger effect on the $\delta^{13}C$ of atmospheric CO_2 than the influence of photorespiration.

From the beginning of the Permian, the mean $\delta^{13}C_{TOM}$ is again increased and reached a mean value of −21.8‰ during the Cisuralian, before declining to values near -24‰ in the Guadalupian and Lopingian (Fig. 1). This increase probably mirrors a time of maximum sequestration of light carbon in terrestrial and shelf sediments (Berner, 2003). The subsequent trend to more negative $\delta^{13}C$ values long before the Permian-Triassic boundary carbon isotope excursion recorded in various marine and terrestrial sections might be due to global tectonics and the final consolidation of Pangaea. Several authors (Faure et al., 1995; Kerp, 1996; Hallam and Wignall, 1997; Kidder and Worsley, 2004) have suggested that the tectonic and climatic processes accompanying the formation of the supercontinent led to a reduction of foreland coal basins, ultimately causing a reduction in organic carbon burial (Berner, 2005). An additional consequence may have been retreating or diminishing forest vegetation, also a mechanism for the global coal-hiatus (Faure et al., 1995). An increase in weathering of coal bearing sediments could have also released isotopically depleted carbon into the atmosphere. de Wit et al. (2002) favor the episodic release of methane from clathrates as the reason for the gradual decline of carbon isotope values prior to the P/T-boundary, although they do not exclude the oxidation of organic matter. Both scenarios are consistent with our record and serve as potential negative feedback mechanisms that were capable to reduce atmospheric O_2 well before the end of the Palaeozoic.

The Late Palaeozoic is thought to be a time of rapidly declining pCO_2 to levels near those in the modern world (François et al., 1993; Berner and Kothavala, 2001). Increased photosynthetic fixation and subsequent organic carbon burial is widely acknowledged as being the main cause for $p\text{CO}_2$ lowering — together with land plant induced silicate weathering (Algeo and Scheckler, 1998). Falling atmospheric $p\text{CO}_2$ had considerable influence on land plant evolution in the Devonian (Beerling and Chaloner, 1993; Beerling et al., 2001) but it is not clear whether $p\text{CO}_2$ is linked to the $\delta^{13}\text{C}_{\text{TOM}}$ values. According to Farquhar et al. (1989), an increase in $p\text{CO}_2$ without change in $\delta^{13}\text{C}_{\text{CO2}}$ will only have a minor effect on plant carbon isotopic composition. Arens et al. (2000) showed that the majority of variations in δ^{13}C of modern C_3 plants were due to variations in the isotopic composition of CO_2 rather than the CO_2 level. On the other hand, Van der Water et al. (1994) found that an increase in CO_2 level results in a negative carbon isotope shift whereas Körner et al. (1991) reported a shift to ^{13}C enriched plant organic matter with decreasing $p\text{CO}_2$.

In order to assess whether gross climate conditions might be detectable in our isotope record we have assigned every sample locality to a respective past global climate belt on the basis of the palaeoclimatic maps provided by Scotese (2002). Unfortunately, we do not have reliable information about local environmental conditions for most of the samples. Hence, our classification is only a provisional and rough estimate of the influence from climate conditions. Still, it potentially provides an insight into underlying variations in the record that are generally difficult to obtain for a large heterogeneous data set. The distribution of $\delta^{13}\text{C}_{\text{TOM}}$ values according to different climatic conditions (Fig. 5) reveals that the carbon isotope values from the different climate belts are statistically indistinguishable. It should be noted, however, that warm temperate is underrepresented in our data set.

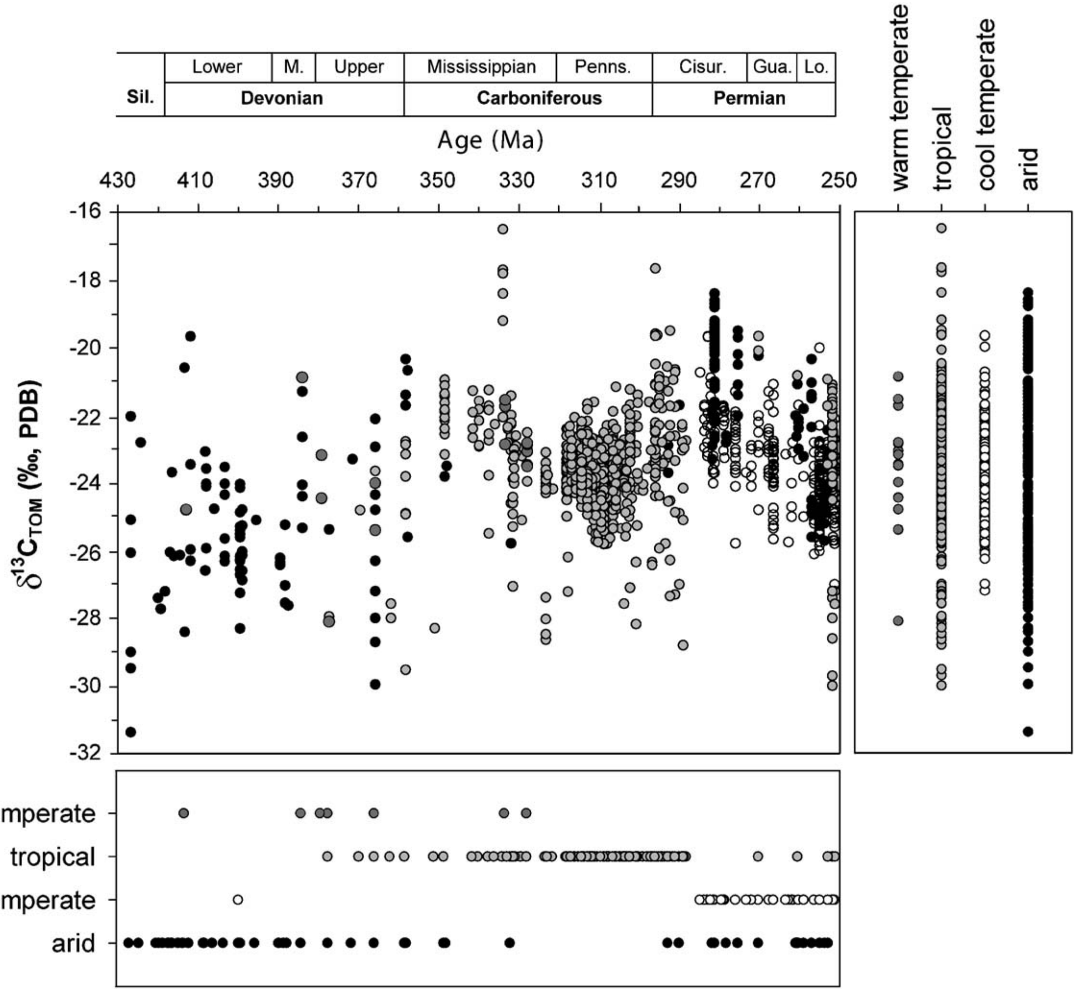

Fig. 5. Provenance of samples with respect to gross climate conditions in the Palaeozoic. For each sampling location palaeogeographic position was identified (palaeogeographic maps and global distribution of climate belts from Scotese, 2002).

