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THE RISE OF FIRE: FOSSIL CHARCOAL IN LATE DEVONIAN MARINE SHALES AS AN INDICATOR OF EXPANDING TERRESTRIAL ECOSYSTEMS, FIRE, AND ATMOSPHERIC CHANGE

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ABSTRACT. Fossil charcoal provides direct evidence for fire events that, in turn, have implications for the evolution of both terrestrial ecosystems and the atmosphere. Most of the ancient charcoal record is known from terrestrial or nearshore environments and indicates the earliest occurrences of fire in the Late Silurian. However, despite the rise in available fuel through the Devonian as vascular land plants became larger and trees and forests evolved, charcoal occurrences are very sparse until the Early Mississippian where extensive charcoal suggests well-established fire systems. We present data from the latest Devonian and Early Mississippian of North America from terrestrial and marine rocks indicating that fire became more widespread and significant at this time. This increase may be a function of rising O_2 levels and the occurrence of fire itself may have contributed to this rise through positive feedback. Recent atmospheric modeling suggests an O_2 low during the Middle Devonian (around 17.5%), with O_2 rising steadily through the Late Devonian and Early Mississippian (to 21–22%) that allowed for widespread burning for the first time. In Devonian-Mississippian marine black shales, fossil charcoal (inertinite) steadily increases upsection suggesting the rise of widespread fire systems. There is a concomitant increase in the amount of vitrinite (preserved woody and other plant tissues) that also suggests increased sources of terrestrial organic matter. Even as end Devonian glaciation was experienced, fossil charcoal continued to be a source of organic matter being introduced into the Devonian oceans. Scanning electron and reflectance microscopy of charcoal from Late Devonian terrestrial sites indicate that the fires were moderately hot (typically 500 – 600 °C) and burnt mainly surface vegetation dominated by herbaceous zygopterid ferns and lycopsids, rather than being produced by forest crown fires. The occurrence and relative abundance of fossil charcoal in marine black shales are significant in that these shales may provide a more continuous record of fire than is preserved in terrestrial environments. Our data support the idea that major fires are not seen in the fossil record until there is both sufficient and connected fuel and a high enough atmospheric O_2 content for it to burn.

Keywords: wildfire, charcoal, black shale, Devonian, oxygen levels

INTRODUCTION

Fire plays a significant role in the Earth system (Bowman and others, 2009; Scott and others, 2014) not only in the regulation of plant biome distribution (Bond and Keeley, 2005) and in the evolution of plants and fire-prone vegetation (Pausas and Keeley, 2009; Bond and Scott, 2010), but also in the regulation of atmospheric oxygen

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(O_2) (Lenton and Watson, 2000; Berner and others, 2003; Lenton, 2013). The origin of widespread fire systems is significant in our understanding of the evolution of both terrestrial ecosystems and the atmosphere (Blecher and others, 2013; Scott and others, 2014). Berner and others (2003) discussed an important positive feedback loop in the relationship between fire and O_2. As O_2 rises, more fires occur, leading to increased charcoal production and burial; this carbon burial would contribute to further increases in O_2. Subsequent to the fire events, there would also be a positive feedback resulting from increased P flux to the oceans through enhanced erosion, which in turn enhances marine productivity resulting in increased carbon burial and O_2 rise in the atmosphere (Berner and others, 2003). Fossil charcoal (a pyrolysis residue of wildfire) provides evidence for the earliest fires in the latest Silurian (Glasspool and others, 2004), yet records of charcoal through the Devonian remain rare (Rowe and Jones, 2000; Cressler, 2001, 2006; Scott and Glasspool, 2006; Scott, 2009, 2010; Glasspool and Scott, 2010; Prestianni and others, 2010), possibly reflecting low fuel supplies and low levels of atmospheric O_2 (Scott and Glasspool, 2006).

The occurrence and spread of wildfire in recent and ancient vegetation has been discussed widely (Pyne and others, 1996; Scott, 2000, 2009; Scott and Glasspool, 2006; Belcher and others, 2013; Scott and others, 2014). Under modern atmospheric O_2 conditions [Present Atmospheric Level (PAL) = 21%], low plant-moisture content is necessary for fire to spread (Wildman and others, 2004) as is a sufficient fuel build-up and an ignition source (usually lightning) (Pyne and others, 1996; Scott and others, 2014). Atmospheric O_2 levels are crucial: fires will not ignite below 13 percent (according to Chaloner, 1989) or 15 percent (Belcher and McElwain, 2008) and below 17 percent fires will not spread (Belcher and others, 2010), whereas at high oxygen levels (above 35%) plants may burn irrespective of fuel moisture, resulting in an upper limit for atmospheric oxygen concentrations as above this level it would be impossible to sustain forest growth (Watson and others, 1978; Lenton and Watson, 2000; Lenton, 2001). This led to the concept of the "fire window", which was originally set between 13 and 35 percent oxygen levels (Jones and Chaloner, 1991); more recent work suggests that the base of this fire window may be closer to 15 to 17 percent (Belcher and others, 2013; Lenton, 2013).

The Devonian saw a rapid rise and spread of vegetation into a wide range of habitats (Kenrick and Crane, 1997; Edwards and Wellman, 2001; Hotton and others, 2001). Plant size rose dramatically, resulting in increased fuel loads. By the Middle Devonian (Givetian) there is evidence for woody shrubs and small tree-sized plants (Algeo and others, 2001), and by the Middle Frasnian there were lowland forests dominated by the progymnosperm tree *Archaeopteris* (Meyer-Berthaud and others, 1999; Scheckler, 2001). However, only scattered terrestrial records of Late Devonian charcoal exist and it is not until the Carboniferous that extensive evidence of widespread fire systems is seen (Scott and Glasspool, 2006). Thus, there appears to be a significant 'charcoal gap' in the latest Middle Devonian and earliest Upper Devonian coinciding with a suggested O_2 low of 17 percent (Scott and Glasspool, 2006; Berner, 2009).

To date, most of the fossil charcoal has been studied in nearshore or terrestrial rocks (Skolnick, 1958; Scott, 2000, 2009, 2010) or in lacustrine deposits (for example, Falcon-Lang, 2000; Edwards and Whittington, 2000; Scott, 2010); however, organic petrographic studies have suggested that significant inertinite accumulations can occur in Devonian marine shales (Robl and others, 1992; Calder and others, 2003; Thompson, ms, 2004; Rimmer and others, 2004), providing an as yet unexplored repository of terrestrial organic matter (OM). Once incorporated into marine sediments, fossil charcoal is very stable over very long time periods (Herring, 1985) due to its refractory nature. We demonstrate here that the marine fossil record may provide a more continuous record of Late Devonian-Early Mississippian fire systems. We suggest widespread burning may have played a significant role in the rise in atmospheric O_2 levels through charcoal burial (Berner and others, 2003) as well as through enhanced soil erosion and supply of P to the oceans, which itself led to increased burial of marine organic carbon (Kump, 1988). The appearance of the first forests followed by a subsequent rise in atmospheric oxygen allowed fires to make significant feedbacks on the Earth system processes from then onwards (Scott, 2000; Belcher and others, 2013).

