



## SYMPOSIUM

# INVESTIGATING DEVONIAN TREES AS GEO-ENGINEERS OF PAST CLIMATES: LINKING PALAEOOLS TO PALAEOBOTANY AND EXPERIMENTAL GEOBIOLOGY

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**Abstract:** We present the rationale for a cross-disciplinary investigation addressing the ‘Devonian plant hypothesis’ which proposes that the evolutionary appearance of trees with deep, complex rooting systems represents one of the major biotic feedbacks on geochemical carbon cycling during the Phanerozoic. According to this hypothesis, trees have dramatically enhanced mineral weathering driving an increased flux of Ca<sup>2+</sup> to the oceans and, ultimately, a 90% decline in atmospheric CO<sub>2</sub> levels through the Palaeozoic. Furthermore, experimental studies indicate a key role for arbuscular mycorrhizal fungi in soil–plant processes and especially in unlocking the limiting nutrient phosphorus in soil via Ca-phosphate dissolution mineral weathering. This suggests co-evolution of roots and symbiotic fungi since the Early Devonian could well have triggered positive feedbacks on weathering rates whereby

root–fungal P release supports higher biomass forested ecosystems. Long-standing areas of uncertainty in this paradigm include the following: (1) limited fossil record documenting the origin and timeline of the evolution of tree-sized plants through the Devonian; and (2) the effects of the evolutionary advance of trees and their *in situ* rooting structures on palaeosol geochemistry. We are addressing these issues by integrating palaeobotanical studies with geochemical and mineralogical analyses of palaeosol sequences at selected sites across eastern North America with a particular focus on drill cores from Middle Devonian forests in Greene County, New York State.

**Key words:** Devonian plant hypothesis, Devonian trees, arbuscular mycorrhiza, mineral weathering, climate change, land plant evolution.

THE evolution and geographical spread of trees with deep, complex rooting systems and their role in the development of soils is widely regarded as the ‘Devonian engine’ that drove major changes in global biogeochemical cycles as the planet became increasingly forested. This is known as the ‘Devonian plant hypothesis’ (Berner 1997; Retallack 1997; Algeo and Scheckler 1998; Beerling and Berner 2005; Beerling 2007). Fossil (Remy *et al.* 1994; Kenrick

and Strullu-Derrien 2014; Strullu-Derrien *et al.* 2014) and molecular clock (Simon *et al.* 1993) evidence indicates that the rooting systems of land plants co-evolved and maintained symbiotic arbuscular mycorrhizal (AM) associations that have played an important role in land colonization and phosphorus uptake by most plants since at least the Early Devonian, even before true roots evolved (Pirozynski and Malloch 1975; Smith and Read 2008;

Humphreys *et al.* 2010; Field *et al.* 2015). The Devonian plant hypothesis suggests that the evolutionary rise of Devonian forests, in conjunction with their AM fungal partners, enhanced weathering of continental Ca and Mg silicates and increased the fluvial flux of nutrients to the oceans, causing major perturbations of the long-term carbon cycle (Bernier *et al.* 2003; Bernier 2004; Taylor *et al.* 2009). In particular, enhanced land–ocean fluxes of weathered cations (e.g. Ca<sup>2+</sup>), in combination with bicarbonate ions, are likely to have driven a 90% reduction in atmospheric CO<sub>2</sub>, as recorded by  $\delta^{13}\text{C}$  isotope signatures of palaeosol carbonates (Mora *et al.* 1996) and the increased frequency of stomatal pores on plant cuticles (McElwain and Chaloner 1995). The drop in CO<sub>2</sub> ultimately triggered global cooling (Popp *et al.* 1986; Joachimski and Buggisch 2002) and possibly glaciation at the end of the Devonian (Caputo 1985).

The rise of Devonian forests probably entrained a further suite of positive feedback mechanisms linked to chemical weathering processes. Phosphorus is the key limiting nutrient in many soils, especially those that have experienced long periods of weathering (Walker and Syers 1976). AM fungi are highly adapted for P uptake, which they transfer to their photosynthesizing hosts in exchange for autotrophic carbon (Smith and Read 2008). Plant-available P is ultimately derived from the weathering of calcium phosphate minerals such as apatite (Jobbágy and Jackson 2001) either by roots and mycorrhizal fungi (Quirk *et al.* 2012) or by organic ligands of the kinds produced by microorganisms (Neaman *et al.* 2005, 2006). The release of P from Ca phosphates therefore largely controls the long-term productivity and biomass of forest ecosystems that in turn intensify weathering through increasingly well-established mechanisms (Bernier *et al.* 2003; Leake *et al.* 2008; Taylor *et al.* 2009). Enhanced terrestrial weathering can lead to increases in land-to-ocean nutrient fluxes that have been linked to ocean eutrophication and anoxic conditions across ocean bottom waters (Murphy *et al.* 2000). This is evidenced by widespread occurrences of organic-rich black shales (e.g. end-Frasnian Kellwasser horizons) and contemporaneous positive  $\delta^{13}\text{C}$  excursions of marine carbonate, with elevated burial rates of organic isotopically light carbon (Sandberg *et al.* 1988; Joachimski and Buggisch 1993; Joachimski *et al.* 2002; Bond *et al.* 2004).

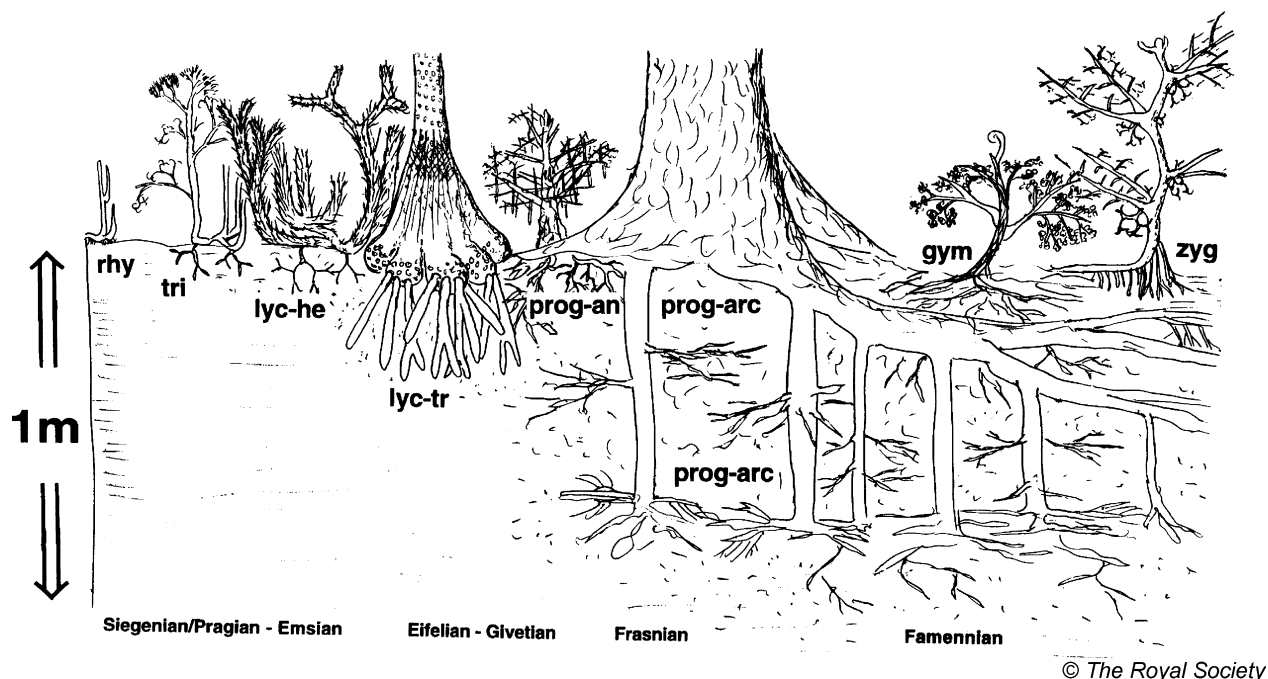
Challenging and long-standing areas of uncertainty in this paradigm concern the limited data from the fossil record documenting the Devonian origin and evolution of tree-sized plants and the identity of the mechanisms of plant–soil interactions by which they influenced the geochemical and climatic evolution of the Earth. Understanding this transition has been hampered by poor palaeontological evidence of the vegetation that formed the earliest forests before the Late Devonian establishment of

widespread deep-rooting *Archaeopteris* forests. In particular, our knowledge of the origin and morphology of roots belonging to arborescent plants is currently based on very limited fossil evidence (Fig. 1). Although there are few sites where fossilized roots and stumps have been determined as *in situ* within palaeosols (Fig. 2 and references therein), only a few have been geochemically analysed, leaving major gaps in our knowledge (Fig. 2). Crucially, no direct link has yet been established between the evolutionary advance of trees and their geochemical impacts on palaeosols in terms of mineral weathering, largely because of the lack of cross-disciplinary investigations. Additionally, geochemical models describing how they affected the Earth's surface and atmospheric CO<sub>2</sub> are based largely on weathering processes inferred from contemporary ecosystems lacking in evolutionary context (Bernier and Kothalava 2001; Bernier 2006).