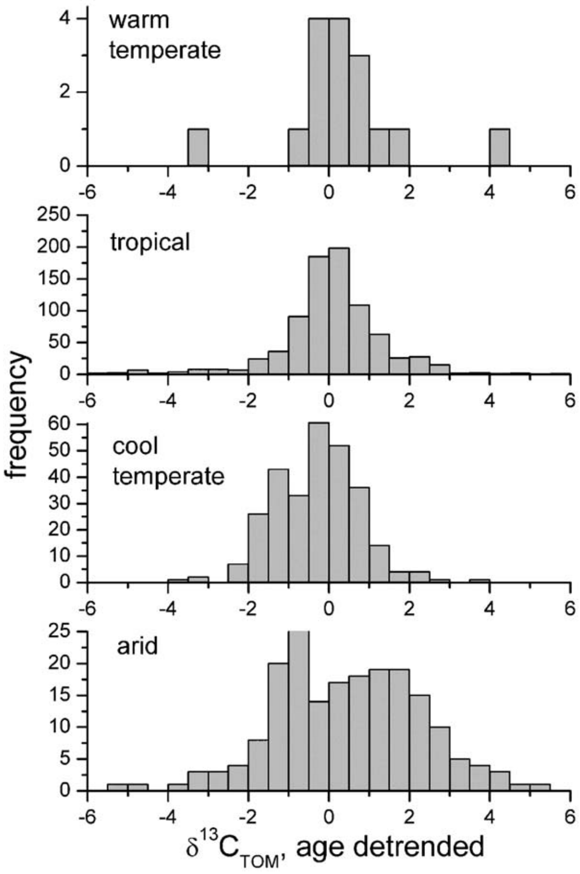

Fig. 6. Frequency distributions of age detrended $\delta^{13}C_{TOM}$ values for climate belts from Fig. 5. Isotope data were normalized to mean $\delta^{13}C_{TOM}$ value inside a 10 Ma window in order to remove possible errors due to age distribution.

Furthermore, nearly all samples from cool temperate climates originate from Permian coal bearing strata whereas tropical samples predominantly are derived from coal basins of the Carboniferous. The distribution of samples from the arid climate belt is bimodal between the Silurian–Devonian and the Permian, which helps explain the wide scatter of isotope data in the right upper box of the diagram (Fig. 5).

We calculated the difference in isotopic composition of TOM between different climates for a 10 Ma window in order to remove age related trends in our record (Fig. 6). Nonparametric testing (Kruskal–Wallis test, Mann–Whitney test) of the age detrended data shows statistically significant differences between the groups ($P<0.01$). The sample distribution from the warm temperate belt was not significantly different from the data representing arid and tropical locations ($P>0.05$), whereas arid samples were significantly different from tropical samples ($P<0.01$). Data from the cool temperate climate belt differed from all other samples. The results do not reveal a clear systematic signal that could be related to ecological effects on carbon isotopes like temperature or light (see, e.g., the compilation in Arens et al., 2000). The absence of explicit geographic variability with respect to $\delta^{13}C$ values is a feature that has also been observed in present day biomes. While differences in leaf $\delta^{13}C$ have been correlated with plant functional type within a given ecosystem (Brooks et al., 1997), between broadleaf tropical forests and coniferous forests (Broadmeadow and Griffiths, 1993), and by latitude (Körner et al., 1991), no clear separations emerge when all data are analysed (Pataki et al., 2003). In general, the ecophysiological significance of the results might be dampened by the fact that all samples originate from rather wet environments. For example, almost all Silurian–Devonian samples have been collected from locations that were positioned in the broad arid climate belt during this time, but it is suspected that early land plants were adapted to moist conditions (DiMichele and Hook, 1992; Algeo and Scheckler, 1998), hence a typical feature of arid environment – osmotic stress – was absent in the actual habitat.

2.5. Taxonomic differences in $\delta^{13}C_{TOM}$

In addition to evaluating climatic effects on carbon isotope values, we investigated isotopic composition among fossil taxa from four systematic groups that originate from the tropical belt of the Carboniferous Euramerican Phytogeographic Province. Fig. 7 shows a box whisker plot of the data distribution for

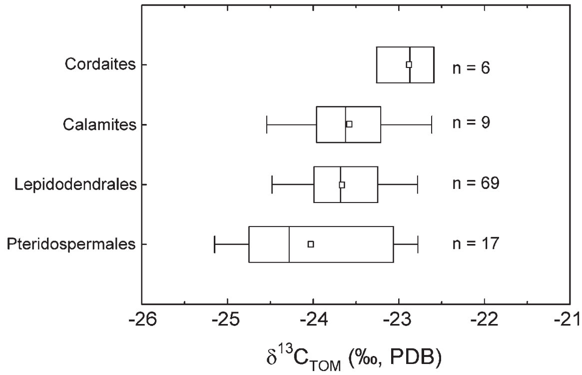

Fig. 7. Range of $\delta^{13}C_{TOM}$ values for different plant groups from the Euramerican Phytogeographic Province. All samples are Carboniferous in age. $\delta^{13}C_{TOM}$ of the Lepidophytes include 18 data from Beerling (2002). The boxes enclose 50% of the data population, with the centerline showing the median value and the square showing the mean value. The error bars show 5% and 95% percentile, respectively.

$\delta^{13}C_{TOM}$. The median values for all groups lie within a remarkably narrow range of 1.5‰ and 50% of the data plot between −22.6‰ and −24.8‰. On the other hand nonparametric comparison tests show that isotope values are significantly different between the studied groups. Pteridosperms have significantly lighter values than Lycopsdis, calamites and cordaites ($P<0.05$). Lycopsids and calamites are statisitically indistinguishable ($P>0.05$) but differ significantly from cordaites ($P<0.05$) which have the most positive values. We suggest that the fairly narrow range of all data might be a consequence of generally comparable regional or local humid climate conditions and that the small but significant differences between the groups mirror different habitat conditions that were typical for each group.