STUDY SITES AND METHODS

Four cores through Devonian-Mississippian marine black shales were sampled for this study: the IRQ core, New Albany Shale (Frasnian through Famennian) from the eastern flank of the Illinios Basin; the D4 and D6 cores from the western flank of the Appalachian Basin, New Albany Shale (Famennian) through the Sunbury Shale (Tournaisian); and the OHLO2 from the northern part of the Appalachian Basin, Ohio Shale (Famennian) (figs. 1 and 2) [see Rimmer and others (2004) and Hawkins (ms, 2006) for additional sampling information]. Additional samples were obtained from two well-documented terrestrial environments, Red Hill (Famennian, Duncannon Member, Catskill Fm., PA) (Cressler, 2001, 2006) and Elkins (Famennian, Hampshire Fm., WV) (Gillespie and others, 1981; Scheckler, 1986) (figs. 1 and 2). These terrestrial sites represent floodplain and deltaic deposits on the Catskill Delta, including some of the earliest known peat (coal) swamps (Hampshire Fm.) (Scheckler, 1986; Greb and others, 2006). They are time-correlative (Famennian 2c) (Gillespie and others, 1981; Cressler, 2001) with the upper parts of the black shale cores from central Kentucky and northern Ohio, and thus represent areas from which terrestrial OM likely originated during accumulation of the marine black shales.

For organic petrographic analysis, shale kerogen concentrates were obtained via HCl-HF-HCl treatment and then embedded in epoxy resin and polished. A combined white-light, blue-light (450–490 nm excitation) quantitative point-count analysis (300 points) was performed on each kerogen concentrate using a Zeiss Universal microscope (640x magnification) [see Rimmer and others (2004) and Hawkins (ms, 2006) for details of analytical techniques]. As inertinite reflectance is indicative of formation temperature (Scott, 2000; Scott and Glasspool, 2007), reflectance analyses (min. 100 readings) were performed on the three terrestrial samples and a subset of the marine shale samples (6 samples per core) using a Zeiss Universal scope fitted with a photomultiplier tube; data collection was controlled by custom computer hardware and software. SEM analysis provided additional support for a charcoal origin of the inertinites; homogenization of cell walls and loss of the middle lamella (300–325 °C) are indicative of charcoal (Scott, 2000; Glasspool and Scott, 2013).

RESULTS

Variations in OM Type in Late Devonian Black Shales

The Late Devonian-Early Mississippian black shales of the Appalachian Basin contain a predominance of marine liptinitic OM (bituminite and alginite, both telaginite, including *Tasmanites*, and lamalginite), along with lesser amounts of terrestrially derived OM including vitrinite [preserved woody and other plant-derived tissues such as cortical tissues (Scott, 2002)] and inertinite (fossil charcoal). This inertinite occurs within the shales as inertodetrinite, mostly with well-developed cell structure and with varying reflectances (ranging from that of semifusinite to fusinite); as such this is considered fossil charcoal (Guo and Bustin, 1998; Scott and Glasspool, 2007). Some other inertinites, such as funginite and some macrinite, do not have a fire origin but are formed due to degradation, usually by bacterial and fungal activity (for

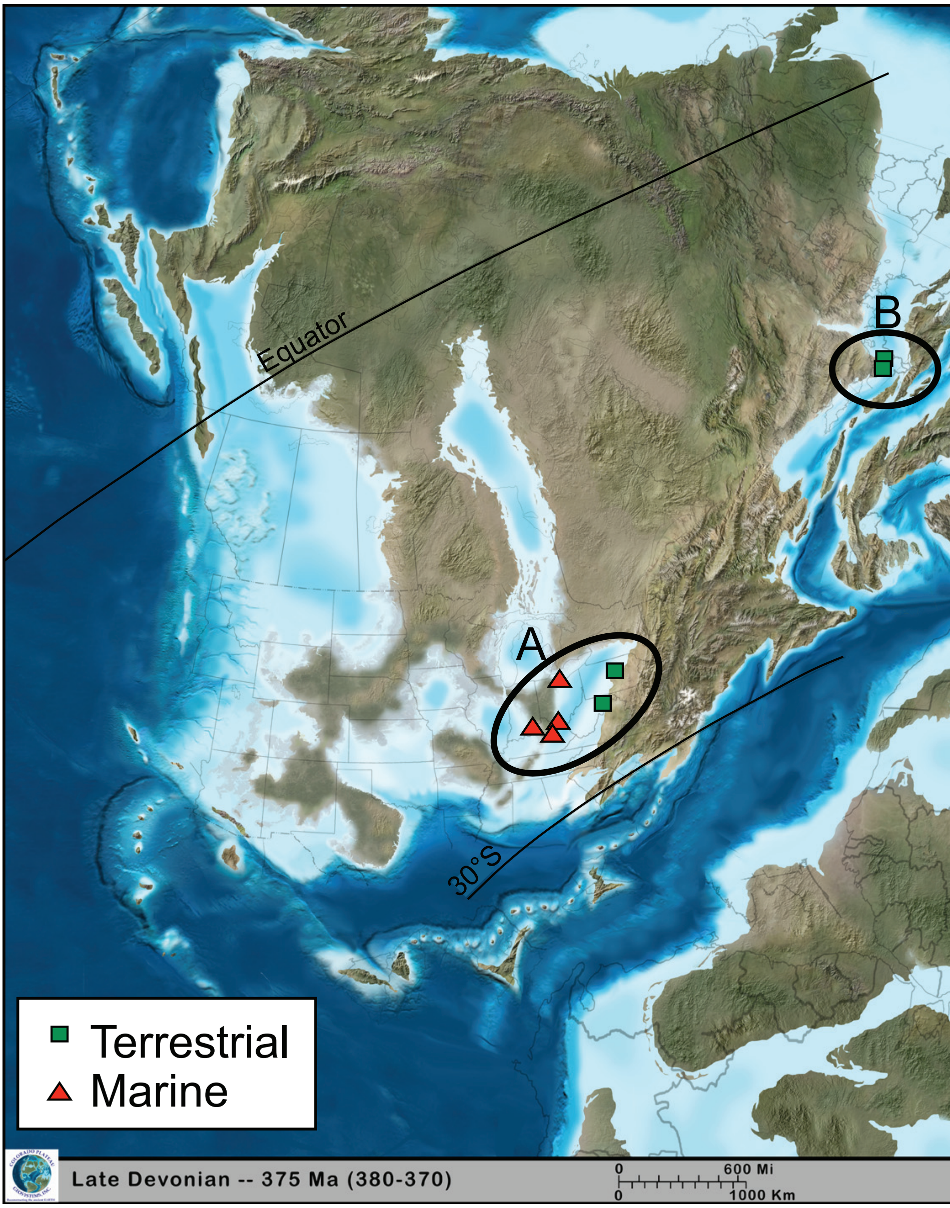

Fig. 1. Late Devonian paleogeography indicating Famennian locations of (A) terrestrial and marine charcoal sites from current study, and (B) Belgian terrestrial charcoal sites (Prestianni and others, 2010). Base map used with permission (Scotese, 2011).

example, Hower and others, 2009, 2013) and possibly insect activity (Richardson and others, 2012; Hower and others, 2013), but these macerals were not identified in our samples and are not included in our inertinite counts.

