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Devonian landscape heterogeneity recorded by a giant fungus

C. Kevin Boyce

Department of the Geophysical Sciences, University of Chicago, 5734 South Ellis Ave, Chicago, Illinois 60637, USA

Carol L. Hotton

Department of Paleobiology, NHB MRC 121, National Museum of Natural History, Washington, D.C. 20560, USA

Marilyn L. Fogel

George D. Cody

Robert M. Hazen

Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, D.C. 20015, USA

Andrew H. Knoll

Department of Organismic and Evolutionary Biology, Harvard University, 26 Oxford Street, Cambridge, Massachusetts 02138, USA

Francis M. Hueber

Department of Paleobiology, NHB MRC 121, National Museum of Natural History, Washington, D.C. 20560, USA

ABSTRACT

The enigmatic Paleozoic fossil *Prototaxites* Dawson 1859 consists of tree-like trunks as long as 8 m constructed of interwoven tubes <50 μm in diameter. *Prototaxites* specimens from five localities differ from contemporaneous vascular plants by exhibiting a carbon isotopic range, within and between localities, of as much as 13‰ $\delta^{13}C$. Pyrolysis–gas chromatography–mass spectrometry highlights compositional differences between *Prototaxites* and co-occurring plant fossils and supports interpretation of isotopic distinctions as biological rather than diagenetic in origin. Such a large isotopic range is difficult to reconcile with an autotrophic metabolism, suggesting instead that, consistent with anatomy-based interpretation as a fungus, *Prototaxites* was a heterotroph that lived on isotopically heterogeneous substrates. Light isotopic values of *Prototaxites* approximate those of vascular plants from the same localities; in contrast, heavy extremes seen in the Lower Devonian appear to reflect consumption of primary producers with carbon-concentrating mechanisms, such as cryptobiotic soil crusts, or possibly bryophytes. *Prototaxites* biogeochemistry thus suggests that a biologically heterogeneous mosaic of primary producers characterized land surfaces well into the vascular plant era.

Keywords: *Prototaxites*, terrestrial ecosystems, isotope geochemistry, Paleozoic, paleobotany, paleoecology.

INTRODUCTION

From its origin in the Late Silurian more than 420 m.y. ago until the evolution of large trees ~50 m.y. later, *Prototaxites* was the largest organism known to have lived on land (Fig. 1A; GSA Data Repository Fig. DR1[1]). It produced unbranched trunks as long as 8 m and 1 m in diameter, constructed only of a relatively homogenous tissue of interwoven tubes of three size classes, 5–50 µm in diameter (Fig. 1B). Although originally described as a conifer (Dawson, 1859), its distinctive anatomy is utterly unlike any living or fossil land plant. Subsequent interpretations as a lichen, a red, green, or brown alga, or a fungus (Carruthers, 1872; Church, 1919; Jonker, 1979; Hueber, 2001) are also problematic. For example, interpretation of *Prototaxites* as a giant fungal fruiting body (Hueber, 2001) accounts for its hyphae-like anatomy, but remains controversial (e.g., Selosse, 2002) because its sheer size and lack of clear reproductive structures are more difficult to reconcile. The identity of *Prototaxites* may never be proven by anatomy alone (save for consensus it was not a vascular plant); its bizarre form is the very source of its enduring interest. Carbon isotopic and organic analyses of *Prototaxites* fossils provide a morphology-independent assessment of its evolutionary relationships and indirect evidence for the nature of its surrounding ecosystem.