Pteridosperms or seed ferns constituted a dominant group of lowland gymnosperms during the Late Carboniferous. The broad variety of growth strategies and potential habitats might be the explanation for the data scatter seen in the length of the respective box (Fig. 7). Arborescent lycopsids are typical representatives from the low-lying foreland or intramontane coal basins. The Late Carboniferous arborescent lycopsids *Lepidodendron*, *Lepidophloios* and *Sigillaria* are typical elements from the basinal peat-swamp floras and hence indicate wet habitat conditions. The arborescent lycopods differ from modern trees in having stems which largely consisted of cortex instead of xylem like in modern woody trees. Our analyses were performed on OM from compression fossils that resemble the outer cortex of the plants.

Calamites were also bound to wet conditions, which probably explain the isotopic similarity to the Lepidodendrales. They belong to the group of the sphenopsids, had widespread rhizome systems, and were typical flood-plain elements, mostly occurring in areas of substrate aggradation, e.g. along stream and lake margins, where they often formed monospecific stands (Scott, 1979; DiMichele and Phillips, 1994). An ecological characterization of Cordaites is difficult because this group has been reported from different environments, varying from hinterland habitats to coal swamps. Some species even had mangrove like root systems, indicating a brackish habitat. Cordaite trees which have been analyzed in this study all grew in peat mires like the plants from the other groups. Nonetheless, they show a slight ^{13}C enrichment which might point to changes in leaf gas exchange metabolism that were preferentially dependent upon ecological causes other than humidity, e.g. the canopy architecture.

3. Conclusions

Close inspection of the late Palaeozoic organic carbon isotope record from terrestrial organic matter (plant fossils, cuticules, humic coals, bulk organic carbon) reveals that land plants had a C_3 metabolism. Relatively positive $\delta^{13}C$ values (e.g. data from Jones, 1994) are believed to reflect extreme habitats rather than C_4 metabolism. Carbon isotope values for samples from different climatic zones (warm temperate, tropic, cool temperate, arid) do not reveal a systematic influence of gross climate. In part, this might be a consequence of a preference of early land plants for moist environments. Carbon isotope measurements for a variety of fossil taxa from four systematic groups reveal small but significant differences with $\delta^{13}C$ values for pteridosperms < arborescent lycopsids = calamites < cordaites. This result might point to different ecophysiological strategies. The long term trend of increasing $\delta^{13}C_{TOM}$ values is a consequence of increased carbon burial. This trend is possibly superimposed by a maximum pO_2 peak in the Permian atmosphere which increased isotopic discrimination for ~40 Ma. It is not clear whether a concomitant minimum CO_2 level in the atmosphere had direct impact on $\delta^{13}C_{TOM}$. Laboratory growth experiments on land plants using varying O_2/CO_2 may be a valuable tool to understand the influence of atmospheric composition on land plant evolution.

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Appendix A

Stable carbon isotopic composition of Palaeozoic plant taxa.

Fossil taxon	Sample	Age (Ma)	Organic matter type	$\delta^{13}C_{TOM}$ (‰)
Bitelaria dubjanskii	0016	399.5	Cuticles	−24.1
Crucicalamites cruciatus	0850	305.5	Coalified tissue	−23.3

(continued on next page)

Appendix A (*continued*)