These substantial gaps in our knowledge during Earth's transition to a forested planet provide the rationale for the UK-funded palaeosol drilling programme, which builds upon recent discoveries of one of the world's oldest known *in situ* forests in North America (*c.* 387 Ma; Stein *et al.* 2012). The project aims to investigate the evolution of forests and complex rooting systems through the critical Silurian–Devonian interval and quantify their effects on the Earth system using advanced geochemical and mineralogical analyses of palaeosol weathering profiles, which can be related to the *in situ* occurrence of vegetation and rooting depths, where preserved. Here, we first outline evidence for trees as geo-engineers of the Earth's Devonian environment and then describe the goals of the project. Finally, we outline experimental evidence for the co-evolution of trees and their mycorrhizal partners as the primary driver of biological weathering processes.

## DEVONIAN TREES AS GEO-ENGINEERS

Land plants probably originated in the Middle Ordovician (evidenced by spores; Rubinstein *et al.* 2010), with vascular (tracheid-bearing) plants evolving and radiating rapidly in the Silurian to Early Devonian. Vascular plants became the primary producers of emerging terrestrial ecosystems (Edwards and Selden 1992; Edwards 1996). In the Early Devonian, competitive pressures for light and space favoured axial sporophytes with an indeterminate growth habit (i.e. the zosterophylls and trimerophytes), which ultimately led to an overall increase in height and biomass (Edwards 1994; Morris and Edwards 2014). However, it is likely that these plants remained ecologically restricted to moist environments, such as wetlands and riverbanks, and were relatively small in stature (<1 m), and therefore of low biomass, with limited geochemical effects on soils.



**FIG. 1.** The relative sizes, morphologies and rooting depths of rooting systems through the Early to Late Devonian, as envisaged and drawn by Algeo and Scheckler (1998, fig. 3, p. 117; reproduced by permission from The Royal Society). *Abbreviations:* gym, early gymnosperms; lyc-he, early herbaceous lycopods; lyc-tr, early tree lycopods; prog-an, aneurophyte progymnosperms; prog-arc, *Archaeopteris* progymnosperms; rhy, rhyniophytes; tri, trimerophytes; zyg, zygopterid ferns.

By the Middle Devonian, land plants developed several strategic innovations in growth. With the evolution of secondary vascular tissues, arborescence was achieved in some clades (namely the pseudosporochnalean cladoxylsids, lycopsids and archaeopteridalean progymnosperms) within the Eifelian and Givetian stages (Berry and Fairon-Demaret 2002; Stein *et al.* 2007; Meyer-Berthaud *et al.* 2010). Concurrently, with a greater need for nutrients, water and structural support, rooting systems evolved from simple, hairless rhizomatous axes that were shallow to subaerial in the Early Devonian (Kerp *et al.* 2001; Raven and Edwards 2001) to true roots by the Middle Devonian (Meyer-Berthaud *et al.* 1999; Giesen and Berry 2013).

A key factor in the success of the transition to arborescence is thought to be the mutualistic symbioses between vascular plants and AM fungi (Kenrick and Strullu-Derrien 2014), which evolved in basal land plants even before the development of roots (Strullu-Derrien *et al.* 2014; Field *et al.* 2015). Despite evidence from fossils and/or extant genera of AM-like colonization in early rooting plants such as lycopods (e.g. Lycopodiaceae) and trimerophytes (e.g. Psilophytaceae) and the later gymnosperms (cordaites and coniferophytes), as yet the mycorrhizal status of progymnosperms such as *Archaeopteris* remains unknown (Wang and Qiu 2006; Krings *et al.* 2007; Strullu-Derrien and Strullu 2007). Given the long fossil record of AM-like fungi and fossils of early coniferous gym-

nosperms, such as the now-extinct *Notophytum krauselii* (Podocarpaceae) from the middle Triassic (245–230 Ma; Schwendemann *et al.* 2011) and *Metasequoia milleri* (Cupressaceae) from the middle Eocene (49 Ma; Stockey *et al.* 2001), it is likely that Earth's first forested ecosystems were dominated by AM-associating trees. Moreover, arborescence appears tightly associated with mycorrhization in contemporary floras (Strullu-Derrien and Strullu 2007; Smith and Read 2008).

Evolutionary advancement of terrestrial vegetation is linked to the development of soils and the appearance of major soil orders through time (Fig. 2). Before vascular plants evolved, soils were weakly developed (identified as entisols and inceptisols according to the modern soil taxonomy) with no evidence of rooting (Feakes and Retallack 1988). Additionally, palaeosols interpreted as aridisols, oxisols and vertisols are all known soil types prior to the advent of forests in the Devonian (Driese *et al.* 1992; Retallack 2003). There are Early Devonian examples of coaly shale deposits prior to the evolution of arborescence, interpreted as organic accumulations of early vascular plant phytodebris in wetlands (Kennedy *et al.* 2013). However, these are meagre compared with organic-rich soils interpreted as histosols of Middle with Late Devonian age, linked to the evolution of arborescence. Alfisols and spodosols, which develop primarily (though not exclusively) under modern forests, appeared

Era	Stage	Unit	Location	Environmental setting	Palaeosol type* / key features	Pedogenesis / Geochemical profiling	Evidence of <i>in situ</i> rooting	Rooting dimensions / depth	Fossil evidence for vegetation from aerial parts ( <i>in situ</i> )	RCO <sub>2</sub>	References	
Devonian	Silurian	Bloomsburg Fm	Lehigh Gap, PA, USA	Fluvial-alluvial system	160 cm thick, red, clay-rich profile, with calcrete nodules	Clay production, calcification at depth	Questionable tubular features	Unknown	None	3200–5200 <sup>†</sup>	Retallack (1985)	
												Milton & Danville, PA, USA
	Emsian	Battery Point Fm	Gaspé Bay, QC, Canada	Fluvial-alluvial system	Mudstone with no observed pedogenic alteration	Unknown geochemical profile	Downward orientated root casts and moulds.	Root traces D = 0.5–2 cm L = 10–90 cm	Plant casts, D = 10–15 cm Trimerophytes, lycophytes and rhyniopsids known in the region	~3600 <sup>‡</sup>	Gensel and Andrews (1984); McElwain and Chaloner (1995); Elick <i>et al.</i> (1998)	
												West Saugerites, Plattekil Creek, NY, USA
	Givetian	Manorkill Fm	East Windham, NY, USA	Deltaic to fluvial-alluvial system	Inceptisols in palaeosol sequence; clay-rich profile with ped structure, slickensided argillan cutans	Geochemistry of palaeosol sequences indicate losses of Si and nutrient cations	Stump casts and drab halbed root traces that extend downwards	Stumps D = 25–30 cm Roots D = 3–5 cm	Stumps and roots of archaeopteridalean progymnosperms	~3900 <sup>†</sup>	Cox <i>et al.</i> (2001); Mintz <i>et al.</i> (2010); Retallack and Huang (2011)	
												Schoharie Creek, Gilboa, NY, USA
	Frasnian	Walton Fm	Peas Eddy, NY, USA	Deltaic to fluvial-alluvial system	? Inceptisol; 1 m thick profile (compacted), weakly pedified, surface waterlogged, clay-rich B horizon	Production and illuviation of clays, gleying, ferruginization	Drab-halbed root traces, root sheath within carbonate nodules	Stump and large root traces	Stump D = 30 cm Roots 14 cm in depth mottled traces to 96 cm depth	Callixylon logs, <i>Archaeopteris</i> leaves in palaeo-channels above	~2800 <sup>†</sup>	Retallack (1985)

**FIG. 2.** Selection of relevant Silurian to Middle Devonian sites across the Appalachian belt, North America, where palaeosol research, including the collection of palaeobotanical and geochemical data, has been conducted. Unknowns are highlighted in bold. *Abbreviations:* D, diameter; Bkss, soil taxonomy code for a B horizon with an accumulation of carbonates (k) and with slickensides (ss); L, length; NY, New York, USA; PA, Pennsylvania, USA; Q, Quebec, Canada; RCO<sub>2</sub>, ratio of palaeo-CO<sub>2</sub> concentration against pre-industrial levels. \*Palaeosol type based on modern soil taxonomy of the USDA; †RCO<sub>2</sub> calculated from calcrete nodules; ‡RCO<sub>2</sub> calculated from cuticle stomatal densities.

in the Late Devonian to early Carboniferous, respectively (Retallack 1986, 2003).