The organic composition of fossils can be influenced as much by locality of preservation as by original biology (Abbott et al., 1998), but comparison of multiple specimens within individual localities controls for factors that might influence preserved C isotopic or organic chemistry, including diagenesis and variations in climate, background inorganic $^{12}C/^{13}C$, or atmospheric CO_2 concentration (Boyce et al., 2002, 2003). To this end, organic and isotopic comparisons were made between *Prototaxites* and associated vascular plants (two vascular plant derived coals, silicified *Callixylon*, and carbonate-permineralized *Psilophyton*) within one Upper Devonian and two Lower Devonian localities (ca. 375 Ma and 405–400 Ma, respectively). *Prototaxites* isotopes also were analyzed from two Lower Devonian localities for which no other fossils were associated. Carbon isotopes reflect in part the organism's metabolism. Organic analyses further constrain the risk that isotopic composition was unduly affected by differential taphonomic history within a locality. All *Prototaxites* samples are permineralized by silica and preserve anatomy in fine detail, with organic material confined to the tube walls (e.g., Fig. 1C). Samples for isotopic analysis were treated in acid to eliminate any carbonate. Further information concerning samples and methods is in the GSA Data Repository (see footnote 1).

Comparative Geochemistry of Fossils

In the Upper Devonian Kettle Point flora, *Prototaxites* is isotopically similar to the associated woody plant *Callixylon* (and Devonian plants more broadly; Beerling et al., 2002;

Boyce et al., 2003), consistent with either a C_3-like photosynthetic organism or a heterotroph that consumed C_3 plants (Fig. 2). In contrast, *Prototaxites* samples from the Lower Devonian (Emsian, ca. 400 Ma) Gaspé south shore flora are either isotopically similar to co-occurring *Psilophyton* and coal or as much as 11‰ heavier. This enormous range is replicated in other Lower Devonian localities: *Prototaxites* isotopes resemble those of C_3 plants at two localities, but are 8‰ heavier than a surrounding coal composed of spiny vascular plant axes at a third locality (Fig. 2).

Molecular structural information derived from pyrolysis–gas chromatography–mass spectrometry of the Gaspé coal (Fig. 3) is consistent with a predominance of lignin-derived geopolymers. The strong prevalence of alkylphenols over dihydroxy aromatics (note trace of eugenol) as well as a complete lack of levoglucosan (a pyrolytic product of cellulose) indicates that the original peat was altered diagenetically to high-rank subbituminous to low-rank high volatile bituminous coal. Although Gaspé *Prototaxites* samples also yield predominantly alkylbenzene, alkylphenol, and alkylnaphthalene moieties, their relative distributions are distinct from the coal and are dominated by alkyl benzenes rather than phenol derivatives. *Prototaxites* and the vascular plant *Callixylon* are similarly distinct at the Upper Devonian locality (Fig. 3). A robust molecular interpretation linking original biochemistry to the specific distribution of molecular species in diagenetically altered material is incomplete even in the well-studied system of vascular plant–derived coal (Hatcher and Clifford, 1997), much less the various potential relatives of *Prototaxites*. However, this consistent predominance of akyl-phenols versus alkyl-benzenes in organic matter from the same strata and geologic histories must reflect derivation from biochemically distinct original source organisms.

Extensive taphonomic alteration of organic C isotopic ratios typically involves loss of compounds or constituent functional groups with distinct biosynthetic fractionations (Benner et al., 1987). *Prototaxites* samples spanning a C isotopic range from −15.6‰ to −26.6‰ are all similarly dominated by alkyl benzenes and are clearly differentiated from a local, vascular plant–derived coal, reflecting differences maintained from their original biochemical inheritance. Any extreme and divergent taphonomic modification between specimens—such as methanogenic decay of some, but not all of the individuals—also should have been reflected in the final organic composition, but is not seen. This, along with the uniformly high quality of anatomic preservation, argues that isotopically distinct populations record underlying features of original physiology, not differential taphonomy.

Biological Affinity of *Prototaxites*

For each *Prototaxites* sample, photosynthetic organisms with similar isotopic discriminations can be identified: lighter values are consistent with terrestrial C_3 photosynthesis and heavier values are consistent with various groups with carbon-concentrating mechanisms. Nonetheless, the overall isotopic range of the *Prototaxites* population is difficult to reconcile with autotrophy. C_4 and CAM **[[Q: spell out CAM first time used?]]**plants concentrate carbon, but in neither does isotopic variation resemble that of *Prototaxites* (O'Leary, 1988). Macrophytic marine algae can accommodate a larger range of values (Raven et al., 2002), but *Prototaxites* is usually preserved in terrestrial deposits (Griffing et al., 2000; Hotton et al., 2001), and both ecological and geochemical arguments suggest that it was subaerial (Niklas, 1976; Edwards and Richardson, 2000; Hueber, 2001). Moreover, the broad isotopic spread of algae is related to variations in inorganic carbon source—ranging from HCO_3^- pumping to aqueous diffusion of

CO_2—unlikely to be encompassed by a single population, particularly of large terrestrial organisms.