Fossil taxon	Sample	Age (Ma)	Organic matter type	$\delta^{13}C_{TOM}$ (‰)
Calamites cruciatus	0100	306.5	Coalified tissue	−24.1
Calamites sp.	0059	302.3	Coalified tissue	−22.6
Calamites sp.	0097	306.5	Coalified tissue	−24.5
Calamites sp.	0754	314.3	Coalified tissue	−23.2
Calamites sp.	0680	314.3	Coalified tissue	−23.6
Calamites sp.	0675	314.3	Coalified tissue	−23.8
Calamites undulatus	0848	308.7	Coalified tissue	−23.3
Coniferales	0116	257.0	Coalified tissue	−21.5
Coniferales	0015	260.8	Cuticles	−22.6
Coniferales	0050	296.0	Coalified tissue	−21.7
Cordaites sp.	0828	302.3	Coalified tissue	−22.4
Cordaites sp.	0890	302.3	Coalified tissue	−22.7
Cordaites sp.	0770	302.3	Coalified tissue	−22.8
Cordaites sp.	0645	309.5	Coalified tissue	−23.5
Cordaites sp.	0617	310.3	Coalified tissue	−23.0
Cordaites sp.	0867	310.8	Coalified tissue	−23.2
Crenaticaulis verruculosus	0787	399.5	Coalified tissue	−24.9
Cyperites bicarinatus	0648	309.5	Coalified tissue	−23.7
Eskdalia sp.	0007	332.0	Cuticles (Papercoal)	−24.6
Leclercqia complexa	0019	384.0	Cuticles	−20.9
Lepidocarpon linearifolium	0832	311.2	Coalified tissue	−23.7
Lepidodendron aculeatum	0044	310.3	Coalified tissue	−24.3
Lepidodendron aculeatum	0852	312.0	Coalified tissue	−24.1
Lepidodendron aculeatum	0859	314.3	Coalified tissue	−24.5
Lepidodendron aculeatum	0753	315.8	Coalified tissue	−23.8
Lepidodendron cf. *aculeatum*	0620	310.3	Coalified tissue	−25.7
Lepidodendron dichotomum	0757	313.7	Coalified tissue	−24.2
Lepidodendron lossenii	0231	331.5	Coalified tissue	−23.9
Lepidodendron obovatum	0776	310.8	Coalified tissue	−23.6
Lepidodendron obovatum	0611	312.9	Coalified tissue	−22.7
Lepidodendron obovatum	0592	312.9	Coalified tissue	−24.0
Lepidodendron sp.	0070	303.0	Coalified tissue	−24.3
Lepidodendron sp.	0062	306.5	Coalified tissue	−24.6
Lepidodendron sp.	0649	309.5	Coalified tissue	−23.7
Lepidodendron sp.	0591	310.3	Coalified tissue	−23.8
Lepidodendron sp.	0776b	310.8	Coalified tissue	−23.9
Lepidodendron sp.	0766	314.3	Coalified tissue	−23.1
Lepidodendron sp.	0777	314.3	Coalified tissue	−24.7
Lepidodendron sp.	0755	315.8	Coalified tissue	−24.2
Lepidophloios laricinus	0612	313.5	Coalified tissue	−23.4
Lepidophylloides	0648	309.5	Coalified tissue	−23.7
Neuropteris ovata	0565	304.8	Cuticles	−22.9
Palaeostachya sp.	0779	312.9	Coalified tissue	−23.7
Pertica varia	0788	399.5	Cuticles	−27.3
Pteridospermales	0784	302.3	Coalified tissue	−22.5
Pteridospermales	0782	302.3	Coalified tissue	−22.9
Pteridospermales	0814	302.3	Coalified tissue	−24.8
Pteridospermales	0346	303.2	Coalified tissue	−24.1
Pteridospermales	0065	305.8	Coalified tissue	−23.0
Pteridospermales	0329	305.8	Coalified tissue	−24.0
Pteridospermales	0868	306.5	Coalified tissue	−25.4
Pteridospermales	0863	310.8	Coalified tissue	−24.7
Pteridospermales	0864	310.8	Coalified tissue	−25.0
Pteridospermales	0001c	311.3	Coalified tissue	−24.3
Pteridospermales	0001d	311.3	Cuticles	−24.6
Pteridospermales	0001b	311.3	Cuticles	−24.6
Pteridospermales	0001e	311.3	Cuticles	−24.6
Pteridospermales	0001f	311.3	Cuticles	−25.1
Pteridospermales	0766b	314.3	Coalified tissue	−23.1
Pteridospermales	0756	315.8	Coalified tissue	−23.5
Quadrocladus sp.	0095	253.8	Cuticles	−24.0
Renalia hueberi	0018	399.5	Cuticles	−26.2
Rhacophyton condrusorum	0037	365.8	Coalified tissue	−22.1
Sigillaria boblayi	0849	312.3	Coalified tissue	−23.4
Sigillaria boblayi	0613	314.3	Coalified tissue	−23.7
Sigillaria cancriformis	0609	316.8	Coalified tissue	−22.7
Sigillaria cf. *boblayi*	0614	314.3	Coalified tissue	−24.0
Sigillaria elegans	0842	312.7	Coalified tissue	−23.1
Sigillaria elongata	0845	312.3	Coalified tissue	−23.9
Sigillaria hexagona	0844	312.7	Coalified tissue	−23.3
Sigillaria ichthyolepis	0831	302.3	Coalified tissue	−22.0
Sigillaria mamillaris	0843	312.3	Coalified tissue	−23.5
Sigillaria rugosa	0615	312.9	Coalified tissue	−23.6
Sigillaria sp.	0769	296.0	Coalified tissue	−20.5
Sigillaria sp.	0837	302.3	Coalified tissue	−23.1
Sigillaria sp.	0324	305.8	Coalified tissue	−24.5
Sigillaria sp.	0094	306.5	Coalified tissue	−23.8
Sigillaria sp.	0661	308.8	Coalified tissue	−23.6
Sigillaria sp.	0659	308.8	Coalified tissue	−23.7
Sigillaria sp.	0647	309.5	Coalified tissue	−23.5
Sigillaria sp.	0644	309.5	Coalified tissue	−23.8
Sigillaria sp.	0646	309.5	Coalified tissue	−24.5
Sigillaria sp.	0772	310.8	Coalified tissue	−23.3
Sigillaria sp.	0778	312.3	Coalified tissue	−24.0
Sigillaria sp.	0667	314.3	Coalified tissue	−23.8
Sigillaria sp.	0058	315.8	Coalified tissue	−22.8
Sigillaria sp.	0860	316.8	Coalified tissue	−23.6
Sigillaria tesselata	0847	312.3	Coalified tissue	−22.8
Sigillaria tesselata	0851	312.3	Coalified tissue	−23.6
Sigillaria tesselata	0759	315.0	Coalified tissue	−23.6
Sphenophyllum sp.	0780	314.3	Coalified tissue	−23.0
Tetraxylopteris schmidtii	0017	384.0	Cuticles	−22.6
Trigonocarpus starkianus	0692	303.3	Coalified tissue	−23.6
Ulodendron sp.	0857	312.3	Coalified tissue	−22.8
Whittleseya sp.	0774	302.3	Coalified tissue	−23.0

References

Ader, M., Boudou, J.-P., Javoy, M., Goffe, B., Daniels, E., 1998. Isotope study on organic nitrogen of Westphalian anthracites from the Western Middle field of Pennsylvania (U.S.A.) and from the Bramsche Massif (Germany). Organic Geochemistry 29, 315–323.

Algeo, T.J., Scheckler, S.E., 1998. Terrestrial-marine teleconnections in the Devonian: links between the evolution of land plants, weathering processes, and marine anoxic events. Philosophical Transactions of the Royal Society of London. B 353, 113–130.

Ando, A., Kakegawa, T., Takashima, R., Saito, T., 2002. New perspective on Aptian carbon isotope stratigraphy: data from $\delta^{13}C$ records of terrestrial organic matter. Geology 30, 227–230.

Arens, N.C., Jahren, A.H., 2000. Carbon isotope excursion in the atmospheric CO_2 at the Cretaceous-Tertiary boundary: evidence from terrestrial sediments. Palaios 15, 314–322.

Arens, N.C., Jahren, A.H., Amundson, R., 2000. Can C_3 plants faithfully record the carbon isotopic composition of atmospheric carbon dioxide? Paleobiology 26, 137–164.

Beerling, D.J., 2002. Low atmospheric CO_2 levels during the Permo-Carboniferous glaciation inferred from fossil lycopsids. Proceedings of the National Academy of Sciences 99, 12567–12571.

Beerling, D.J., Chaloner, W.G., 1993. Evolutionary responses of stomatal density to global CO_2 change. Biological Journal of the Linnean Society 48, 343–353.

Beerling, D.J., Royer, D.L., 2002. Fossil plants as indicators of the Phanerozoic global carbon cycle. Annual Review of Earth and Planetary Sciences 30, 527–556.

Beerling, D.J., Berner, R.A., 2005. Feedbacks and the coevolution of plants and atmospheric CO_2. Proceedings of the National Academy of Sciences 102, 1302–1305.

Beerling, D.J., Osborne, C.P., Chaloner, W.G., 2001. Evolution of leaf-form in land plants linked to atmospheric CO_2 decline in the Late Palaeozoic era. Nature 410, 352–354.

Beerling, D.J., Lake, J.A., Berner, R.A., Hickey, L.J., Taylor, D.W., Royer, D.L., 2002. Carbon isotope evidence implying high O_2/CO_2 ratios in the Permo-Carboniferous atmosphere. Geochimica et Cosmochimica Acta 66, 3757–3767.

Benner, R., Fogel, M.L., Sprague, E.K., Hodson, R.E., 1987. Depletion of ^{13}C in lignin and its implications for stable carbon isotope studies. Nature 329, 708–710.

Berner, R.A., 2003. The long-term carbon cycle, fossil fuels and atmospheric composition. Nature 426, 323–326.

Berner, R.A., 2004. The Phanerozoic Carbon Cycle: CO_2 and O_2. Oxford University Press, Oxford.