Devonian forests are thought to have profoundly altered soils, sediment transportation, the hydrological cycle, terrestrial geomorphology and ecological habitats (Algeo and Scheckler 1998). As a result of their large biomass and organic matter inputs into soil, trees drive the progressive mobilization of soil exchangeable base cations (such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) through soil acidification, weathering and leaching. Aluminium and iron can also be mobilized from topsoil, but to a lesser extent than base cations. The liberated iron and aluminium are normally reprecipitated deeper in the soil profile where conditions are drier and less acidic. Base cations are sometimes reprecipitated at depth, but a greater proportion is typically leached out into catchments. In both modern and fossil soils, these changes in soil profile geochemistry can be systematically measured and characterized using element and cation ratios, for example  $\text{Al}_2\text{O}_3/\text{bases}$  or  $\text{Ba}/\text{Sr}$  (Retallack 1988, 1997; Sheldon and Tabor 2009).

Chronosequences of soil development in contemporary ecosystems (Walker and Syers 1976; Smeck 1985; Wardle *et al.* 2004) show unifying features critically linking plants and their roots and mycorrhizas to weathering of Ca phosphates and soil development. Soils developing on primary minerals such as those left by many retreating glaciers initially contain almost all their phosphorus in acid-soluble Ca-phosphate minerals, such as apatite. However, within 500 years the acid-soluble Ca-phosphate minerals are dissolved in temperate forest environments (Walker and Syers 1976), and there is substantial accumulation of organic P, much of which is contained in microbial biomass including mycorrhizas (Turner *et al.* 2013). Almost identical processes of rapid calcium phosphate transformation have been seen in a 600-year-old river alluvium forest chronosequence (Zehetner *et al.* 2009). Dissolution of calcium phosphates is correlated with simultaneous dissolution of calcium silicates under forests (Yanai *et al.* 2005).

We can hypothesize therefore that intensification of soil weathering processes resulting from the evolution of deeper, more complex rooting systems is reflected in the changes observed in the palaeosol record. These might be particularly evident through the Devonian and early Carboniferous, together with an overall increase in soil thickness and the appearance of new palaeosol types (Retallack 1986, 2003; Algeo *et al.* 2001). The establishment of more extensive soil-binding root systems as the continental land area became increasingly forested would have reduced surface runoff, erosion rates and land–ocean sediment fluxes (Schumm 1968). This resulted in more stabilized landscapes, leading to changes in fluvial geomorphology (the appearance and increased occurrence of meandering river channels compared to braided channels;

Davies and Gibling 2010; Gibling and Davies 2012) and higher rates of weathering and pedogenesis.

The appearance of new soil types in the Devonian–Carboniferous, such as histosols and alfisols (organic-rich and clay-enriched soils, respectively), developed in part because of an increase in organic matter contribution and changes in the clay mineral composition, thought to be driven by intensification of weathering by the evolution of forested ecosystems. Biologically active soils are effective in clay mineral formation and linked to the activities of fine roots and fungi associated with forest soils (Pate and Verboom 2009; Verboom *et al.* 2010). It has recently been hypothesized that the rise of forests enhanced the biotic processes that promote pedogenic clay mineral production, as vegetation reduced soil erosion and the rapid loss of clays, while organic matter debris retained cations and increased fluid residence time (Hillier 2006; Kennedy *et al.* 2006). In effect, forests act as ‘clay mineral factories’ driving increased formation of clay minerals with a relatively low negative layer charge (moles per formula unit), including expandable mixed-layer clays of the smectite group, with mineralogical shifts from mica-illite and chlorite towards smectitic and kaolinitic assemblages typical of pedogenic clay minerals (Weaver 1989; Hillier 2006; Kennedy *et al.* 2006).

The ‘clay mineral factory’ (CMF) hypothesis (Kennedy *et al.* 2006) requires that the kinds of clay minerals formed in well-drained soil profiles become more complex in nature, origin and organization as the ‘factory’ processes become more advanced and efficient over time (Weaver 1989; Hillier 2006), although its inception as early as the Neoproterozoic as suggested by Kennedy *et al.* (2006) is disputed by Tosca *et al.* (2010). By analogy with modern soil chronosequences, the origins of the clay minerals are anticipated to change from simple detrital inheritance from the parent material, to progressively more complex transformations (including elemental substitutions within sheet silicate structures) and eventual neoformations (precipitation from a soil solution; Hillier 2006). Additionally, increases in the variety of pedogenic mixed-layer clays, and more obvious changes in mineralogy with soil horizonation, would be expected. The CMF hypothesis therefore provides a tractable framework for quantitatively documenting enhancements in biotic weathering processes recorded in palaeosols.

## EVALUATING THE DEVONIAN PLANT HYPOTHESIS WITH DRILL CORES FROM EARLY FOREST SOILS

We are investigating the evolution of forests and complex rooting systems through the critical Silurian–Devonian interval and their interaction with the Earth system. The



project links these fields into a unifying framework that bridges between palaeontology, soil biogeochemistry and ecosystem processes, to develop a rigorous investigation into the effects of the evolution of forest ecosystems on soils and the geochemical carbon cycle. The central thrust of this project is to integrate palaeontological, mineralogical and geochemical analyses of palaeosol sequences via a mechanistic understanding of the effects of trees, their roots and mycorrhizas on the weathering and fate of Ca-silicate and Ca-phosphate minerals as drivers of Earth's atmospheric CO<sub>2</sub> history.

#### *Palaeontological and geological approaches*

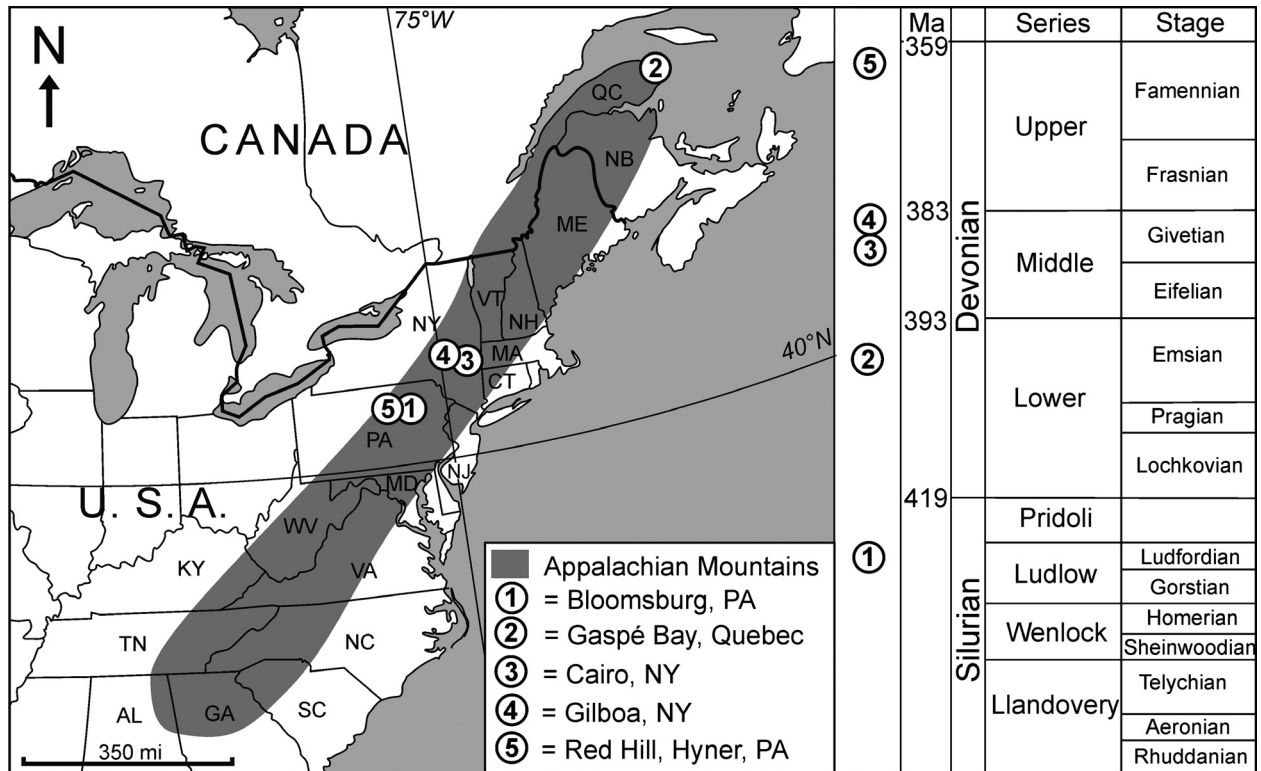
As part of the wider palaeobotanical and palaeopalynological community, three team members, WES, CMB and JEAM, are generating a significant new understanding of the plants and communities of the earliest forests leading increasingly to the revised view that large trees gradually evolved through the Middle Devonian in monospecific or mixed forests, rather than in a step change with the sudden appearance of *Archaeopteris* forests (Stein *et al.* 2012). Important new megafossils with exceptional preservation are shedding light on this transition, in terms of both the aerial parts of the plants and their rooting structures, to allow accurate whole plant reconstructions (Stein *et al.* 2007; Giesen and Berry 2013). Additionally, by recognizing the *in situ* spore taxa of individual plants, the palaeogeography and radiation of these forests are currently being tracked through the Middle to Late Devonian by comparisons to the dispersed spore record.