Both CO_2 limitation and a shift in background inorganic $^{13}C/^{12}C$ could result in more enriched values within an organism, but neither was likely in a Lower Devonian world with an atmospheric CO_2 concentration of 8–10 times modern levels (McElwain and Chaloner, 1995) and C isotopic values of 0‰ to +2‰ for marine carbonates (Veizer et al., 1999), and neither could explain observed isotopic variation within a single assemblage. Rather, the large C isotopic range measured for Lower Devonian *Prototaxites* strongly suggests that this organism was a heterotroph that lived on isotopically distinct substrates: in this context, a fungus. Given its survival of fluvial transport and deposition (Griffing et al., 2000), *Prototaxites*, if fungal, was more akin to a robust, perennial bracket fungus than an ephemeral mushroom.

Early Devonian Ecosystems

The isotopic range of Lower Devonian *Prototaxites* is difficult to reconcile with consumption of a uniform photosynthetic substrate. Lower Devonian terrestrial faunas were vertebrate free and consisted primarily of arthropod detritivores and predators (Shear and Selden, 2001), so trophic enrichment is an unlikely source for variation. Substantial isotopic distinctions between fungi growing on the same substrate could result from digestion of different biochemical components (Hobbie et al., 1999), such as cellulose versus lignin—as in brown and white wood rots. However, most Devonian fungi are small and contained within the host (Taylor et al., 2004) and only white rot is known among the larger fungi capable of extensive translocation (Stubblefield and Taylor, 1988). Furthermore, distinct saprophytic metabolisms are typically employed by different higher-level fungal lineages (Eriksson et al., 1990), not different individuals of the same population. Even if distinct metabolisms were assumed for *Prototaxites* individuals, 4‰–8‰ would be the maximum expected isotopic range for degradation of distinct plant components (Benner et al., 1987), not the 11‰ seen among Gaspé specimens.

Depleted *Prototaxites* isotopic values are consistent with consumption of C_3 land plants, but enriched Early Devonian specimens require consumption of autotrophs with a carbon-concentrating mechanism. All CAM and C_4 plants appeared long after the Devonian. Terrestrial lichens have intermediate C isotope discrimination, whether with chlorophyte or cyanobacterial symbionts, and are not consistent with enriched *Prototaxites* values (Jahren et al., 2003; Fletcher et al., 2004). Most bryophytes are even more depleted than C_3 tracheophytes (Jahren et al., 2003; Fletcher et al., 2004), but the enriched *Prototaxites* values can be approached by some hornworts when water saturated due to a pyrenoid-based carbon-concentration mechanism (Smith and Griffiths, 1996). Hornworts are unknown before the Cretaceous, but stem-group embryophytes in general extend back at least to the Ordovician (Gray, 1993; Edwards et al., 1995; Wellman et al., 2003).

Enriched *Prototaxites* isotopic values are broadly consistent with consumption of cyanobacteria-dominated microbial soil crusts (Evans and Belnap, 1999). Moreover, mats can be prolific sources of sugars, a preferred substrate for fungal growth that tends to have ^{13}C enriched relative to total biomass (van der Meer et al., 2003). Today, microbial crusts and bryophytes dominate only where vascular plants are excluded (Campbell, 1979; Evans and Belnap, 1999), but they were likely distributed broadly prior to vascular plant evolution (Horodyski and Knauth, 1994; Tomescu and Rothwell, 2006). These alternative sources of primary production are rarely considered for ecosystems that postdate the Silurian appearance of vascular plants, except for some mention of intercalation among vascular plant dominants and debate over how rapidly vascular plants spread from wet lowland environments (Griffing et al., 2000; Edwards and