Berner, R.A., 2005. The carbon and sulfur cycles and atmospheric oxygen from middle Permian to middle Triassic. Geochimica et Cosmochimica Acta 69, 3211–3217.

Berner, R.A., Kothavala, Z., 2001. GEOCARB III: a revised model of atmospheric CO_2 over Phanerozoic time. American Journal of Science 301, 182–204.

Berner, R.A., Raiswell, R., 1983. Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: a new theory. Geochimica et Cosmochimica Acta 47, 855–862.

Berner, R.A., Petsch, S.T., Lake, J.A., Beerling, D.J., Popp, B.N., Lane, R.S., Laws, E.A., Westley, M.B., Cassar, N., Woodward, F. I., Quick, W.P., 2000. Isotope fractionation and atmospheric oxygen: implications for Phanerozoic O_2 evolution. Science 287, 1630–1633.

Berner, R.A., Beerling, D.J., Dudley, R., Robinson, J.M., Wildman, R.A., 2003. Phanerozoic atmospheric oxygen. Annual Review of Earth and Planetary Sciences 31, 105–134.

Berry, J.A., Troughton, J.H., Björkman, O., 1972. Effect of oxygen concentration during growth on carbon isotope discrimination in C_3 and C_4 species of Atriplex. Year Book - Carnegie Institution of Washington 71, 158–161.

Bocherens, H., Friis, E.M., Mariotti, A., Pedersen, K.R., 1993. Carbon isotopic abundances in Mesozoic and Cenozoic fossil plants: palaeoecological implications. Lethaia 26, 347–358.

Botz, R., Müller, G., 1981. Mineralogie, Petrographie, anorganische Geochemie und Isotopen-Geochemie der Karbonatgesteine des Zechstein: 2. Geologisches Jahrbuch. Reihe D, Mineralogie, Petrographie, Geochemie, Lagerstättenkunde 47, 3–112.

Boyce, C.K., Cody, G.D., Fogel, M.L., Hazen, R.M., Alexander, C.M. O'D., Knoll, A.H., 2003a. Chemical evidence for cell wall lignification and the evolution of tracheids in Early Devonian plants. International Journal of Plant Science 164, 691–702.

Boyce, C.K., Hotton, C., Fogel, M.L., Cody, G.D., Hazen, R.M., Knoll, A.H., 2003b. Comparative geochemistry suggests Prototaxites was a gigantic fungus. Abstracts with Programs - Geological Society of America Meeting 34 (7), 587.

Broadmeadow, M.S.J., Griffiths, H., 1993. Carbon isotope discrimination and the coupling of CO_2 fluxes within forest canopies. In: Ehleringer, J.R., Hall, A.E., Farquhar, G.D. (Eds.), Stable Isotopes and Plant Carbon–Water Relations. Academic, San Diego, USA, pp. 109–129.

Brooks, J.R., Flanagan, L.B., Buchmann, N., Ehleringer, J.R., 1997. Carbon isotope composition of boreal plants: functional grouping of life forms. Oecologia 110, 301–311.

Bruckschen, P., Oesmann, S., Veizer, J., 1999. Isotope stratigraphy of the European Carboniferous: proxy signals for ocean chemistry, climate and tectonics. Chemical Geology 161, 127–163.

Calder, J.H., Gibling, M.R., 1994. The Euramerican Coal Province: controls on Late Paleozoic peat accumulation. Palaeogeography, Palaeoclimatology, Palaeoecology 106, 1–23.

Kotarba, M.J., Clayton, J.L., 2003. A stable carbon isotope and biological marker study of Polish bituminous coals and carbonaceous shales. International Journal of Coal Geology 55, 73–94.

Czimczik, C.I., Preston, C.M., Schmidt, M.W.I., Werner, R.A., Schulze, E.-D., 2002. Effects of charring on mass, organic carbon, and stable carbon isotope composition of wood. Organic Geochemistry 33, 1207–1223.

de Wit, M.J., Gosh, J.G., de Villiers, S., Rakotosolofo, N., Alexander, J., Tripathi, A., Looy, C., 2002. Multiple organic carbon isotope reversals across the Permo-Triassic boundary of terrestrial Gondwana sequences: clues to extinction patterns and delayed ecosystem recovery. The Journal of Geology 110, 227–240.

DiMichele, W.A., Hook, R.W., 1992. Paleozoic terrestrial ecosystems. In: Behrensmeyer, A.K., Damuth, J.D., DiMichele, W.A., Potts, R., Sues, H.-D., Wing, S.L. (Eds.), Terrestrial Ecosystems Through Time. University of Chicago Press, Chicago, pp. 205–325.

DiMichele, W.A., Phillips, T.L., 1994. Paleobotanical and paleoecological constaints on models of peat formation in the Late Carboniferous of Euramerica. Palaeogeography, Palaeoclimatology, Palaeoecology 106, 39–90.

Dudley, R., 1998. Atmospheric oxygen, giant Paleozoic insects and the evolution of aerial locomotor performance. Journal of Experimental Biology 201, 1043–1050.

Elick, J.M, 1999. Elevated atmospheric CO_2 levels and expansion of early vascular land plants; stable isotope evidence from the Battery Point Fm. (Early to Middle Devonian), Gaspe Bay, Canada. GSA Annual Meeting Abstracts, vol. 31, p. 159.

Farquhar, G.D., Ehleringer, J.R., Hubick, K.T., 1989. Carbon isotope discrimination and photosynthesis. Annual Review of Plant Physiology and Plant Molecular Biology 40, 503–537.

Faure, K., Cole, D., 1999. Geochemical evidence for lacustrine microbial blooms in the vast Permian Main Karoo, Paraná, Falkland Islands and Huab basins of southwestern Gondwana.

Palaeogeography, Palaeoclimatology, Palaeoecology 152, 189–213.

Faure, K., de Wit, M.J., Willis, J.P., 1995. Late Permian global coal hiatus linked to ^{13}C depleted CO_2 flux into the atmosphere during final consolidation of Pangea. Geology 23, 507–510.

Fernandez, I., Mahieu, N., Cadisch, G., 2003. Carbon isotopic fractionation during decomposition of plant materials of different quality. Global Biogeochemical Cycles 17 (3), 1–11 (2001GB001834).

Fletcher, B.J., Beerling, D.J., Chaloner, W.G., 2004. Stable carbon isotopes and the metabolism of the terrestrial Devonian organism Spongiophyton. Geobiology 2, 107–119.

François, L.M., Walker, J.C.G., Opdyke, B.N., 1993. The history of global weathering and the chemical evolution of the ocean-atmosphere system. Geophysical Monograph 74, 143–159 (IUGG Vol. 14).

Gensel, P.G., Andrews, H.N., 1984. Plant Life in the Devonian. Praeger, New York.