Exciting discoveries of *in situ* fossil forest 'floors' in the Middle Devonian rocks of New York State, where the 'footprints' of the position of individual trees within a forested ecosystem have been preserved, are now allowing inferences of forest composition and ecology (Gilboa Forest, Stein *et al.* 2012). At a site near Cairo, NY, the uppermost surface of a single palaeosol is extensively exposed across a quarry floor, revealing the *in situ* moulds of pseudo-sporochnalean cladoxylopsid and early archaeopteridalean rooting structures (Stein *et al.* 2012). Through meticulous mapping of the surface, this remarkable locality is revealing the rooting behaviours of these two tree types, which will improve our understanding of root morphologies and rooting behaviours of Middle Devonian trees (Algeo and Scheckler 1998, fig. 3; Fig. 1). Root measurements and spatial data from the mapped surface are providing information on the composition and structure of a new type of mixed Middle Devonian forest. Critically, this work provides opportunities for relating the *in situ* occurrence of the rooting structures of trees of different types and statures to palaeosol weathering profiles beneath, characterized by detailed geochemical and mineralogical analyses.

#### *Palaeopedology and geochemical studies*

Recent experimental studies (Quirk *et al.* 2014a, b) have demonstrated a direct link between rates of photosynthate carbon allocation to mycorrhizal fungal networks and enhanced mineral weathering rates (see experimental approaches below). We therefore hypothesize that the evolutionary advance of trees left geochemical and mineralogical effects detectable in palaeosols as forested ecosystems increased the quantity and depth of photosynthate chemical energy transported into the soil through roots, mycorrhizal fungi and litter organic matter inputs. The evolutionary sequence from shallow-rooted herbaceous-sized plants to deep-rooted forests through the Silurian and Devonian probably intensified soil acidification and strengthened elemental enrichments and depletions in surface soil horizons compared with underlying parent material, especially increasing the loss of bases, such as Ca, relative to Al and Fe. An increase in clay mineral production is also expected through time, especially the formation of smectitic and kaolinitic assemblages. In theory, these changes should be reflected in palaeosol profiles from the Silurian into the Devonian. One major challenge for detecting such changes is the possible alteration of clay minerals during burial diagenesis, in particular smectite to illite (Hillier 2006). However, via quantitative analysis of bulk and clay mineralogical composition of the palaeosols in a profile framework, we aim to identify potential diagenetic changes to the original (weathered) phase assemblage (as the overall phase assemblage is constrained by bulk chemical composition) and hence control for differences in the nature and extent of potentially confounding postdepositional changes in mineralogy.

Recent developments in the field of isotope biogeochemistry (Pett-Ridge *et al.* 2009) have created the additional opportunity to develop <sup>87</sup>Sr/<sup>86</sup>Sr isotopic ratios of plant fossils and palaeosols as novel geochemical proxies of biological weathering over geological time. As plants take up Sr isotopes with minimal fractionation (Kennedy *et al.* 1998), measurements of the <sup>87</sup>Sr/<sup>86</sup>Sr ratio of foliage and bedrock allow determination of the proportion of foliar Sr derived from bedrock by weathering (as opposed to an atmospheric source) via mass balance calculations. Thus, changes in fossil foliar <sup>87</sup>Sr/<sup>86</sup>Sr ratios during the colonization of the land, and subsequent rise of forests through the Silurian and Devonian, are likely to reflect enhanced biological weathering processes. Depth-dependent changes in <sup>87</sup>Sr/<sup>86</sup>Sr ratios are also seen in modern forest soils with actively weathering minerals (Pett-Ridge *et al.* 2009). We will therefore investigate how foliar and palaeosol depth-profiles of <sup>87</sup>Sr/<sup>86</sup>Sr ratios changed through time as forests and their rooting systems evolved through the Silurian–Devonian.



**FIG. 3.** Five localities selected across the Appalachian ‘Old Red Sandstone’ belt of eastern North America for the drilling and sampling of palaeosols of late Silurian to Late Devonian age.

To establish the intensity and depth of plant-driven changes in palaeosol profiles linked to the evolution and rise of forest ecosystems, we have sampled a 60-Ma time-series of late Silurian to Late Devonian palaeosols at five localities on the Appalachian ‘Old Red Sandstone’ belt of eastern North America (Fig. 3). Detailed sedimentological and depth-dependent clay mineralogical (X-ray diffraction, XRD) and bulk geochemical (X-ray fluorescence and inductively coupled plasma mass spectrometry) analyses on uncontaminated and unweathered surfaces and drilled cores are providing a unique resource to investigate plant–mineral interactions beneath Devonian forests. Biotic weathering by Middle Devonian forests from New York State will be compared with evidence for weathering by pre-forest, early vascular land plants with diminutive rooting systems, and shallow rooting vegetation from Silurian and Early Devonian localities at Bloomsburg, Pennsylvania and Gaspé Bay, Canada, respectively, covering the period 420–390 Ma (Fig. 3). These strata were targeted because they: (1) provide a relatively complete Silurian–Devonian time-series; (2) are well characterized in terms of their stratigraphy, sedimentology, palaeopedology and palaeontology; (3) contain abundant terrestrial deposits including palaeosols; (4) yield abundant plant megafossils and dispersed microfossils (spores); and (5)

contain a time-series of palaeosols that developed within the same climatic belt and on regolith derived from the same source-uplift of the Appalachian Mountains (Woodrow and Sevon 1985). Both major and trace element profiles are known to be preserved within Appalachian Palaeozoic palaeosols (Driese *et al.* 1992; Mora and Driese 1999; Retallack and Huang 2011). Importantly, the sites currently being investigated have only been subjected to relatively shallow post-Palaeozoic burial (Sarwar and Friedman 1995).

State-of-the-art full pattern-fitting XRD methods (Omotoso *et al.* 2006) are revealing the ‘speciation’ of major elements into different minerals. This includes all the clay minerals and hydrous oxides, which can be validated by comparison with independently determined bulk chemical compositions. These bulk analyses define the soil profile development in terms of relative gains and losses of major elements in relation to the mineralogical phases formed or altered by weathering with respect to the soil parent material. This ‘mineralogical budgeting’ approach has been successfully applied to modern soils (Andrist-Rangel *et al.* 2007), but is yet to be applied to palaeosols. Furthermore, by quantitatively analysing the bulk mineralogical composition of the palaeosols in a profile framework, we are able to identify potential diagenetic changes

to the original (weathering) phase assemblage, as the overall phase assemblage is constrained by bulk chemical composition. This approach allows and controls for differences in the nature and extent of potentially confounding postdepositional changes in mineralogy for each site. Additionally, precise clay mineral identification using XRD on oriented clay fractions will test the clay mineral factory hypothesis (Kennedy *et al.* 2006) in relation to known communities of terrestrial plants in different evolutionary stages through the critical transition to the development of forested ecosystems and different tree types.