Richardson, 2004). Sedimentology may constrain this transition (Retallack, 1985; Love and Williams, 2000), but the overall narrative is driven by a megafossil record dominated by vascular plants, rather than any positive evidence for displacement of other primary producers. Given prodigious nutrient translocation in fungal mycelia (Boswell et al., 2002), consumption of a substrate consisting of soil crusts intercalated between vascular plants would result in a *Prototaxites* of an averaged intermediate isotopic composition, as would an ephemeral cyanobacterial scum before vascular plants are reestablished after disturbance. Instead, enriched *Prototaxites* values suggest a strict absence of C_3 photosynthesis in persistent, spatially contiguous landscape patches (perhaps quite large given the potential of modern colonies; Smith et al., 1992). One-third of our upper-Lower Devonian *Prototaxites* specimens provide an isotopic record of heterotrophic growth on a nonvascular, non-C_3 substrate, 30–40 m.y. after the Silurian appearance of vascular plants, sampling communities that otherwise would have little chance of fossil preservation. Isotopic analysis of terrestrial arthropods may provide independent evidence for varied sources of Devonian primary production and, together with further sampling of *Prototaxites*, may reveal changing patterns of substrate use through time.

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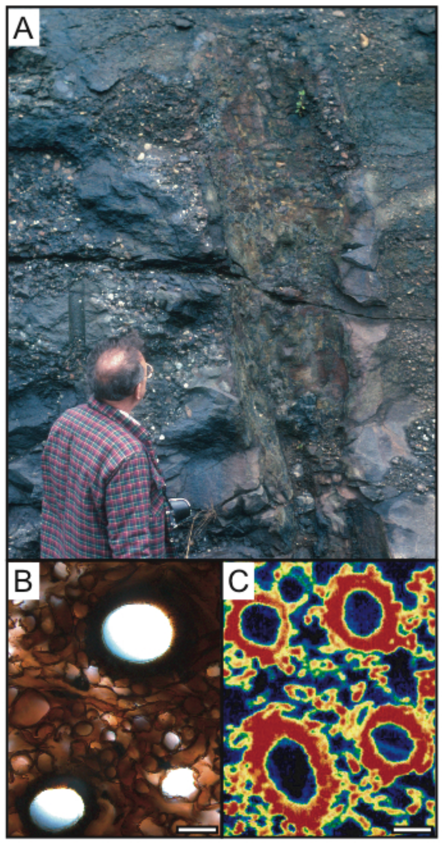
FIGURE CAPTIONS

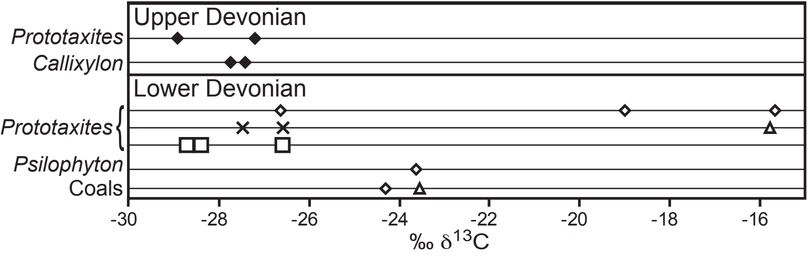
Figure 1. A: Lower Devonian *Prototaxites* fossil in situ, Bordeaux Quarry, Quebec. B: Optical image of carbon abundance of *Prototaxites* anatomy in cross section. Scale bar = 20 μm. C: Electron probe map of carbon abundance of *Prototaxites* anatomy in cross section. Scale bar = 20 μm. In electron probe map, red indicates high and blue-black indicates slow abundance of carbon, qualitatively demonstrating confinement of organic matter to tube walls. **[[Q: In figure A, person in photo could be sitting or standing, so scale really should be more specific; would be helpful if specific area of fossil was indicated or outlined]]**

Figure 2. Carbon isotopic values for *Prototaxites* and associated vascular plants *Callixylon* and *Psilophyton* and coal. Upper Devonian fossils are from Kettle Point, Ontario (Frasnian–lower Fammenian). Lower Devonian (primarily Emsian) fossils are from south shore of Gaspé Peninsula, Quebec (diamonds), north shore of Gaspé Peninsula (squares), Baxter State Park, Maine (Xs), and Pin Sec Point, New Brunswick (triangles). Each symbol represents average of two samples from single specimen. Based on acetanilide standards, analytical error associated with each measurement is ±0.2‰. Details in Table DR1 (see footnote 1).