Gensel, P.G., Edwards, D. (Eds.), 2001. Plants Invade the Land, Evolutionary and Environmental Perspectives. Columbia University Press, New York.

Ghosh, Pr., Ghosh, P., Bhattacharya, S.K., 2001. CO_2 levels in the Late Paleozoic and Mesozoic atmosphere from soil carbonate and organic matter, Satpura basin, Central India. Palaeogeography, Palaeoclimatology, Palaeoecology 170, 219–236.

Gorter, J.D., Foster, C.B., Summons, R.E., 1994. Carbon isotopes and the Permian-Triassic boundary in the north Perth, Bonaparte and Carnarvon Basins, Western Australia. PESA Journal 23, 21–38.

Graham, J.B., Dudley, R., Aguilar, N.M., Gans, C., 1995. Implications of the late Palaeozoic oxygen pulse for physiology and evolution. Nature 375, 117–120.

Gröcke, D.R., 2002. The carbon isotope composition of ancient CO_2 based on higher-plant organic matter. Philosophical Transactions of the Royal Society of London. A 360, 633–658.

Grossman, E.L., Bruckschen, P., Mii, H.-S., Chuvashov, B.I., Yancey, T.E., Veizer, J., 2002. Carboniferous paleoclimate and global change: isotopic evidence from the Russian Platform. Carboniferous Stratigraphy and Paleogeography in Eurasia. Institute of Geology and Geochemistry, Russian Academy of Sciences, Urals Branch, Ekaterinburg, pp. 61–71.

Hallam, A., Wignall, P.B., 1997. Mass Extinctions and their Aftermath. Oxford University Press, Oxford.

Hansen, H.J., Lojen, S., Toft, P., Dolenec, T., Tong, J., Michelsen, P., Sarkar, A., 2000. Magnetic susceptibility and organic carbon isotopes of sediments across some marine terrestrial Permo-Triassic boundaries. In: Yin, H., Dickins, J.M., Shi, G.R., Tong, J. (Eds.), Permian-Triassic Evolution of Tethys and Western Circum-Pacific. Elsevier, Amsterdam, pp. 271–289.

Hasegawa, T., 2003. Cretaceous terrestrial paleoenvironments of northeastern Asia suggested from carbon isotope stratigraphy: increased atmospheric $p\mathrm{CO_2}$-induced climate. Journal of Asian Earth Sciences 21, 849–859.

Hatch, J.R., Avcin, M.J., Van Dorpe, P.E., 1984. Element Geochemistry of Cherokee Group Coals (Middle Pennsylvanian) from South-Central and Southeastern Iowa. Iowa Geological Survey Technical Paper, vol. 5. Iowa Geological Survey, Iowa City.

Hayes, J.M., 2001. Fractionation of Carbon and Hydrogen isotopes in biosynthetic processes. In: Valley, J.W., Cole, D.R. (Eds.), Stable Isotope Geochemistry. Reviews in Mineralogy and Geochemistry, vol. 43. Mineralogical Society of America, Washington, D.C., pp. 225–277.

Hayes, J.M., Strauss, H., Kaufman, A.J., 1999. The abundance of ^{13}C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma. Chemical Geology 161, 103–125.

Hedges, J.I., Cowie, G.L., Ertel, J.R., Barbour, R.J., Hatcher, P.G., 1985. Degradation of carbohydrates and lignins in buried woods. Geochimica et Cosmochimica Acta 49, 701–711.

Heimhofer, U., Hochuli, P.A., Burla, S., Andersen, N., Weissert, H., 2003. Terrestrial carbon-isotope records from coastal deposits (Algarve, Portugal): a tool for chemostratigraphic correlation on an intrabasinal and global scale. Terra Nova 15, 8–13.

Hemsley, A.R., Poole, I. (Eds.), 2004. The Evolution of Plant Physiology. From Whole Plants to Ecosystems. Linnean Society Symposium Series, vol. 21. Academic Press, London.

Hesselbo, S.P., Morgans-Bell, H.S., McElwain, J.C., McAllister Rees, P., Robinson, S.A., Ross, C.E., 2003. Carbon-cycle perturbation in the Middle Jurassic and accompanying changes in the Terrestrial Paleoenvironment. The Journal of Geology 111, 259–276.

Hilton, J., 1998. Review of the fossil evidence for the origin and earliest evolution of the seed-plants. Acta Botanica Sinica 40, 981–987.

Hoefs, J., Frey, M., 1976. The isotopic composition of carbonaceous matter in a metamorphic profile from the Swiss Alps. Geochimica et Cosmochimica Acta 40, 945–951.

Jahren, A.H., Porter, S., Kuglitsch, J.J., 2003. Lichen metabolism identified in Early Devonian terrestrial organisms. Geology 31 (2), 99–102.

Jones, T.P., 1994. ^{13}C enriched Lower Carboniferous fossil plants from Donegal, Ireland: carbon isotope constraints on taphonomy, diagenesis and palaeoenvironment. Review of Palaeobotany and Palynology 81, 53–64.

Jones, T.P., Chaloner, W.G., 1991. Fossil charcoal, its recognition and palaeoatmospheric significance. Global and Planetary Change 97, 39–50.

Keeley, J.E., Rundel, P.W., 2003. Evolution of CAM and C_4 carbon concentrating mechanisms. International Journal of Plant Sciences 164 (3 Suppl.), 555–577.

Kerp, H., 1990. The study of fossil gymnosperms by means of cuticular analysis. Palaios 5, 548–569.

Kerp, H., 1996. Post-Variscan late Palaeozoic Northern Hemisphere gymnosperms: the onset to the Mesozoic. Review of Palaeobotany and Palynology 90, 263–285.

Kidder, D.L., Worsley, T.R., 2004. Causes and consequences of extreme Permo-Triassic warming to globally equable climate and relation to the Permo-Triassic extinction and recovery. Palaeogeography, Palaeoclimatology, Palaeoecology 203, 207–237.

Körner, C., Farquhar, G.D., Wong, S.C., 1991. Carbon isotope discrimination by plants follows latitudinal and altitudinal trends. Oecologia 88, 30–40.

Korte, C., Veizer, J., Leythaeuser, D., Below, R., Schwark, L., 2001. Evolution of Permian and Lower Triassic δ^{13}C in marine and terrigenous organic material. Terra Nostra 2001/4, 30–34.

Kotarba, M.J., 1990. Isotopic geochemistry and habitat of the natural gases from the Upper Carboniferous Zacler coal-bearing formation in the Nowa Ruda coal district (Lower Silesia, Poland). Organic Geochemistry 16, 549–560.