The base of the Huron Shale contains as much as 95 percent (by volume) marine liptinitic OM, but inertinite increases from 5 percent at the base of the section to as much as 15 to 20 percent towards the top of the section (in the Cleveland and Sunbury

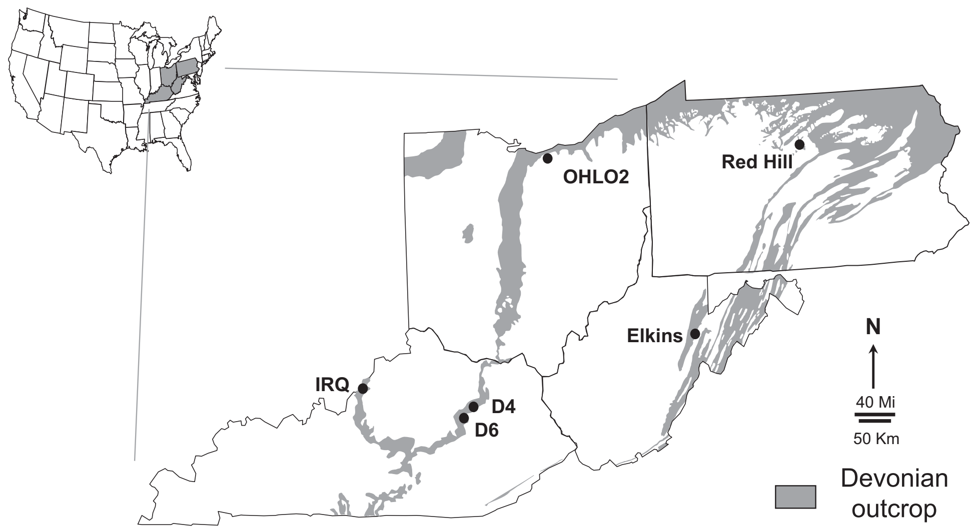

Fig. 2. Location of terrestrial and marine black shale sites. Red Hill and Elkins represent Upper Devonian terrestrial environments that could have sourced inertinite (fossil charcoal). At core locations OHLO-2, D-4, D-6, and IRQ Upper Devonian marine black shales were sampled to evaluate marine/terrestrial OM contributions.

shales) at the expense of marine OM; vitrinite content is lower but also shows a slight increase upwards (Thompson, ms, 2004; Rimmer and others, 2004; Hawkins, ms, 2006). The inertinite consists of small fragments (2–50 μm) that often show discernable cell structure (fig. 3). Fragments appear to include lower reflecting semifusinite and more highly reflecting fusinite, with 2 percent being the boundary between the two (Scott and Glasspool, 2007).

As the section shows considerable variation in lithology and organic carbon (C_{org}) content (with leaner intervals containing more inertinite, on a relative basis), and to avoid the problems of closure posed by maceral volume (V) data, the relative volume for each maceral (V_i) was converted to grams of organic carbon present in the sample as that maceral (W_i) using the method of Robl and others (1992). Values for the density of each maceral (σ_i) and respective average carbon composition (MC_i) were based on data from Robl and others (1987). The relative number of grams of carbon for each maceral (OC*i*) was calculated:

$$OC_i = V_i \sigma_i MC_i \tag{1}$$

The fraction of that maceral relative to the total grams of carbon (ΣOC_i) was multiplied by C_{org} to determine W_i:

$$W_i = C_{org} OC_i / \Sigma OC_i \tag{2}$$

This conversion allows comparison of the influx of inertinite (measured as the weight percent carbon as inertinite) between sites and avoids any bias introduced by lithological variations in maceral composition (similarly for vitrinite) (fig. 4). All locations show a general upward increase in the amount of inertinitic carbon, particularly above the *Foerstia* zone [a biostratigraphic marker (Schopf and Schwietering, 1970)] that occurs within the Huron Shale Member in the Appalachian Basin and the Clegg Creek Member in the Illinois Basin (*FZ* in fig. 4). The increase in vitrinitic carbon is less

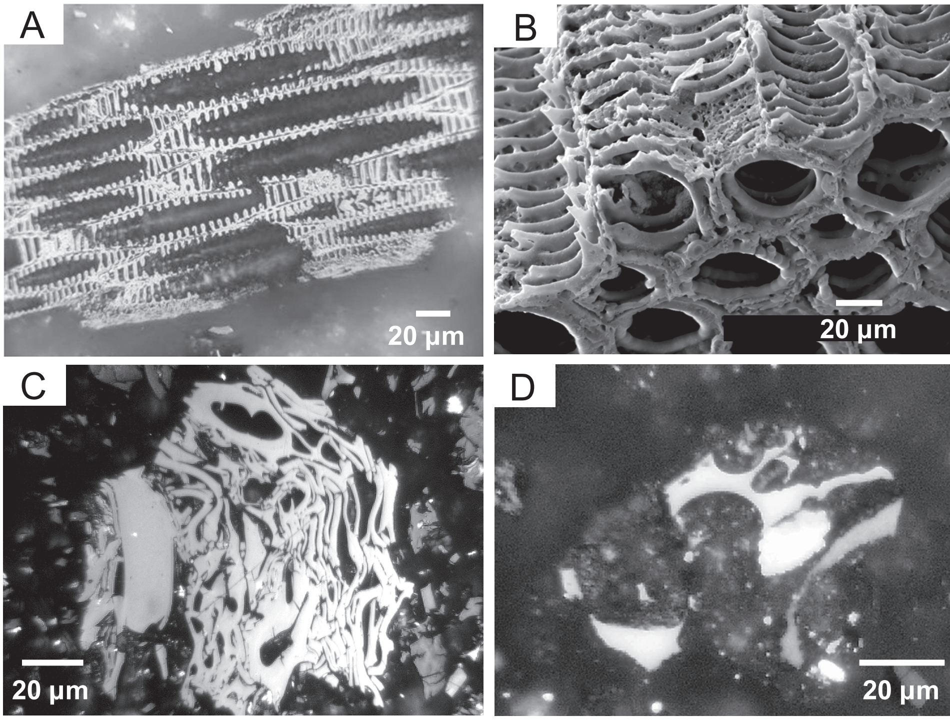

Fig. 3. Photomicrographs of inertinite in (A) Red Hill (reflected-light microscopy); (B) Red Hill (SEM); (C) Elkins siltstone (reflected-light microscopy); and (D) Cleveland Shale (reflected-light microscopy).

pronounced than that seen in inertinitic carbon, but is still evident in all four cores (fig. 4).

Reflectance and SEM Analysis of Inertinites

Inertinite reflectances of 2 percent correspond to combustion temperatures of ~ 400 °C, 5 percent to temperatures of 600 °C or higher, and 6 percent to 850 °C or higher (Scott and Jones, 1994; Guo and Bustin, 1998; Scott, 2000). Regardless of the duration of heating, reflectances will not exceed 2 percent at temperatures $<$ 400 °C (Guo and Bustin, 1998; Scott and Glasspool, 2007; McParland and others, 2009). Reflectance levels for semifusinite and fusinite from both the Red Hill (mean R_o = 4.4%) and Elkins (mean R_o = 3.2%) sites confirm that these materials are fossil charcoal and were produced at relatively high temperatures, ~ 600 °C at Red Hill and 575 °C at Elkins (table 1). Mean random reflectance provides a minimum temperature if the duration of charring is unknown (McParland and others, 2007, 2009), thus the data given here are for minimum fire temperatures. Surface charring temperatures are often around 400 °C (Scott and others, 2000) but the temperatures and hence reflectance relates also to the type of fuel and fuel load (Hudspith and others, 2014). Note that burial maturation produced vitrinite reflectances of 1.5 percent and 1.1 percent at the Red Hill and Elkins sites, respectively. The absence of lower reflectance inertinite from the Red Hill site may be due to the higher level of burial maturation at this location; as maturation increases, lower reflectance inertinite can increase in reflectance (Taylor and others, 1998).