#### *Palaeosols beneath the Middle Devonian fossil forest at Cairo, NY*

The Middle Devonian fossil forest ‘floor’ at Cairo, NY (Fig. 3), mapped by Stein, Berry and others, provides a unique opportunity to quantitatively analyse ancient plant–soil interactions from two major groups of early arborescent plants in relation to their rooting structures, namely archaeopteridalean progymnosperms and pseudo-sporochnalean cladoxylopsids. This locality shows exceptional preservation of *in situ* root morphology and palaeosol structure as a result of a rapid flooding and burial event, covering the rooting horizon of the trees with a sealing layer of clay-rich green siltstone that includes fish remains. This layer has a sharp lower boundary with no evidence of downwards movement of material, although the degree of possible associated hydromorphy will be assessed geochemically. Two drilling programmes (in 2012 and 2013) extracted a total of 18 cores of 1.8–3 m length via a mobile drill rig (Fig. 4A) through the forest floor (Fig. 4B) into the palaeosol beneath (Fig. 4C). Core positions were carefully selected to establish pedological variation across the mapped palaeosol surface, particularly beneath different tree types and statures. Five cores were positioned between main roots close to the basal trunk moulds of five individual archaeopteridaleans of varying size based on the lateral extent of root moulds observed at the surface. A further core was taken directly through a horizontally running primary root at a distance of ~6 m from the centre of the largest archaeopteridalean root mould. Seven cores were positioned close to seven individual cladoxylopsids (Fig. 4B) of various sizes, with an additional core taken directly through the centre of the largest individual. A further four cores were extracted across the palaeosol horizon and surrounding area to elucidate the lateral extent of the palaeosol and the stratigraphic relationship with the quarry limiting walls. The cores were transported to the New York State Museum, Albany, where they were split lengthways (Fig. 4D). Detailed analyses of pedologi-

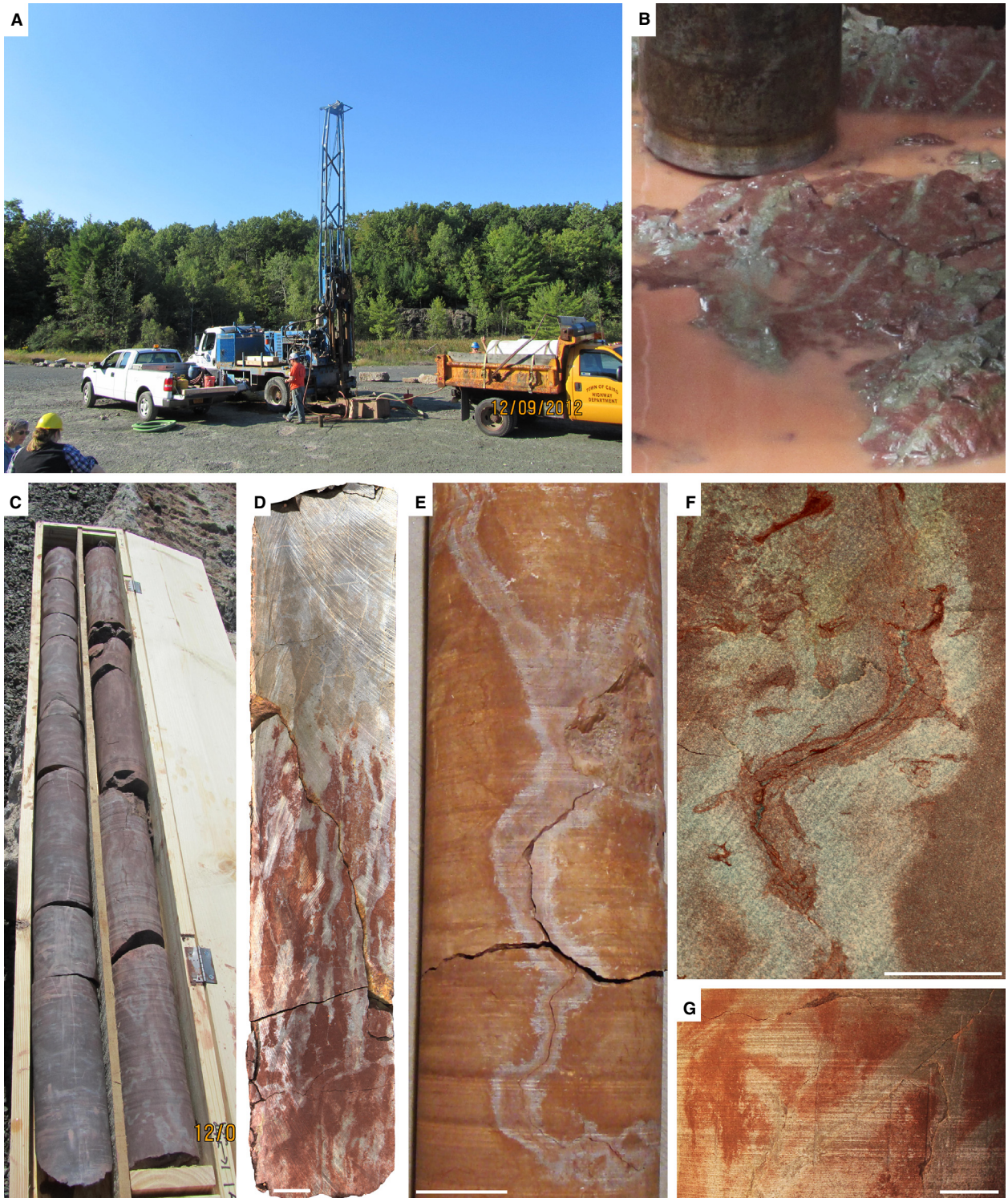
cal features (both macro- and micromorphological) at depth include analyses of texture (grain size), structure (including the presence of features such as slickensided surfaces or carbonate nodules), horizon thickness and horizon boundary types. Particular attention is drawn to any rooting structures (Fig. 4E–G): their morphology, preservation, dimensions, abundance and the maximum depth of rooting.

Initial observations indicate the presence of at least two palaeosols, either stacked directly on top of one another, or separated by parallel-bedded fine-grained heterolithics that represent unweathered parent material. The uppermost palaeosol is approximately 1.66 m thick, interpreted as a palaeo-vertisol, with evidence of a clay-rich middle (B) horizon comprised of wedge-shaped pedes with slickensided clay skins. Although there is some evidence of surface gleying in the uppermost (A) horizon, the majority of the palaeosols are bright red. Numerous root traces, or ‘rhizoliths’, are preserved throughout, mostly as rhizohaloes (diffuse, blue-grey, chemically altered zones sometimes referred to as drab-haloes) that develop around the root and may remain even after all other traces have gone (Retallack 1988; Wright 1992; Kraus and Hasiotis 2006). Some rhizohaloes, however, possess a central carbonaceous strand (Fig. 4F–G) and/or clay-rich internal cast (Fig. 4E–F). At least four rhizolith morphologies have been identified, and work is in progress to relate these back to the structures observed at the surface.

#### **EXPERIMENTAL APPROACHES TO ESTABLISHING THE ROLE OF MYCORRHIZAL FUNGI IN WEATHERING**

Mechanistic insights into the role of AM fungal partners of early trees in driving weathering and biogeochemical cycles over evolutionary time are being gained with carefully designed field and controlled-environment laboratory experiments. These experiments using extant mycorrhizal trees selected to represent exemplar taxa of past forests are important for establishing cause and effect because plant root–fungal relationships are rarely preserved in the fossil record. In Devonian palaeosols, *in situ* tree roots are often preserved only as moulds and casts (voids filled with sediment or mineral concretions; Driese *et al.* 1997; Elick *et al.* 1998; Mintz *et al.* 2010; Stein *et al.* 2012), or simply the geochemical traces of their decay (i.e. rhizohaloes, Fig. 4D, G). At best the lignified parts are permineralized, preserving the original anatomy in three dimensions (Meyer-Berthaud *et al.* 2013), or as coalified compressions (Giesen and Berry 2013), although both types are usually found in allochthonous deposits (i.e. not in life position). In most cases, the resolution of





**FIG. 4.** Middle Devonian palaeosols from a locality near Cairo, New York State. A, extraction of drill cores using a mobile drill rig. B, core drilling through red palaeosol near the mould of a cladoxylopsid stump, penetrating through radially orientated 'drab-haloed' roots. Drill bit diameter = 8 cm. C, extracted core, up to 3 m in length. D, split core of the top ~37 cm of a core drilled beneath a cladoxylopsid rooting structure; scale bar represents 2 cm. E–G, examples of rhizolith types preserved in the palaeosol beneath the 'forest floor'; E, archaeopteridalean-type rhizolith, preserved as clay cast, surrounded by 'drab-halo', scale bar represents 3 cm; F, small archaeopteridalean-type rhizolith, preserved as clay cast with central carbonaceous strand, surrounded by a 'drab-halo', scale bar represents 1 cm; G, cladoxylopsid rhizolith, preserved as rhizohalo, with some preservation of carbonaceous material, scale bar represents 1 cm.



preservation is too coarse for much finer root hairs or fungal hyphae, unless preserved in exceptional taphonomic circumstances such as the Lower Devonian Rhynie Chert (late Pragian to early Emsian hot spring deposits that predate the evolution of arborescence; Taylor *et al.* 2004; Strullu-Derrien *et al.* 2014).