Krull, E.S., 1998. Paleoenvironmental and carbon isotopic studies (δ^{13}Corg) from terrestrial and marine strata across the Permian-Triassic boundary in Antarctica and New Zealand. Ph.D. Thesis, University of Oregon, Eugene, USA.

Kump, L.R., Brantley, S.L., Arthur, M.A., 2000. Chemical Weathering, Atmospheric CO_2, and Climate. Annual Review of Earth and Planetary Sciences 28, 611–667.

Kuypers, M.M.M., Pancost, R.D., Sinninghe-Damsté, J.S., 1999. A large and abrupt fall in atmospheric CO_2 concentration during Cretaceous times. Nature 399, 342–345.

Lasaga, A.C., Ohmoto, H., 2002. The oxygen geochemical cycle: dynamics and stability. Geochimica et Cosmochimica Acta 66, 361–381.

Lecuyer, C., Paris, F., 1997. Variability in the δ^{13}C of lower Palaeozoic palynomorphs; implications for the interpretation of ancient marine sediments. Chemical Geology 138, 161–170.

Lehmann, M.F., Bernasconi, S.M., Barbieri, A., McKenzie, J.A., 2002. Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. Geochimica et Cosmochimica Acta 66, 3573–3584.

Lenton, T.M., Watson, A.J., 2000. Redfield revisited: 2. What regulates the oxygen content of the atmosphere? Global Biogeochemical Cycles 14, 249–268.

Lorimer, G.H., 1981. The carboxylation and oxygenation of ribulose-1,5-bisphosphate: the primary events in photosynthesis and photorespiration. Annual Review of Plant Physiology 32, 349–382.

Maass, I., Künstner, E., Hübner, H., Nitzsche, H.-M., Schütze, H., Zschiesche, M., 1975. Der Einfluβ der petrographischen Zusammensetzung von Kohlen und bituminösen Sedimenten auf die stoffliche und isotope Zusammensetzung von Inkohlungsgasen künstlicher Nachinkohlungsreaktionen. Zeitschrift für angewandte Geologie 21, 472–481.

Mastalerz, M., Kvale, E.P., Stankiewicz, B.A., Portle, K., 1999. Organic geochemistry in Pennsylvanian tidally-influenced sediments from SW Indiana. Organic Geochemistry 30, 57–73.

Maynard, J.B., 1981. Carbon isotopes as indicators of dispersal patterns in Devonian–Mississippian shales of the Appalachian Basin. Geology 9, 262–265.

Menning, M., German Stratigraphic Commission, 2002. A geologic timescale 2002. In: German Stratigraphic Commission (Ed.), Stratigraphic Table of Germany 2002. GeoForschungsZentrum (GFZ), Potsdam.

Mii, H.-S., Grossman, E.L., Yancey, T.E., Chuvashov, B., Egorov, A., 2001. Isotopic records of brachiopod shells from the Russian Platform — evidence for the onset of mid-Carboniferous glaciation. Chemical Geology 175, 133–147.

Monin, J.C., Boudou, J.P., Durand, B., Oudin, J.L., 1981. Example of the enrichment of carbon-13 in coals in the process of coalification. Fuel 60, 957–960.

Montañez, I.P., Tabor, N.J., Ekart, D., Collister, J.W., 2000. Evolution of Permian atmospheric pCO_2 as derived from Permo-Pennsylvanian pedogenic proxies. In: (anonymous) IGC 31, Rio de Janeiro, August 2000, extended abstracts volume.

Mora, C.I., Driese, S.G., Colarusso, L.A., 1996. Middle to Late Paleozoic atmospheric CO_2 levels from soil carbonate and organic matter. Science 271, 1105–1107.

Morante, R., Veevers, J.J., Andrew, A.S., Hamilton, P.J., 1994. Determination of the Permian-Triassic boundary in Australia from carbon isotope stratigraphy. The APEA Journal 34, 330–336.

Nambudiri, E.M.V., Tidwell, W.D., Smith, B.N., Hebbert, N.P., 1978. A C_4 plant from the Pliocene. Nature 276, 816–817.

Nguyen Tu, T.T., Kvaèek, J., Ulièný, D., Bocherens, H., Mariotti, A., Broutin, J., 2002. Isotope reconstruction of plant palaeoecology: a case study of Cenomanian floras from Bohemia. Palaeogeography, Palaeoclimatology, Palaeoecology 183, 43–70.

O'Leary, M.H., 1988. Carbon isotopes in photosynthesis. Bioscience 38, 328–336.

Pataki, D.E., Ehleringer, F.R., Flanagan, L.B., Yakir, D., Bowling, D.R., Still, C.J., Buchmann, N., Kaplan, J.O., Berry, J.A., 2003. The application and interpretation of Keeling plots in terrestrial carbon cycle research. Global Biogeochemical Cycles 17 (1), 1–15 (2001GB001850.9).

Poole, I., Van Bergen, P.F.,Kool, J., Schouten, S., Cantrill, D.J., 2004. Molecular isotopic heterogeneity of fossil organic matter: implications for $\delta^{13}C_{\text{biomass}}$ and $\delta^{13}C_{\text{palaeoatmosphere}}$ proxies. Organic Geochemistry 35, 1261–1274.

Popp, B.N., Anderson, T.F., Sandberg, P.A., 1986. Brachiopods as indicators of original isotopic compositions in some Paleozoic limestones. Geological Society of America Bulletin 97, 1262–1269.

Raven, J.A., 1991. Plant responses to high O_2 concentrations: relevance to previous high O_2 episodes. Global and Planetary Change 97, 19–38.

Raven, J.A., 2002. Evolutionary options. Nature 415, 375–376.

Raven, J.A., Edwards, D., 2001. Roots: evolutionary origins and biogeochemical significance. Journal of Experimental Botany 52, 381–401.

Redding, C.E., Schoell, M., Monin, J.C., Durand, B., 1980. Hydrogen and carbon isotopic composition of coals and kerogens. Physics and Chemistry of the Earth 12, 711–723.

Robinson, J.M., 1990. The burial of organic carbon as affected by the evolution of land plants. Historical Biology 3, 189–201.

Robinson, S.A., Hesselbo, S.P., 2004. Fossil-wood carbon-isotope stratigraphy of the non-marine Wealden Group (Lower Cretaceous, southern England). Journal of the Geological Society (London) 161, 133–145.

Rowe, N.P., 2000. The insides and outsides of plants: the long and chequered evolution of secondary growth. In: Spatz, H.-C., Speck, T. (Eds.), Plant biomechanics 2000. Proceedings of the 3rd plant biomechanics conference, Freiburg-Badenweiler. Thieme, Stuttgart, New York, pp. 129–140.