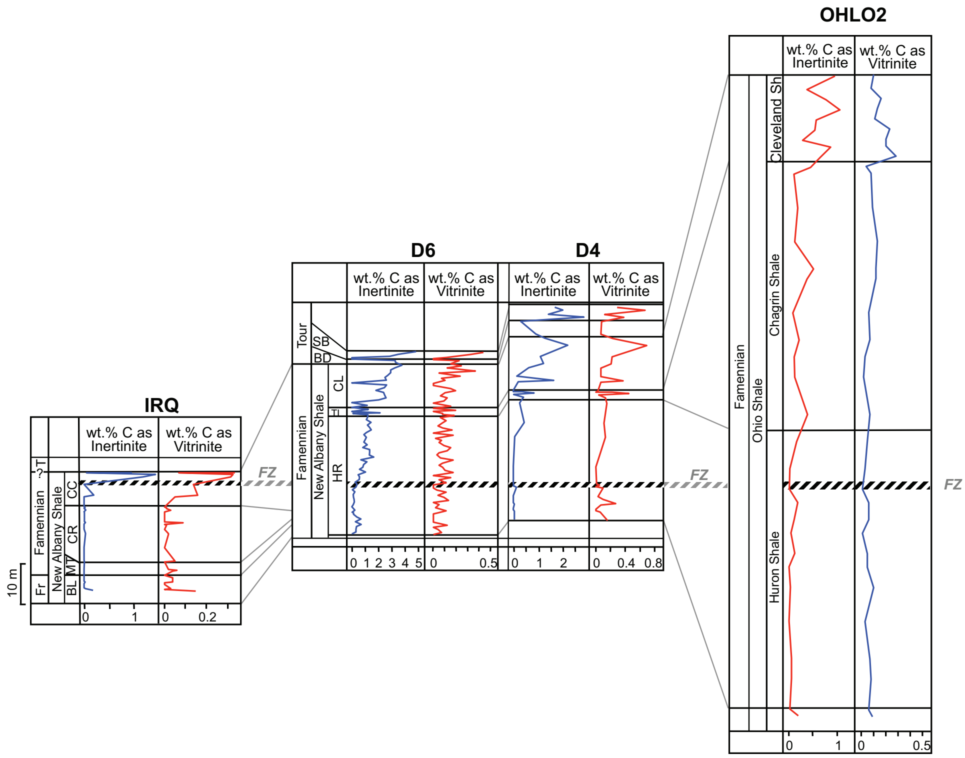

Fig. 4. Stratigraphic variability in wt. % carbon as inertinite and wt. % carbon as vitrinite for cores from the Illinois and Appalachian basins (data from Rimmer and others, 2004, and Hawkins, ms, 2006). (Abbreviations: FZ = *Foerstia* Zone, BL = Blocher Member, MT = Morgan Trail Member, CR = Camp Run Member, CC = Clegg Creek Member, HR = Huron Shale Member, TL = Three Lick Bed, CL = Cleveland Shale Member, BD = Bedford Shale, SB = Sunbury Shale).

The small fragments of inertinite in the marine shales show cell structure (fig. 3) and are considered to be fossil charcoal that was transported from co-eval terrestrial environments and deposited in the marine shales (after Scott and Glasspool, 2007). The reflectance levels of these inertinites are consistent with a wildfire origin (table 1). In all four cores studied, reflectance distributions show a bimodal distribution (fig. 5) with a mode around 2 percent and a second one around 4 or 5 percent, most likely due to temperature variations within the fire; such non-normal and bimodal inertinite reflectance distributions are thought to be common in coals (Bustin and Guo, 1999) and this bimodal distribution of inertinite reflectances has been observed in fusain-rich rocks, for example, the Lower Carboniferous Upper Shalwy beds, Donegal (Scott and Jones, 1994). These modes correspond to temperatures of approximately 485 to 600 °C. Mean values (2.17–4.15%) correspond to temperatures between 500 and 600 °C, comparable to those suggested for the terrestrial sites at Red Hill and Elkins (table 1). Thus, reflectance data are consistent with a terrestrial wildfire origin for the inertinites seen in the marine black shales. For comparison, vitrinite in the marine shales typically has reflectance levels of 0.5 to 0.6 percent in the outcrop belt of Kentucky, corresponding to maturity levels just inside the oil window (Rimmer and others, 1993, 2004). Rock-Eval T_{max} values for the Cleveland Shale and equivalents in these cores are ~430, which is consistent with this level of vitrinite reflectance (Rimmer and others, 1993; Hawkins, ms, 2006).

TABLE 1

Inertinite reflectance (R_o) data for terrestrial and marine samples. Estimated minimum fire temperatures based on means using data for Sequoia in Scott and Glasspool, 2007

Sample	Unit	Age	Inertinite R_o (%)			Est. Min. Temp. °C
			Min	Mean	Max	
Terrestrial samples:						
Red Hill siltstone	Catskill Fm.	Fam	2.32	4.40	5.51	600
Elkins coal	Hampshire Fm.	Fam	1.48	3.14	5.06	575
Elkins siltstone	Hampshire Fm.	Fam	1.05	3.19	4.48	575
Marine samples:						
Central Appalachian Basin:						
DN6-2	Sunbury	Tour	1.39	3.95	5.62	600
DN6-4	Sunbury	Tour	1.44	3.99	6.27	600
DN6-9	Cleveland	Fam	1.47	3.44	5.51	575
DN6-16	Cleveland	Fam	0.98	3.26	5.37	575
DN6-22	Cleveland	Fam	1.25	4.15	6.11	600
D6R-7	Huron	Fam	1.33	4.11	5.64	600
DR4-10	Sunbury	Tour	0.96	2.86	4.40	550
DR4-14	Sunbury	Tour	0.99	3.05	4.64	550
DR4-18	Bedford	Tour	0.90	2.17	4.36	500
DR4-27	Bedford	Tour	1.05	2.76	5.16	550
DR4-33	Cleveland	Fam	1.00	3.04	5.55	550
DR4-51	Cleveland	Fam	1.04	2.95	4.93	550
Northern Appalachian Basin:						
OHLO2-4	Cleveland	Fam	1.06	2.26	4.82	500
OHLO2-12	Cleveland	Fam	0.96	2.65	4.95	525
OHLO2-16	Cleveland	Fam	0.91	2.82	4.54	550
OHLO2-20	Cleveland	Fam	0.94	2.89	5.11	550
OHLO2-39	Cleveland	Fam	1.59	3.24	4.83	575
OHLO2-42	Cleveland	Fam	1.28	2.91	4.72	550
Illinois Basin:						
IRQ-2	Clegg Creek	Fam	0.93	3.36	5.69	575
IRQ-3	Clegg Creek	Fam	0.80	2.31	5.22	500
IRQ-4	Clegg Creek	Fam	0.91	3.56	5.50	575
IRQ-6	Clegg Creek	Fam	1.11	3.66	6.41	600
IRQ-10	Clegg Creek	Fam	0.71	2.91	5.41	550
IRQ-18	Clegg Creek	Fam	0.96	2.96	5.38	550

Fam = Famennian
Tour = Tournaisian

Morphological evidence (from SEM and organic petrography) suggests that charcoal fragments from the terrestrial sites are derived mostly from herbaceous and shrubby plants rather than from large pieces of wood from trees (fig. 3), possibly from the fern *Rhacophyton* that has been identified as a major component at both sites (Scheckler, 1986; Cressler, 2001). This concurs with observations by Cressler (2001) who reported that the fossil charcoal from the Red Hill site was likely derived from the fern *Rhacophyton*, rather than from the trees forming the canopy (*Archaeopteris*). Scheckler (1986) reported that the mire that produced the peat (coal) at the Elkins site was dominated by *Rhacophyton*. The surface fuel type has been shown in modern fire systems to have had an effect upon fire temperatures and hence reflectance values (Hudspith and others, 2014).