Roots and mycorrhizal fungi are the main conduits through which chemical energy fixed by shoot photosynthesis is transported into the soil, contributing to soil acidification and mineral weathering (Taylor *et al.* 2009). To isolate the activities of AM fungal partners from those of the host roots, we have implemented experiments that use fungal-ingrowth mesh bags and mesh-walled cores. In these systems, the mesh pore size allows fine-diameter hyphal mycelium, but not larger diameter roots, to penetrate and interact with the contents of the bags or cores (Johnson *et al.* 2001; Quirk *et al.* 2012). By filling the mesh with well-characterized grains of silicate rocks and minerals, and burying them beneath mycorrhizal plants and trees, we are able to quantify mycorrhizal AM hypha–mineral interactions. This includes measurements of AM hyphal networks colonizing various rock types, assessment of direct physical disruption of mineral surfaces by AM hyphae and chemical dissolution of basalt grains following interactions with AM fungi (Quirk *et al.* 2012; Quirk *et al.* 2014a, b).

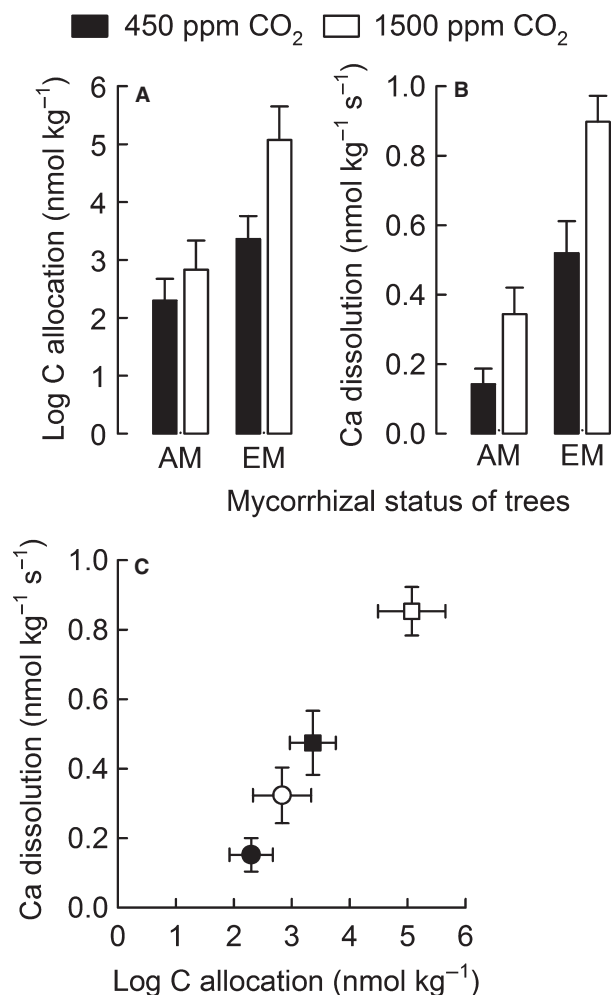
A field experiment at the UK National Arboretum at Westonbirt in Gloucestershire demonstrated preferential colonization of basalt grains by the AM fungal partners of established *Metasequoia* and *Sequoia* (Cupressaceae) trees over less easily weathered granite and pure quartz grains (Quirk *et al.* 2012). The crushed grains were of uniform size and buried 5–10 cm deep below the trees within mesh bags. This targeted proliferation is indicative of positive feedbacks between elemental uptake from basalt (as a more exploitable nutrient element resource compared with granite and quartz) by hyphal networks in return for increasing carbon provision from tree roots. *Metasequoia* and *Sequoia* are AM-associating gymnosperms and were selected as representatives of extant tree types that are amongst the closest modern analogues to Devonian forest trees. This is important because gymnosperms from the Pinaceae (*Pinus* and *Larix*) form mycorrhizal associations known as ectomycorrhizas with soil fungi from later-evolving ‘higher’ clades, including the basidiomycetes and ascomycetes, whereas the main AM-forming fungi are from the glomeromycetes (Schußler *et al.* 2001; Taylor *et al.* 2009 and references therein) that co-evolved with early land plants.

Ectomycorrhizas are thought to have emerged in the Early Cretaceous, and the first unequivocal fossil evidence suggests they were extant by 50 Ma (LePage *et al.* 1997), with molecular clock evidence indicating they existed by at least 200 Ma (Berbee and Taylor 1993). Critically, in

the arboretum study where climate and substrate are consistent across taxa, *Pinus* and *Larix* were associated with greater hyphal colonization and weathering of the basalt grains, highlighting fundamental functional differences between the two types of mycorrhizal symbioses (ancestral AM and later, independently evolved ectomycorrhiza; Quirk *et al.* 2012). Nevertheless, the key point is that AM fungi in association with gymnosperm trees exhibited mineral-specific foraging behaviour, and prior to this demonstration, their weathering capabilities had been dismissed (Lambers *et al.* 2009). Moreover, an independent study of 24 paired forest plots in New Zealand, comparing weathering under trees that associate with AM or with EM fungi, revealed clear evidence of crystalline apatite weathering, presumably for P uptake, by both kinds of trees (Koele *et al.* 2014).

The capacity of AM fungi to physically alter silicate mineral surfaces has been revealed through the application of vertical scanning interferometry (VSI) to characterize the microscale surface topography of muscovite – an atomically smooth potassium-bearing phyllosilicate – co-buried inside the mesh bags beneath the trees. VSI measurements provided direct evidence of localized physical alteration and loss of the muscovite where colonizing AM hyphae contacted the mineral surface (Quirk *et al.* 2012). This so-called fungal trenching behaviour was later verified for AM fungi in association with *Sequoia* and *Acer* saplings in a pot experiment under controlled-environment conditions (Quirk *et al.* 2014b). Critically, the morphological characteristics of the trenches on the mineral were consistent with AM hyphal anatomy. Carefully designed VSI procedures provided quantitative assessment of increases in mineral surface roughness linked to colonization by AM fungal hyphae (Quirk *et al.* 2014a, b). Together with the evidence of direct AM hypha–mineral interaction and physical disruption of the mineral surface, this highlights the potential importance of AM to biotic weathering.