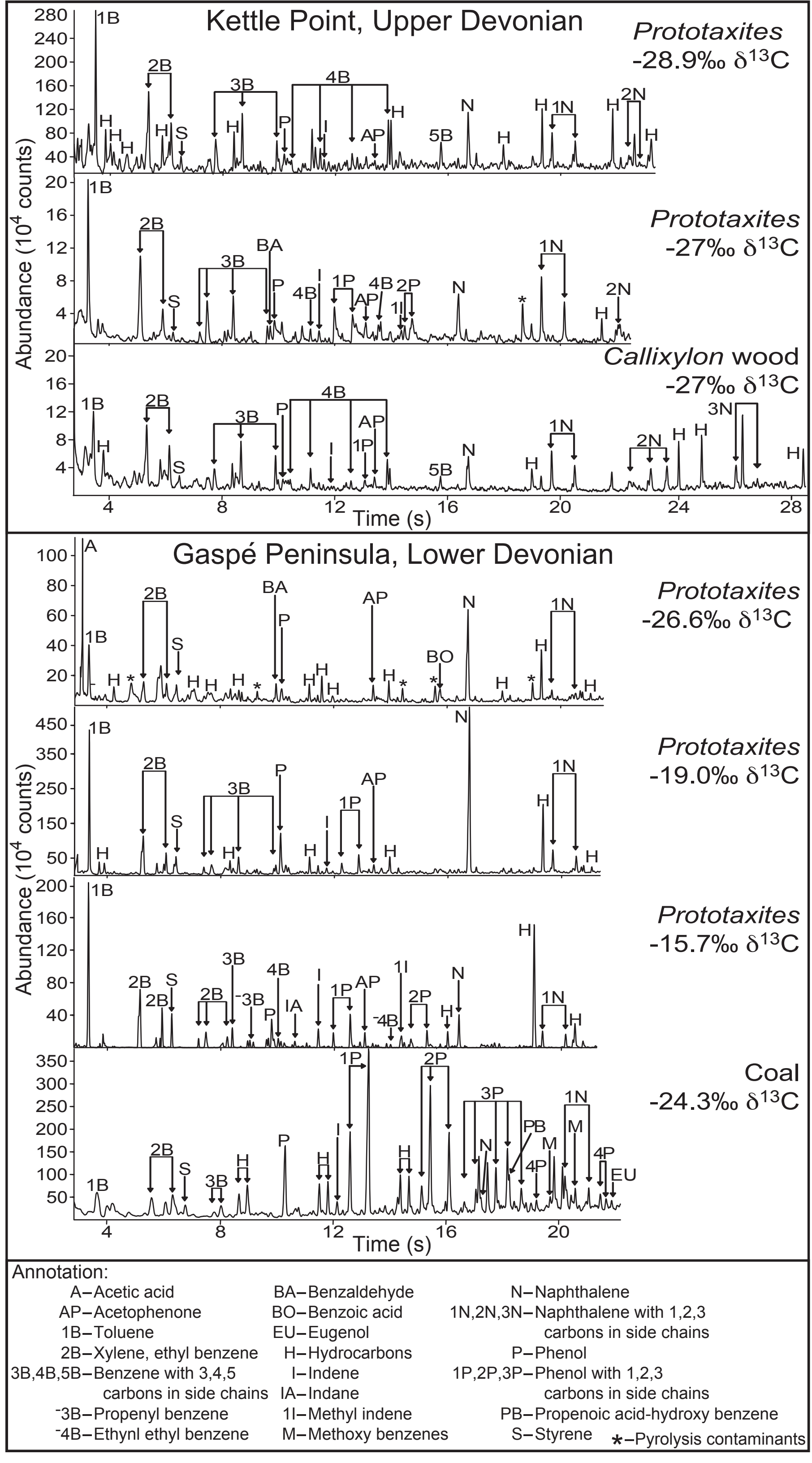
Figure 3. Stacked gas chromatography–mass spectrometry (GC-MS) chromatograms of pyrolysate (plotted as total ion count vs. retention time) of Lower Devonian Gaspé and Upper Devonian Kettle Point samples. Identities of various molecular groups are highlighted and references cited in legend. Labeled contaminants are polydimethyl siloxane products resulting from reaction of HCl released from pyrolyzed minerals with various internal septa of GC-MS; they could not have contributed to isotopic measurements because they are not present in original samples. **[[Q: There are no references cited "in legend" in figure; should this be "Identities…are highlighted and defined in legend"? Or "…highlighted and annotated…"? Note that peninsula should be uppercase; should be 1-ems in key; seconds should be s.]]**