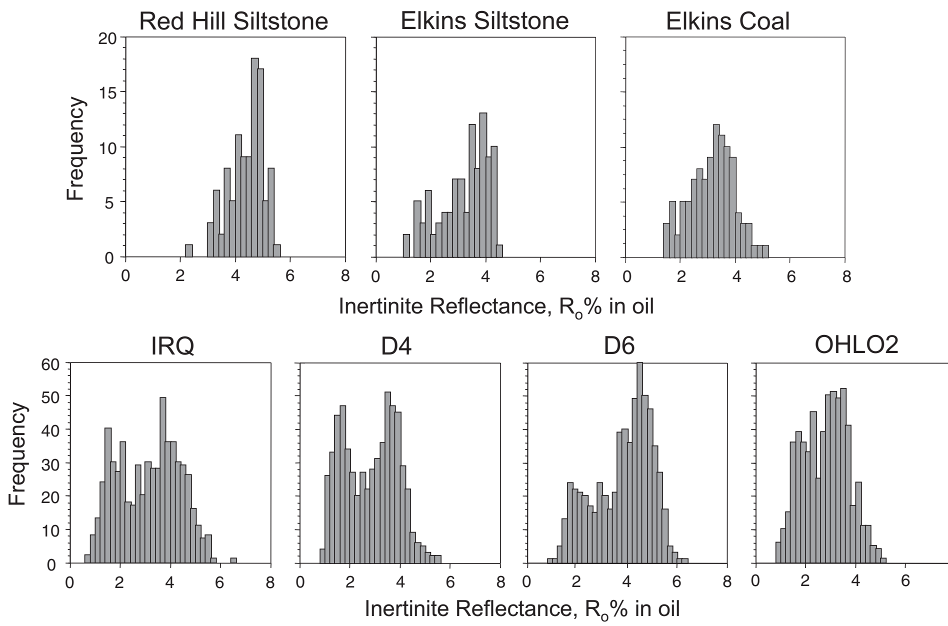

Fig. 5. Histograms showing inertinite reflectance results for both terrestrial and marine samples.

DISCUSSION

Terrestrial OM in Marine Devonian Black Shales

Much of the work to date on the organic-rich, Devonian-Mississippian black shales of the Illinois and Appalachian basins has focused on controls on autochthonous OM that constitutes a major proportion of the OM (for example, Ettensohn and others, 1988; Algeo and others, 2001; Werne and others, 2002; Sageman and others, 2003), but have largely ignored inputs from expanding terrestrial ecosystems that may have added an important, recalcitrant component to the marine basins of that time (Rimmer and others, 2004). This lignitic material may have been more resistant to decomposition and would have been difficult to degrade under the anoxic conditions (Crawford, 1981) thought to exist at times (seasonal to persistent) in the Devonian seas (for example, Ripley and others, 1990; Algeo and others, 1995; Murphy and others, 2000; Werne and others, 2002; Sageman and others, 2003; Rimmer, 2004). As such, this terrestrial OM could have made a contribution to the OM preserved in marine sediments. This would have been a significant new source of OM introduced to the oceans, despite the potential for decomposition within the terrestrial environment by fungi and bacteria. Fungi and bacteria capable of lignin breakdown were already in existence at this time (Stubblefield and others, 1985; Taylor and others, 2009a, 2009b), however it is unknown how extensive a role they played in the decomposition of terrestrial plant materials during the Late Devonian (Taylor and Osborne, 1996).

Beyond the current study, terrestrial input into the Devonian marine black shales is indicated by various lines of evidence, including megascopic (fossilized tree logs) (Cross and Hoskins, 1951; Chitaley, 1982, 1988; Robl and others, 1992; Chitaley and Cai, 2001), petrographic (including vitrinite, or preserved woody and other cortical tissue, and inertinite, partially pyrolyzed OM) (Robl and others, 1987, 1992; Ripley and others, 1990; Rimmer and others, 1993, 2004; Thompson, ms, 2004), palynological

(Winslow, 1962), geochemical (Breger and Brown, 1962; Breger and others, 1983), and isotopic (Maynard, 1981) evidence. The primary source of this vitrinite would have been the Catskill Delta during accumulation of the Catskill and Hampshire formations, the latter containing sediments that represent some of the earliest known peat-forming mires. The site at Elkins is thought to represent mires developing along a deltaic shoreline (Scheckler, 1986). Additional coaly horizons are seen in the Rockwell Formation (time correlative with the basinal Early Mississippian Sunbury Shale) (Brezinski and others, 2011).

Whereas this study provides the first systematic examination of inertinite trends in the Devonian-Mississippian shales of the Appalachian and Illinois basins, there have been other reports of such an increase. Ripley and others (1990) noted an increase in the modal abundance of vitrinite plus inertinite upsection in the Clegg Creek Member of the New Albany Shale within the Illinois Basin. The increase in terrestrial OM in these cores occurs in a zone of metal enrichment in the Clegg Creek, suggesting deposition of these macerals in a euxinic environment (Ripley and others, 1990). Robl and others (1987) reported that in some intervals within the Cleveland Shale of northeastern Kentucky (Appalachian Basin), vitrinite plus inertinite account for as much as 21 to 34 percent of the kerogen. Additionally, Winslow (1962) noted "unidentified vascular fragments" within the Upper Devonian and Lower Mississippian rocks of Ohio within the Appalachian Basin; most abundant within this classification were "splinters of tissue preserved as fusain or semifusain." Solomon and others (1984) provided yet another account of inertinite within the Cleveland Shale Member of the Ohio Shale in east-central Kentucky as well as the time-correlative Chattanooga Shale in Tennessee, where vitrinite plus inertinite accounts for as much as 5 to 6 volume percent of whole-rock samples, with inertinite reflectances as high as 4.91 percent.

Thus, it appears that there is ample evidence from the present study and various other reports in the literature for an increase in both inertinite and vitrinite in these Appalachian Basin marine shales towards the end of the Devonian and into the Early Mississippian. Any discussion of reasons for these increases must account for changes in both the vitrinitic and inertinitic components.