Experiments under controlled-environment conditions in an elevated CO<sub>2</sub> atmosphere have allowed plant–mycorrhiza–mineral interactions to be investigated in conditions approximating those during the Devonian rise in forested ecosystems. These experiments have demonstrated that an atmosphere enriched in CO<sub>2</sub> allows trees to support larger hyphal networks and intensifies physical alteration of silicate mineral surfaces by AM fungi (Quirk *et al.* 2014b). The link between carbon-energy fluxes into mycorrhizal networks and the intensity of biological weathering rates has been established with <sup>14</sup>C tracer experiments (Quirk *et al.* 2014a). The radioactive CO<sub>2</sub> is fixed by the tree canopy and the assimilated <sup>14</sup>C is monitored as it is transported through the plant, below ground into the roots and mycorrhizal hyphal networks within hyphal-ingrowth mesh-covered cores containing basalt



**FIG. 5.** The linkage between: A, autotrophic carbon provision into networks of arbuscular mycorrhizal (AM) and ectomycorrhizal (EM) fungi partnering trees; and B, dissolution of Ca-silicate minerals in basalt grains. Both the carbon flux and weathering response increase with atmospheric CO<sub>2</sub> enrichment from ambient to Early Palaeozoic CO<sub>2</sub> concentrations of 1500 ppm. C, cross-plots reveal the broad proportionality of the weathering response to the carbon flux (circles are AM species, squares are EM species). The AM trees studied were *Ginkgo biloba*, *Sequoia sempervirens* and *Metasequoia glyptostroboides*; and EM trees were *Pinus sylvestris* and *Betula pendula*. Figure reproduced from Quirk *et al.* (2014a).

grains. The amount of <sup>14</sup>C detected in and around the basalt grains reflects its assimilation into mycorrhizal fungal biomass and exudates and can be linked to rates of Ca dissolution from silicate minerals within the basalt (Quirk *et al.* 2014a; Fig. 5). Both the carbon flux into mycorrhizal networks and the dissolution of Ca-silicate from the basalt were higher under the experimentally simulated high-CO<sub>2</sub> Devonian atmosphere, and the effects are greater for ectomycorrhizal trees than for AM trees (Quirk *et al.* 2014a).

Although these experiments were necessarily conducted using contemporary tree and fungal taxa, the genes controlling functions of AM fungal symbiosis are ancient and highly conserved (Bonfante and Genre 2008, 2010), retaining similarities to fungi in the Mucoromycotina and Chytridiomycota from which they diverged hundreds of millions of years ago (Hibbett and Matheny 2009). These experimental findings offer new insights into the mechanisms underpinning terrestrial biotic feedbacks on long-term carbon cycling associated with evolutionary advancement of trees and their mycorrhizal fungi that cannot be gained from the geological record alone.

## CONCLUSION

The central hypothesis of our drilling project is that the evolutionary advance of trees left geochemical effects detectable in palaeosols as forested ecosystems increased the quantity and depth of chemical energy transported into the soil through roots, mycorrhizal fungi and litter. These effects probably intensified soil acidification, increased the strength of isotopic and elemental enrichment in surface soil horizons and enhanced the weathering of Ca-Si and Ca-P minerals, and the formation of pedogenic clays, leading to long-term sequestration of atmospheric CO<sub>2</sub> through the formation of marine carbonates with the liberated terrestrial Ca. By adopting a unifying framework that bridges between palaeontology, soil biogeochemistry and ecosystem processes, current research studies aim to increase our mechanistic understanding of how the evolutionary rise of deep-rooting forests intensified weathering and pedogenesis. Augmenting this systems palaeobiology approach, are studies of key ecosystem processes within extant communities of trees, mycorrhizal fungi and associated rhizosphere microbial communities. The effects of these interactions at the interface between land plants and the lithosphere are more often than not precluded from traditional palaeontological approaches, yet their probable importance is gaining wider acceptance.

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## REFERENCES

- ALGEO, T. J. and 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, London B*, **353**, 113–130.
- — and MAYNARD J. B. 2001. Effects of the Middle to Late Devonian spread of vascular land plants on weathering regimes, marine biotas, and global climate. 213–236. In GENSEL, P. G. and EDWARDS, D. (eds). *Plants invade the land: evolutionary and environmental perspectives*. Columbia University Press, New York, 304 pp.
- ANDRIST-RANGEL, Y., EDWARDS, A. C., HILLIER, S. and ÖBORN, I. 2007. Long-term K dynamics in organic and conventional mixed cropping systems related to management and soil properties. *Agriculture, Ecosystems & Environment*, **122**, 413–426.
- BEERLING, D. J. 2007. *The emerald planet: how plants changed Earth's history*. Oxford University Press, Oxford, 288 pp.
- — and BERNER, R. A. 2005. Feedbacks and the coevolution of plants and atmospheric CO<sub>2</sub>. *Proceedings of the National Academy of Sciences of the United States of America*, **102**, 1302–1305.
- BERBEE, M. L. and TAYLOR, J. W. 1993. Dating the evolutionary radiations of the true fungi. *Canadian Journal of Botany*, **71**, 1114–1127.
- BERNER, R. A. 1997. The rise of plants and their effect on weathering and atmospheric CO<sub>2</sub>. *Science*, **276**, 544–546.
- — 2004. *The Phanerozoic carbon cycle: CO<sub>2</sub> and O<sub>2</sub>*. Oxford University Press, New York, 158 pp.
- — 2006. GEOCARBSULF: a combined model for Phanerozoic atmospheric O<sub>2</sub> and CO<sub>2</sub>. *Geochimica et Cosmochimica Acta*, **70**, 5653–5664.
- — and KOTHALAVA, Z. 2001. GEOCARB III: a revised model of atmospheric CO<sub>2</sub> over Phanerozoic time. *American Journal of Science*, **301**, 182–204.
- — BERNER, E. K. and MOULTON, K. L. 2003. Plants and mineral weathering: present and past. *Treatise on Geochemistry*, **5**, 169–188.
- BERRY, C. M. and FAIRON-DEMARET, M. 2002. The architecture of *Pseudosporochnus nodosus* Leclercq et Banks: a Middle Devonian Cladoxylopsid from Belgium. *International Journal of Plant Sciences*, **163** (5), 699–713.
- BOND, D., WIGNALL, P. B. and RACKI, G. 2004. Extent and duration of marine anoxia during the Frasnian–Famennian (Late Devonian) mass extinction in Poland, Germany, Austria and France. *Geological Magazine*, **141** (2), 173–193.
- BONFANTE, P. and GENRE, A. 2008. Plants and arbuscular mycorrhizal fungi: an evolutionary-developmental perspective. *Trends in Plant Science*, **13**, 492–498.
- — 2010. Mechanisms underlying beneficial plant–fungus interactions in mycorrhizal symbiosis. *Nature Communications*, **1**, 48. doi:10.1038/ncomms1046
- CAPUTO, M. V. 1985. Late Devonian glaciation in South America. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **51**, 291–317.
- COX, J. E., RAILSBACK, L. B. and GORDON, E. A. 2001. Evidence from Catskill pedogenic carbonates for a rapid Late Devonian decrease in atmospheric carbon dioxide concentrations. *Northeastern Geology & Environmental Sciences*, **23**, 91–102.
- DAVIES, N. S. and GIBLING, M. R. 2010. Paleozoic vegetation and the Siluro–Devonian rise of fluvial lateral accretion sets. *Geology*, **38**, 51–54.
- DRIESE, S. G., MORA, C. I., COTTER, E. and FOREMAN, J. L. 1992. Paleopedology and stable isotope chemistry of Late Silurian vertic paleosols, Bloomsburg Formation, Central Pennsylvania. *Journal of Sedimentary Petrology*, **62**, 825–841.
- — and ELICK J. M. 1997. Morphology and taphonomy of root and stump casts of the earliest trees (Middle to Late Devonian), Pennsylvania and New York, U.S.A. *Palaaios*, **12**, 524–537.
- EDWARDS, D. 1994. Towards an understanding of pattern and process in the growth of early vascular plants. 39–59. In INGRAM, D. S. (ed.). *Shape and form in plants and fungi*. Linnean Society, London, 380 pp.
- — 1996. New insights into early land ecosystems: a glimpse of a Lilliputian world. *Review of Palaeobotany & Palynology*, **90**, 159–174.
- — and SELDEN, P. A. 1992. The development of early terrestrial ecosystems. *Botanical Journal of Scotland*, **46**, 337–366.
- ELICK, J. M., DRIESE, S. G. and MORA, C. I. 1998. Very large plant and root traces from the Early to Middle Devonian: implications for early terrestrial ecosystems and atmospheric p(CO<sub>2</sub>). *Geology*, **26**, 143–146.
- FEAKES, C. R. and RETALLACK, G. J. 1988. Recognition and chemical characterization of fossil soils developed on alluvium; a Late Ordovician example. 35–48. In REINHARDT, J. and SIGLEO, W. R. (eds). *Paleosols and weathering through geologic time: principles and applications*. Geological Society of America Special Paper, **216**, 181 pp.
- FIELD, K. J., RIMINGTON, W. R., BIDARTONDO, M. I., ALLINSON, K. E., BEERLING, D. J., CAMERON, D. D., DUCKETT, J. G., LEAKE, J. R. and PRESSEL, S. 2015. First evidence of mutualism between ancient plant lineages (Haplomitriopsida liverworts) and Mucoromycotina fungi and its response to simulated Palaeozoic changes in atmospheric CO<sub>2</sub>. *New Phytologist*, **205**, 743–756.
- GENSEL, P. G. and ANDREWS, H. N. 1984. *Plant life in the Devonian*. Praeger Publishers, New York, 380 pp.
- GIBLING, M. R. and DAVIES, N. S. 2012. Palaeozoic landscapes shaped by plant evolution. *Nature Geoscience*, **5**, 99–105.
- GIESEN, P. and BERRY, C. M. 2013. Reconstruction and growth of the early tree *Calamophyton* (Pseudosporochnales, Cladoxylopsida) based on exceptionally complete specimens from Lindlar, Germany (Mid-Devonian): organic connection of *Calamophyton* branches and *Duisbergia* trunks. *International Journal of Plant Sciences*, **174**, 665–686.
- HIBBETT, D. S. and MATHENY, B. P. 2009. The relative ages of ectomycorrhizal mushrooms and their plant hosts estimated using Bayesian relaxed molecular clock analyses. *BMC Biology*, **7**, 1–13.
- HILLIER, S. 2006. Formation and alteration of clay materials. 29–71. In REEVES, G. M., SIMS, I. and CRIPPS, J. C.