[1]GSA Data Repository item 2007xxx, Figure DR1 and Table DR1, is available online at www.geosociety.org/pubs/ft2007.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA. **[[Q: any other item to be listed? (Line 66 mentions "samples and methods"; is there a separate appendix?). Need item descriptions.]]**


A
B
C

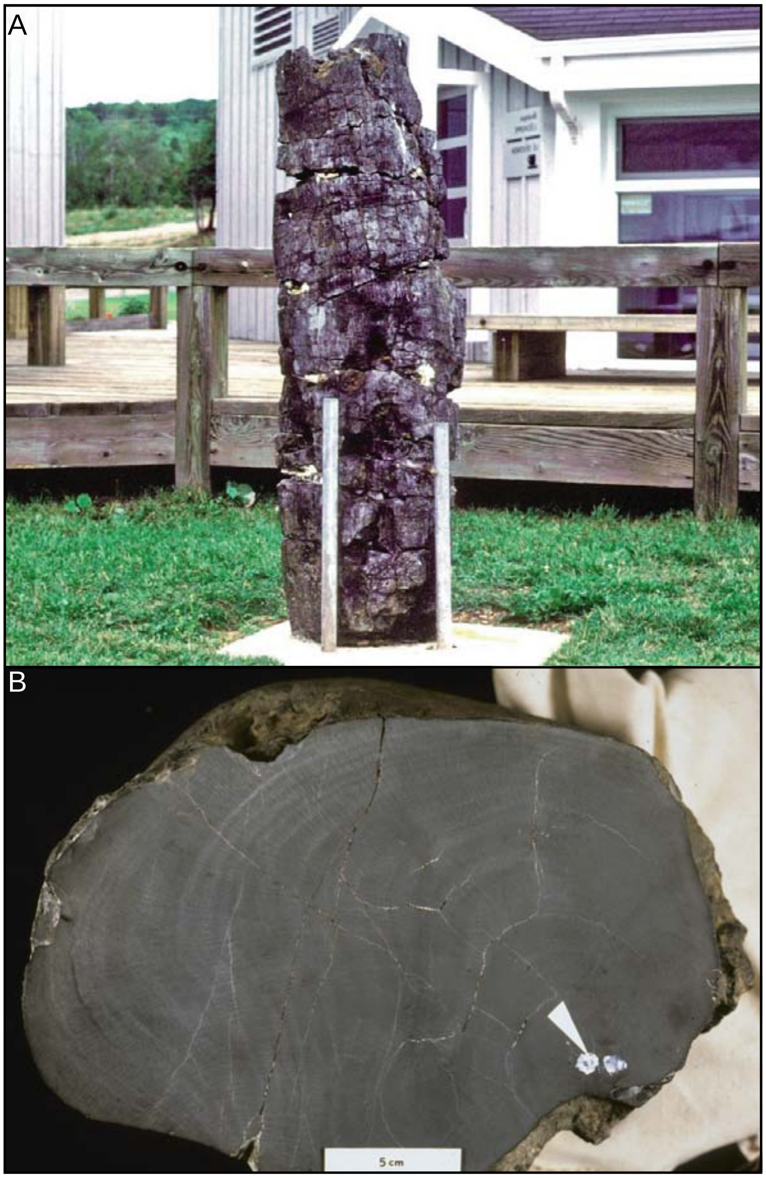


Upper Devonian
Prototaxites
Callixylon
Lower Devonian
Prototaxites
Psilophyton
Coals
-30
-28
-26
-24
-22
-20
-18
-16
‰ δ13C