Possible Causes for an Increase in Inertinite Upsection

Possible causes for this upward increase in fossil charcoal (inertinite) could include proximity to paleoshoreline, climatic and/or latitudinal changes during accumulation, or expanding fire-prone ecosystems under suitable paleoatmospheric oxygen levels, or possibly a combination of these controls. Transport of wildfire-derived inertinite into the marine basin may have been by both water and wind (Rimmer and others, 2004; Scott, 2000, 2010). Studies of modern wind-blown charcoal suggest aeolian transport of fragments ranging from 1 to 150 μm (Patterson and others, 1987; Clark, 1988), encompassing the range of inertinite fragments observed in this study. Aeolian transport of charcoal into the basin from the Catskill Delta would be consistent with paleogeography and prevailing winds (trade winds) during the Late Devonian (Ettensohn, 1985), and such long-distance transport of charcoal has been demonstrated in other marine basins (Smith and others, 1973; Herring, 1985). Charcoal also would have been introduced into the marine basin associated with increased runoff and sediment load following fire events (Kaiho and others, 2013).

Proximity to paleoshoreline.—It has been observed that increased charcoal contributions occur in areas closer to land masses, possibly due to additional input of water-borne charcoal (Herring, 1985). However, in the current study the upward increase in inertinite does not appear to be related to either increased proximity to the paleoshoreline or to increased sediment influx. Rimmer and others (2004) showed no significant correlation between the increase in terrestrial OM and proxies for detrital influx, Ti/Al and K/Al, for core D6 (their fig. 11). Citing data from Ettensohn and others (1988) who mapped the relative positions of the edges of the individual black-shale basins based on the position of the paleo-pycnocline, that is, the transition between black and gray shales, Rimmer and others (2004) provide another argument against the increase in inertinite being due to increased clastic influx. Starting from a more easterly position during accumulation of the lower Huron, the edges of the black-shale basins migrated westwards into eastern Kentucky during middle and upper Huron and Cleveland deposition, but then returned to a more easterly position in West Virginia during accumulation of the Sunbury Shale (Rimmer and others, 2004; their fig. 12). If clastic influx due to proximity to the basin edge was the primary control on terrestrial OM accumulation, then similar terrestrial OM contents would be expected in the Lower Huron and the Sunbury; however, the lower Huron has little or no terrestrial OM, whereas the Sunbury contains significant amounts of terrestrial OM. Thus, it does not appear that the inertinite and vitirinite trends shown here can be attributed to proximity to the paleo-shoreline.

Latitudinal and climatic influences.—Paleogeographic reconstructions suggest that the central Appalachian Basin, and hence the source area for the charcoal seen in the Devonian marine shales, was in the southern mid-latitudes (probably between 45°S and 30°S) (fig. 1) (Blakey, 2008; Scotese, 2011). A subtropical climate was suggested for the Red Hill site by the presence of paleosols with vertic features, indicating seasonally wet and dry periods (Driese and Mora, 1993; Cressler and others, 2010). As there is a significant latitudinal control on charcoal production (Herring, 1985; Power and others, 2008), it is reasonable to ask whether this was a factor in the increase in charcoal that is seen in the marine black shales. For example, migration of a sample site due to plate movements from a low-charcoal-flux wetter, tropical environment into a drier temperate high-charcoal-flux environment would result in increased inertinite in the rock record based on what is observed in modern environments (Herring, 1985). Whereas there was some movement of the source area (Catskill Delta) into lower latitudes during the Late Devonian, the stratigraphic interval over which the increase in inertinite occurs in the black shales is relatively short for latitudinal shifts to have been a major factor. Also, because this occurred at a time when forests were just becoming well established, it would be difficult to find a reasonable modern analogue, so comparisons with charcoal occurrences in modern oceans may be difficult.

Climate can have a significant influence on the frequency of fires (for example, Power and others, 2008; Marlon and others, 2009) and, therefore, the occurrence of charcoal in both the modern and ancient rock record. Recent work has suggested that even at mid-latitudes, there is evidence for extensive low-altitude, Late Devonian glaciation within the Appalachian Basin consistent with global glacial cooling (Brezinski and others, 2011). Additionally, latest Famennian glacial deposits have been noted in other parts of the world, including South America and Africa (Streel and others, 2000), and isotopic studies of European equivalents of the Cleveland and basal Bedford shales suggest deposition under warm climatic conditions, followed by a significant drop in temperature at the close of the Devonian (Kaiser and others, 2006). Therefore, is it possible that the trends in fossil charcoal seen here reflect changing climatic conditions that could have lead to increased fire activity? Assuming a change in climate at the close of the Devonian to cooler, glacially influenced conditions, one might expect a decrease in fire frequency rather than an increase based on studies of fire occurrences since the Last Glacial Maximum (LGM): cooler climates result in a lower level of fire occurrence and hence less charcoal accumulation (Power and others, 2008; Daniau, 2010). The lower charcoal occurrence reported for the LGM may be related to an overall decrease in terrestrial biomass and therefore fuel availability (Power, 2013), along with cooler, drier conditions associated with less convection and a reduction in lightning activity, which in turn would mean fewer ignition sources and fires (Power and others, 2008; Power, 2013). Marlon and others (2009) also suggested, however, that fire increased during periods of rapid climate transition from one climate state to another, but our time resolution does not allow the distinction of any very short-term events linked to short-term climate change.

The increase in inertinite seen in the Devonian marine shales would suggest an increase in charcoal as the climate cooled (the opposite to what is seen in the LGM), therefore it is unlikely that the trends we are seeing are driven solely by climate. Comparisons are difficult, however, as the nature of the vegetation was so different during the Late Devonian compared to that found at the LGM. Other studies have suggested that even though the amount of charcoal produced during glacial periods decreases, the amount that finds its way in to the ocean basin actually increases (Verardo and Ruddiman, 1996). The reasoning suggested for this includes changing wind conditions and remobilization of charcoal originally produced under warmer conditions (Verardo and Ruddiman, 1996). We believe this is an unlikely explanation of the trends seen in the present study. In our cores, an increase in vitrinite accompanies the observed increase in inertinite. Although this is a minor increase, it is seen in all four cores and suggests an increasing total terrestrial contribution (woody tissue and bark plus fossil charcoal). Collectively, the increase in vitrinite and inertinite suggests an increase in available biomass even as the climate cooled, not a decrease. In addition, the Late Devonian was a time of rapid biome changes with the evolution of the seed habit allowing plants to spread into drier environments (Scott, 1980; DiMichele and Hook, 1992; DiMichele and others, 2001; DiMichele and Bateman, 2005; DiMichele and Gastaldo, 2008).

Increase in fire-prone environments under high O_2 levels.—Through the Devonian, terrestrial landscapes evolved from bank-dwelling communities in the early Devonian to the first modern forests by the Late Devonian (Scheckler, 2001). Early Devonian landscapes were likely typified by small plants (mostly rhyniopsids and zosterophylls with some herbaceous lycopsids). These plants grew in close proximity to streams, and inhabited areas that were nearly always moist (Scheckler, 2001). Tree-sized lycopsids were common by the Givetian (Middle Devonian), occurring in diverse forest communities (Stein and others, 2012), and the Late Devonian saw expansion of forests over large areas (Scheckler, 2001). In the Upper Devonian, Archaeopteris, which is thought to have appeared during the Frasnian (Scheckler, 2001) and became extinct around the Devonian-Carboniferous boundary (Scheckler, 1986), would have been the dominant large tree (approximately 30 m) in the forest (Meyer-Berthaud and others, 2010), and had extensive foliage that formed crowns (Meyer-Berthaud and others, 1999). These forested areas also included herbaceous ferns (Rhacophyton) and tree lycopsids (Scheckler, 1986). At the Elkins locality, large deltaic marshes and small inland backswamps were dominated by Rhacophyton (Scheckler, 1986). The Red Hill site was populated by both Archaeopteris and Rhacophyton (Cressler, 2001).