Sage, R.F., 2004. The evolution of C_4 photosynthesis. New Phytologist 161 (2), 341–370.

Saltzman, M.R., Groessens, E., Zhuravlev, A.V., 2004. Carbon cycle models based on extreme changes in δ^{13}C: an example from the lower Mississippian. Palaeogeography, Palaeoclimatology, Palaeoecology 213, 359–377.

Schleser, G.H., Frielingsdorf, J., Blair, A., 1999. Carbon isotope behavior in wood and cellulose during artificial ageing. Chemical Geology 158, 121–130.

Scholle, P., Arthur, M.A., 1980. Carbon isotopic fluctuations in pelagic limestones: potential stratigraphic and petroleum exploration tool. Memoir - American Association of Petroleum Geologists 64, 67–87.

Schwarzkopf, T., Schoell, M., 1985. Die Variation der C-und H-Isotopenverhältnisse in Kohlen und deren Abhängigkeit von Maceralzusammensetzung und Inkohlungsgrad. Fortschritte in der Geologie von Rheinland und Westfalen 33, 161–168.

Scotese, C.R., 2002. Paleomap Project. http://www.scotese.com2002.

Scott, A.C., 1979. The ecology of the coal measures floras from northern Britain. Proceedings of the Geologists' Association 90, 97–116.

Sephton, M.A., Looy, C.V., Veefkind, F.J., Brinkhuis, H., De Leeuw, J.W., Visscher, H., 2002. Synchronous record of δ^{13}C shifts in the oceans and atmosphere at the end of the Permian. In: Koeberl, C., MacLead, K.G. (Eds.), Catastrophic Events and Mass Extinctions: Impacts and Beyond. Geological Society of

America Special Paper, vol. 356. Geological Society of America, Boulder, pp. 455–462.

Stott, L.D., Sinha, A., Thiry, M., Aubry, M.-P., Berggren, W.A., 1996. Global δ^{13}C changes across the Paleocene–Eocene boundary: criteria for terrestrial–marine correlations. In: Knox, W.R.O'B., Corfield, R.M., Dunay, R.E. (Eds.), Correlation of the Early Paleogene in Northwest Europe. Geological Society Special Publication, vol. 101. Geological Society, London, pp. 381–399.

Strauss, H., Peters-Kottig, W., 2003. The Paleozoic to Mesozoic carbon cycle revisited: the carbon isotopic composition of terrestrial organic matter. Geochemistry, Geophysics, Geosystems 4 (10), 1–15 (2003GC000555).

Strauss, H., Des Marais, D.J., Lambert, I.B., Hayes, J.M., Summons, R.E., 1992. Procedures of whole rock and kerogen analysis. In: Schopf, J.W., Klein, C. (Eds.), The Proterozoic Biosphere: A Multidisciplinary Study. Cambridge University Press, Cambridge, New York, pp. 699–707.

Streel, M., Caputo, M.V., Loboziak, S., Melo, J.H.G., 2000. Late Frasnian-Famennian climates based on palynomorph analyses and the question of the Late Devonian glaciations. Earth-Science Reviews 52, 121–173.

Tabor, N.J., Yapp, C.J., Montañez, I.P., 2004. Goethite, calcite, and organic matter from Permian and Triassic soils: carbon isotopes and CO_2 concentrations. Geochimica et Cosmochimica Acta 68, 1503–1517.

Taylor, T.N., Taylor, E.L., 1993. The Biology and Evolution of Fossil Plants. Prentice Hall, New Jersey.

Taylor, G.H, Teichmüller, M., Davis, A., Diessel, C.F.K, Littke, R., Robert, P., 1998. Organic Petrology. Gebrüder Borntraeger, Berlin-Stuttgart.

Thomasson, J.R., Nelson, M.E., Zakrezewski, R.J., 1988. A fossil grass (Gramineae: Chloridoideae) from the Miocene with Krantz anatomy. Science 233, 876–878.

Turekian, V.C., Macko, S., Ballentine, D., Swap, R.J., Garstang, M., 1998. Causes of bulk carbon and nitrogen isotopic fractionations in the products of vegetation burns: laboratory studies. Chemical Geology 152, 181–192.

Tyson, R.V., 1995. Sedimentary Organic Matter. Organic facies and palynofacies. Chapman and Hall, London.

Van Bergen, P.F., Poole, I., 2002. Stable carbon isotopes of wood: a clue to palaeoclimate? Palaeogeography, Palaeoclimatology, Palaeoecology 182, 31–45.

Van der Water, P.W., Leavitt, S.W., Betancourt, J.L., 1994. Trends in stomatal density and ^{13}C/^{12}C ratios of Pinus flexilis needles during last glacial–interglacial cycle. Science 264, 239–243.

Veizer, J., Ala, D., Azmy, K., Bruckschen, P., Buhl, D., Bruhn, F., Carden, G.A.F., Diener, A., Ebneth, S., Godderis, Y., Jasper, T., Korte, C., Pawellek, F., Podlaha, O.G., Strauss, H., 1999. ^{87}Sr/^{86}Sr, δ^{13}C and δ^{18}O evolution of Phanerozoic seawater. Chemical Geology 161, 59–88.

Watanabe, Y., Naraoka, H., Wronkiewicz, D.J., Condie, K.C., Ohmoto, H., 1997. Carbon, nitrogen, and sulfur geochemistry of Archean and Proterozoic shales from the Kaapvaal Craton, South Africa. Geochimica et Cosmochimica Acta 61, 3441–3459.

Wellman, C.H., Richardson, J.B., 1993. Terrestrial plant microfossils from Silurian inliers of the Midland Valley of Scotland. Palaeontology 36, 155–193.

Wellman, C.H., Osterloff, P.L., Mohiuddin, U., 2003. Fragments of the earliest land plants. Nature 425, 282–285.

Wenger, L.M., Baker, D.R., Chung, H.M., McCulloh, T.H., 1988. Environmental control of carbon isotope variations in Pennsylvanian black-shale sequences, Midcontinent, U.S.A. Organic Geochemistry 13, 765–771.

Whiticar, M.J., 1996. Stable isotope geochemistry of coals, humic kerogens and related natural gases. International Journal of Coal Geology 32, 191–215.

Wildman Jr., R.A., Hickey, L.J., Dickinson, M.B., Berner, R.A., Robinson, J.M., Dietrich, M., Essenhigh, R.H., Wildman, C.B., 2004. Burning of forest materials under late Paleozoic high atmospheric oxygen levels. Geology 32 (5), 457–460.

Yapp, C.J., Poths, H., 1996. Carbon isotopes in continental weathering environments and variations in ancient atmospheric CO_2 pressure. Earth and Planetary Science Letters 137, 71–82.