Kettle Point, Upper Devonian
Prototaxites
-28.9‰ δ13C
Prototaxites
-27‰ δ13C
Callixylon wood
-27‰ δ13C
Abundance (10⁴ counts)
Time (s)
Gaspé Peninsula, Lower Devonian
Prototaxites
-26.6‰ δ13C
Prototaxites
-19.0‰ δ13C
Prototaxites
-15.7‰ δ13C
Coal
-24.3‰ δ13C
Abundance (10⁴ counts)
Time (s)
Annotation:
A–Acetic acid
AP–Acetophenone
1B–Toluene
2B–Xylene, ethyl benzene
3B,4B,5B–Benzene with 3,4,5 carbons in side chains
⁻3B–Propenyl benzene
⁻4B–Ethynl ethyl benzene
BA–Benzaldehyde
BO–Benzoic acid
EU–Eugenol
H–Hydrocarbons
I–Indene
IA–Indane
1I–Methyl indene
M–Methoxy benzenes
N–Naphthalene
1N,2N,3N–Naphthalene with 1,2,3 carbons in side chains
P–Phenol
1P,2P,3P–Phenol with 1,2,3 carbons in side chains
PB–Propenoic acid-hydroxy benzene
S–Styrene
*–Pyrolysis contaminants

SUPPLEMENTAL FIGURE 1



Supplemental Figure 1. A, Fragment of a permineralized *Prototaxites* trunk displayed at Parc de Miguasha, from the Lower Devonian Bordeaux Quarry, near Cross Point, Quebec, Canada, approximately 1.5 m high. B, Portion of a large permineralized *Prototaxites* trunk in cross section showing the concentric banding of peripheral accretionary growth. White arrow indicates center of the axis. Specimen from Bordeaux Quarry (Parc de Miguasha collection).

METHODS

Samples for isotopic and organic analyses were obtained from permineralized fossils and powdered with mortar and pestle. Powdered samples for isotopic analysis were treated with 5% HCl to eliminate the possibility of carbonate contamination. All tools were cleaned by sonication in hexane for 15 minutes before use, except for the delicate sample boats for isotopic analyses which were sonicated in hexane for 1 minute. Fossils were washed with hexane but not sonicated. The surfaces of fossils and all equipment were rinsed with ethanol and allowed to air dry after the collection of each sample.

Isotopic measurements were made with a Finnigan Delta Plus Excel isotope ratio mass spectrometer with a CE Instruments, NA 2500 series, elemental analyzer and a Conflo II interface. The gas chromatograph oven was set to 60° C for the fossil samples. Acetanilide standards were only included at the beginning of each set of analyses (followed by 2 or 3 blank sample boats) and at the end after all fossil samples had been run in order to eliminate the possibility that trace residue from the carbon-rich acetanilide standards might contaminate fossil samples.

Pyrolysis Gas Chromatography-Mass Spectrometry (GC-MS) was performed with an Agilient 6890 GC interfaced with an Agilent 5972 quadrupole mass spectrometer. Samples were pyrolyzed using a CDS-1000 pyroprobe where 0.5-3 mg samples were heated to 715 °C with a heating rate of 500 °C/sec under helium at the injection port of the GC. Chromatography was performed with a 50 % phenyl polydimethylsiloxane stationary phase column.