Extensive charcoal occurrence in the Famennian may suggest that land plants had reached sufficient density and size, and had expanded into drier habitants, experiencing forest fires much like those experienced today (Beerbower and others, 1992; Scheckler, 2001). Charred remains of Callixylon (the trunks and branches of Archaeopteris) have been described (Scott and Jones, 1994; Prestianni and others, 2010), as has fossil charcoal from Rhacophyton (Cressler, 2001). Both Archaeopteris and Rhacophyton have been identified at both the Red Hill and Elkins localities (Scheckler, 1986; Cressler, 2001, 2006). Cressler (2001) suggested that the occurrence of only Rhacophyton charcoal at the Red Hill site may indicate wet-and-dry seasonality that led to the development of wildfires in the dry season; Rhacophyton, a shallow-rooted plant (Scheckler, 1986) was likely growing in areas subject to desiccation and ignition, whereas Archaeopteris, being more deeply rooted, would have been less affected by

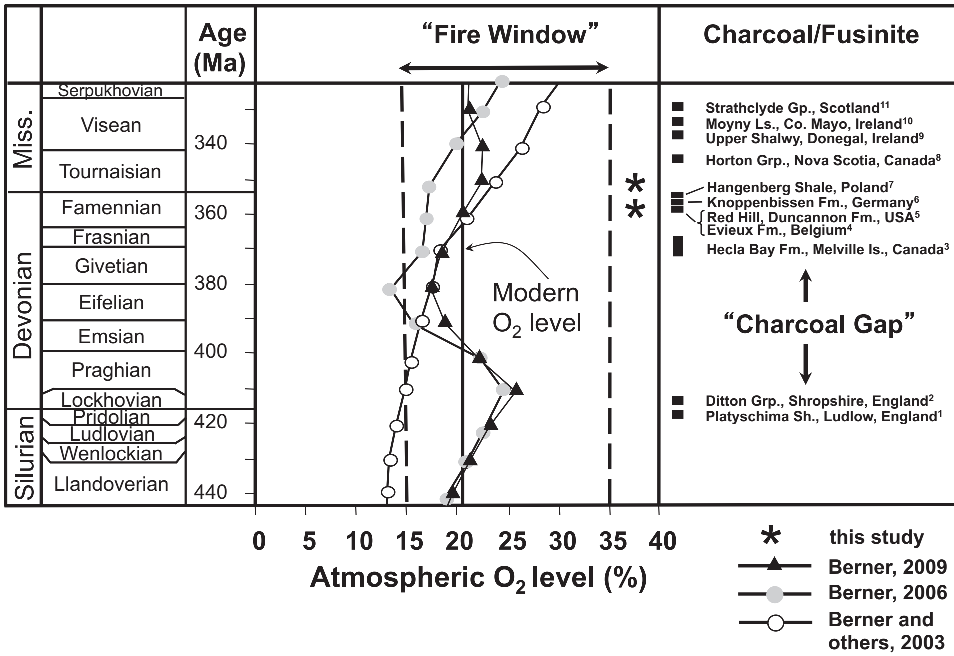

Fig. 6. Atmospheric O_2 levels from the Silurian through the Mississippian, based on Berner, 2009 (black triangles), Berner (2006) (gray solid circles), Berner and others, 2003 (open circles), and known occurrences of fossil charcoal. * = present study, Red Hill site, Catskill Fm., PA, USA; Elkins site, Hampshire Fm., WV, USA; New Albany Shale and Sunbury Shale, KY, USA. (1) Platyschima Shale Member, Dowton Fm., Ludlow, England (Glasspool and others, 2004); (2) Ditton Grp., Shropshire, England (Edwards and Axe, 2004; Glasspool and others, 2006); (3) Hecla Bay Fm., Melville Island, Canada (Goodarzi and Goodbody, 1990); (4) Evieux Fm., Belgium (Prestianni and others, 2010); (5) Red Hill site, Duncannon Fm., PA, USA (Cressler, 2001, 2006); (6) Knoppenbissen Fm., Ardennes-Rhenish Massif, Germany (Fairon-Demaret and Hartkopf-Fröder, 2004); (7) Hangenberg Black Shale, Holy Cross Mountains, Poland (Marynowski and Filipiak, 2007); (8) Horton Grp., Nova Scotia, Canada (Falcon-Lang, 2000); (9) Upper Shalwy Beds, Donegal, Ireland (Nichols and Jones, 1992; Scott and Jones, 1994); (10) Moyny Limestone, Creevagh Head, County Mayo, Ireland (Falcon-Lang, 1998); (11) Strathclyde Group, Scotland (Falcon-Lang, 2000); also see Scott and Glasspool (2006) for additional Mississippian occurrences).

drought. By this time, however, significant areas would have been covered by vegetation allowing fire to spread across the landscape.

The rise in fire activity, as suggested by the black shale inertinite record, appears to have been gradual but sustained, and fits well with the suggested rise in atmospheric O_2 at this time (Berner, 2006, 2009; Scott and Glasspool, 2006; Lenton, 2013). We know of no terrestrial charcoal records from the latest Frasnian or early Famennian, nor from the Early-Middle Devonian (Late Emsian to Givetian) that represent the ‘charcoal gap’ (fig. 6) (Scott and Glasspool, 2006). For example, despite extensive analysis of the Middle Devonian forest community at Gilboa, New York (Stein and others, 2012), this site has provided no evidence of fossil charcoal (W.L.C., personal observation). Macroscopic charcoal records from both Europe and North America appear to be restricted to the latest Famennian. Most of the North American charcoal occurrences are not derived from the tree Archaeopteris/Callixylon, but from herbaceous plants or shrubs such as the zygopterid fern Rhacophyton. Similarly, studies of Famennian sediments in Europe have indicated charcoal assemblages dominated by a range of herbaceous plants, with Callixylon wood being rare (Fairon-Demaret and Hartkopf-Fröder, 2004; Prestianni and others, 2010), a pattern that appears to continue through the Mississippian (Scott and Glasspool, 2006). This suggests extensive surface fires supported by our inertinite reflectance data. If there were extensive forests then at least some crown fires may be expected if there were sufficient ladder fuels to allow a fire to spread from the surface into the crowns (Scott and others, 2014), yet there are no confirmed occurrences of Archaeopteris leaf charcoal from the Appalachian sites. If surface fires spread through the forest, then fallen branches and leaves in the litter would have been burnt and some preserved as charcoal. Possibly forest litter remained moist but open 'scrub-like' vegetation dried out occasionally and burnt after a significant fuel build-up. In modern forests, ground fires smoulder at low temperatures, surface fires burn litter at temperatures $<$350 °C, whereas intense crown fires may exceed 600 °C (Scott and Jones, 1994; Scott, 2000). Possibly, the moderately high temperatures indicated for this herbaceous and shrub-derived charcoal arose because of excessive build-up of litter.

The occurrence of charcoal in marine black shales may not only be significant in the Devonian but also during other periods in Earth history such as the Triassic where there are widespread black shales above the Permian-Triassic boundary (Wignall and Twitchett, 2002). It has been suggested that O_2 levels were around 24 percent (Berner, 2006), a level at which plant material with relatively high moisture contents should burn, but there are no terrestrial records of charcoal in the Early Triassic (see review by Abu Hamad and others, 2012). Macroscopic evidence of wildfire is not seen until the Middle Triassic (Uhl and others, 2010) and Late Triassic (Uhl and Montenari, 2011); however, microscopic evidence (from a palynological report) suggests charcoal occurrence slightly earlier, in late Early to Middle Triassic (Spathian-Anisian) marine shales and siltstones of the Barents Sea (Mangerud and Rømuld, 1991). The microscopic marine charcoal record may thus provide a record of the nature of fire systems at this time and contributes towards our understanding of terrestrial ecosystem recovery in the Paleozoic.

Fire, Post-Fire Erosion, and Oceanic Anoxia

The impact of these first extensive fires may have been felt beyond the terrestrial system and had a direct impact on the marine system. Not only may these wildfires have enhanced erosion, at least some of the soil and charcoal will have entered the marine system through water runoff. Kump (1988) showed the relationship between fire, erosion, and the release of phosphorus (P). Increasing the flux of P into the ocean has a dramatic effect upon marine productivity and carbon burial, which acts as a significant feedback for oxygen levels in the atmosphere (Kump, 1988; Lenton and Watson, 2000). There are numerous studies that suggest Late Devonian marine anoxia was driven by the release of nutrients from evolving terrestrial environments during accumulation of the organic-rich shales of the Appalachian Basin (for example, Algeo and others, 1995; Murphy and others, 2000; Rimmer and others, 2004) and other anoxic basins (for example, Joachimski and others, 2001; Tribovillard and others, 2004), and it has been suggested that widespread fire and subsequent large-scale erosion led to the mass extinction at the Frasnian-Famennian boundary (Kaiho and others, 2013). In addition, recent research has suggested that extensive soluble charcoal-derived organic matter may be transported into the oceans and hence have an impact upon carbon burial (Jaffé and others, 2013).

Thus, the expanding wildfires in the Late Devonian present several potential positive feedbacks on oxygen levels in the atmosphere (fig. 7). Following a fire event, some charcoal would accumulate in terrestrial (for example, in peats) and riverine settings, whereas other charcoal would be transported via the rivers to the sea, both as particulate matter and as solubilized OM (Jaffé and others, 2013). Some additional charcoal could be wind-blown, potentially carrying fine materials considerable distances to the oceans. These represent avenues whereby carbon could be sequestered,

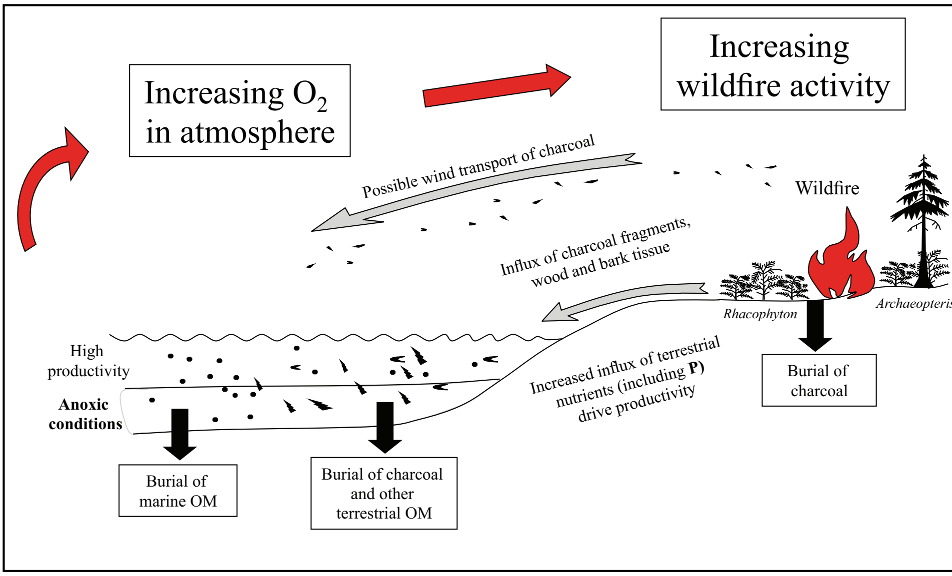

Fig. 7. Positive feedback mechanisms associated with wildfire activity in the Late Devonian-Early Mississippian: increased carbon burial and increase in atmospheric O_2 associated with the expansion of wildfires (plant reconstructions from Greb and others, 2006).

contributing to an increase in atmospheric oxygen (Berner and others, 2003). Primary production of marine OM was likely enhanced by the increase in flux of P associated with increased erosion, driving the seas to anoxia and further enhancing carbon burial. As these increases in carbon burial would have led to increased atmospheric O_2 levels, further promoting wildfire, we suggest that the rise of fire may be significant for the whole Earth system and that this is a topic for further research.

CONCLUSIONS

Despite the occurrence of scattered records of charcoal in the Late Silurian and Early Devonian, evidence of fire through most of the Devonian is rare despite the diversification of land vegetation and the potential build-up of fuel. There is a significant ‘charcoal gap’ in the latest Middle Devonian and earliest Late Devonian, followed by increasing evidence of fire in the latest Famennian. Scanning electron microscopy of macroscopic charcoals from the Late Famennian indicates that herbaceous plants and shrubs were being burnt and thus suggests the occurrence of surface fires, rather than forest crown fires, a pattern that was maintained at least through the Early to Middle Mississippian. The marine record of inertinite (fossil charcoal) in black shales of Kentucky and Ohio, which cross the Devonian-Mississippian boundary, indicates increasing fire activity though this time. Climatic cooling across this time period would have resulted in less charcoal, not more, if climate were the primary driving factor. The increase in both inertinite and vitrinite suggests other factors, and here we suggest that this reflects the expansion of vegetation into fire-prone environments under O_2 conditions high enough to sustain fire. Reflectance data on both terrestrial and marine charcoal indicates minimum fire temperatures of 500 to 600 °C. Atmospheric modeling suggests a rise in O_2 levels from 17.5 to 22 percent through the Late Devonian and the charcoal record is consistent with this prediction indicating that for the first time on the planet there was sufficient fuel and oxygen to allow significant wildfires to occur (for example, Belcher and others, 2013). The expansion of wildfires led to increased carbon burial both as recalcitrant charcoal and through increased marine productivity (resulting from post-fire increased erosion and P influx); this in turn led to increased atmospheric O_2 levels, further promoting wildfire.

The occurrence of charcoal in marine black shales is significant in yielding a more continuous record of fire than is possible in many terrestrial systems. It has been noted that, in fact, charcoal may be more persistent in marine sediments (having a stability of several tens of millions of years) than in terrestrial environments (Herring, 1985). It is probable that the petrographic study of black shales from other ages may provide a similar wildfire record providing constraints on atmospheric models. Our data indicate development of a world where fire was capable of having a major influence on vegetation and earth system processes for the first time in the Late Devonian.

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