Maps of elemental composition in standard fossil thin sections obtained using a JEOL 8900 electron microprobe with five wavelength dispersive spectrometers. Electron probe measurements interact only with the sample surface, are no more than semi-quantitative, and are intended only to illustrate confinement of carbon to the organic tube walls and absence of dispersed carbonate (which would recognizably dwarf organic carbon concentrations if present). Analyses were performed at 15 KeV. Following modifications of standard procedures described previously (Boyce et al. 2001), samples were aluminum coated and an increased electron beam current of approximately 300 nA was employed in order to enhance detection of organic carbon.

Reference cited:

Boyce, C.K., Hazen, R.M., and Knoll, A.H., 2001, Nondestructive, in situ, cellular-scale mapping of elemental abundances including organic carbon in permineralized fossils: Proceedings of the National Academy of Sciences, v. 98, p. 5970-5974.

TABLE 1. SAMPLES AND CARBON ISOTOPIC COMPOSITION

Age*	Locality†	Specimen§	Curation#	δ ^{13}C (‰)
Frasnian/ Famennian	Kettle Point (ON)	*Prototaxites southworthii*	HBM 55852	-28.99 -28.83
Frasnian/ Famennian	Kettle Point (ON)	*Prototaxites southworthii*	USNM 510202	-27.87 -26.49
Frasnian/ Famennian	Kettle Point (ON)	*Callixylon newberryi*	USNM (unnumbered) Southworth collection	-27.79 -27.68
Frasnian/ Famennian	Kettle Point (ON)	*Callixylon newberryi***	USNM (unnumbered) Southworth collection	-27.51 -27.27
L.Emsian/ E.Eifelian	Baxter State Park (ME)	*Prototaxites* sp.	USNM (unnumbered) Hueber collection	-26.56 -26.56
L.Emsian/ E.Eifelian	Baxter State Park (ME)	*Prototaxites* sp.	USNM (unnumbered) Hueber collection	-27.82 -27.07
Emsian	Pin Sec Point (NB)	*Prototaxites loganii*	USNM 510099	-15.69 -15.83
Emsian	Pin Sec Point (NB)	Coal (of cf. *Sawdonia*)	USNM (unnumbered) Hueber locality 91-10	-23.23 -23.84
M./L.Emsian	Gaspé peninsula, North Shore (QC)	*Prototaxites loganii*	USNM (unnumbered) Hueber collection	-28.75 -28.10
M./L.Emsian	Gaspé peninsula, North Shore (QC)	*Prototaxites loganii*	USNM (unnumbered) Hueber collection	-28.61 -28.76
M./L.Emsian	Gaspé peninsula, North Shore (QC)	*Prototaxites loganii*	USNM (unnumbered) GSC locality†† 5388	-26.59 -26.59
M./L.Emsian	Gaspé peninsula, South Shore (QC)	*Prototaxites loganii*	USNM (unnumbered) Hueber locality 66-8	-26.60 -26.62
M./L.Emsian	Gaspé peninsula, South Shore (QC)	*Prototaxites loganii*	USNM 510202	-18.88 -19.07
M./L.Emsian	Gaspé peninsula, South Shore (QC)	*Prototaxites loganii*	USNM (unnumbered) SUNYB†† 1146.C-1.1	-15.64 -15.68
M./L.Emsian	Gaspé peninsula, South Shore (QC)	*Psilophyton princeps*	USNM (unnumbered) Hueber locality 66-8	-24.57 -22.58
L.Pragian/ E.Emsian	Gaspé peninsula, South Shore (QC)	Coal (of cuticularized axes)	USNM (unnumbered) Hueber locality 66-6	-24.32 -24.23

*E-Early, M-Middle, L-Late.
†ME-Maine, United States; NB-New Brunswick, ON-Ontario, QC-Quebec, Canada.
§All specimens silica permineralized (including Pin Sec Point coal) except for the unmineralized Gaspé coal and the Gaspé *Psilophyton,* which is permineralized in carbonate.
#All specimens loaned from USNM-Smithsonian National Museum of Natural History or HBM-Harvard Botanical Museum.
**Wood specimen with some fungal decay.
††GSC-Geological Society of Canada; SUNYB-State University of New York, Binghamton.