- (eds). *Clay materials used in construction*. Geological Society of London, Engineering Geology Special Publications, **21**, 511 pp.
- HUMPHREYS, C. P., FRANKS, P. J., REES, M., BILDARTONDO, M. I., LEAKE, J. R. and BEERLING, D. 2010. Mutualistic mycorrhiza-like symbiosis in the most ancient group of land plants. *Nature Communications*, **1**, 103. doi:10.1038/ncomms1105
- JOACHIMSKI, M. M. and BUGGISCH, W. 1993. Anoxic events in the late Frasnian – causes of the Frasnian–Famennian faunal crisis? *Geology*, **21**, 675–678.
- 2002. Conodont apatite  $\delta^{18}\text{O}$  signatures indicate climatic cooling as a trigger of the Late Devonian mass extinction. *Geology*, **30**, 711–714.
- PANCOST, R. D., FREEMAN, K. H., OSTERTAGHENNING, C. and BUGGISCH, W. 2002. Carbon isotope geochemistry of the Frasnian–Famennian transition. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **181**, 91–109.
- JOBÁGY, E. G. and JACKSON, R. B. 2001. The distribution of soil nutrients with depth: global patterns and the imprint of plants. *Biogeochemistry*, **53**, 51–77.
- JOHNSON, D., LEAKE, J. R. and READ, D. J. 2001. Novel in-growth core system enables functional studies of grassland mycorrhizal mycelial networks. *New Phytologist*, **152**, 555–562.
- KENNEDY, M. J., CHADWICK, O. A., VITOUSEK, P. M., DERRY, L. A. and HENDRICKS, D. M. 1998. Changing sources of base cations during ecosystem development, Hawaiian Islands. *Geology*, **26**, 1015–1018.
- KENNEDY, M., DROSER, M., MAYER, L. M., PEVEAR, D. and MROFKA, D. 2006. Late Precambrian oxygenation; inception of the clay mineral factory. *Science*, **311**, 1446–1449.
- KENNEDY, K. L., GIBLING, M. R., EBLE, C. F., GASTALDO, R. A., GENSEL, P. G., WENER-ZWANZIGER, U. and WILSON, R. A. 2013. Lower Devonian coaly shales of Northern New Brunswick, Canada: plant accumulations in the early stages of terrestrial colonization. *Journal of Sedimentary Research*, **83**, 1202–1215.
- KENRICK, P. and STRULLU-DERRIEN, C. 2014. The origin and early evolution of roots. *Plant Physiology*, **166**, 570–580.
- KERP, H., HASS, H. and MOSSBRUGGER, V. 2001. New data on *Nothia aphylla* Lyon 1964 ex El-Saadawy et. Lacey 1979, a poorly known plant from the Lower Devonian Rhynie Chert. 52–82. In GENSEL, P. G. and EDWARDS, D. (eds). *Plants invade the land: evolutionary and environmental perspectives*. Columbia University Press, New York, 304 pp.
- KOELE, N., DICKIE, I. A., BLUM, J. D., GLEASON, J. D. and DE GRAFF, L. 2014. Ecological significance of mineral weathering in ectomycorrhizal and arbuscular mycorrhizal ecosystems from a field-based comparison. *Soil Biology & Biochemistry*, **69**, 63–70.
- KRAUS, M. J. and HASIOTIS, S. T. 2006. Significance of different modes of rhizolith preservation to interpreting paleoenvironmental and paleohydrologic settings: examples from Paleogene paleosols, Bighorn Basin, Wyoming, U.S.A. *Journal of Sedimentary Research*, **76**, 633–646.
- KRINGS, M., TAYLOR, T. N., HASS, H., KERP, H., DOTZLER, N. and HERMSEN, E. J. 2007. Fungal endophytes in a 400-million-yr-old land plant: infection pathways, spatial distribution, and host responses. *New Phytologist*, **174**, 648–657.
- LAMBERS, H., MOUGEL, C., JAILLARD, B. and HINSINGER, P. 2009. Plant–microbe–soil interactions in the rhizosphere: an evolutionary perspective. *Plant & Soil*, **321**, 83–115.
- LEAKE, J. R., DURAN, A. L., HARDY, K. E., JOHNSON, I., BEERLING, D. J., BANWART, S. A. and SMITS, M. M. 2008. Biological weathering in soil: the role of symbiotic root-associated fungi biosensing minerals and directing photosynthate-energy into grain-scale mineral weathering. *Mineralogical Magazine*, **72**, 85–89.
- LEPAGE, B., CURRAH, R., STOCKEY, R. and ROTHWELL, G. 1997. Fossil ectomycorrhizae from the Middle Eocene. *American Journal of Botany*, **84**, 410–412.
- McELWAIN, J. C. and CHALONER, W. G. 1995. Stomatal density and index of fossil plants track atmospheric carbon dioxide in the Palaeozoic. *Annals of Botany*, **76**, 389–395.
- MEYER-BERTHAUD, B., SCHECKLER, S. E. and WENDT, J. 1999. *Archaeopteris* is the earliest known modern tree. *Nature*, **398**, 700–701.
- SORIA, A. and DECOMBEIX, A.-L. 2010. The land plant cover in the Devonian: a reassessment of the evolution of the tree habit. 59–70. In VECOLI, M., CLÉMENT, G. and MEYER-BERTHAUD, B. (eds). *The terrestrialization process: modelling complex interactions at the biosphere–geosphere interface*. Geological Society, London, Special Publications, **339**, 192 pp.
- DECOMBEIX, A.-L. and ERMACORA, X. 2013. Archaeopterid root anatomy and architecture: new information from permineralized specimens of Famennian age from Anti-Atlas (Morocco). *International Journal of Plant Sciences*, **174**, 364–381.
- MINTZ, J. S., DRIESE, S. G. and WHITE, J. D. 2010. Environmental and ecological variability of Middle Devonian (Givetian) forests in Appalachian Basin paleosols, New York, United States. *Palaios*, **25**, 85–96.
- MORA, C. I. and DRIESE, S. G. 1999. Palaeoenvironment, palaeoclimate and stable carbon isotopes of Palaeozoic red-bed palaeosols, Appalachian Basin, USA and Canada. *Special Publications of the International Association of Sedimentologists*, **27**, 61–84.
- and SEAGER P. A. 1991. Carbon dioxide in the Paleozoic atmosphere: evidence from carbon-isotope composition of pedogenic carbonate. *Geology*, **19**, 1017–1020.
- and COLARUSSO L. A. 1996. Middle to late Paleozoic atmospheric CO<sub>2</sub> levels from soil carbonate and organic matter. *Science*, **271**, 1105–1107.
- MORRIS, J. L. and EDWARDS, D. 2014. An analysis of vegetational change in the Lower Devonian: new data from the Lochkovian of the Welsh Borderland, U.K. *Review of Palaeobotany & Palynology*, **211**, 28–54.
- MURPHY, A. E., SAGEMAN, B. B. and HOLLANDER, D. J. 2000. Eutrophication by decoupling of the marine biogeochemical cycles of C, N, and P: a mechanism for the Late Devonian mass extinction. *Geology*, **28**, 427–430.

- NEAMAN, A., CHOROVER, J. and BRANTLEY, S. L. 2005. Element mobility patterns record organic ligands in soils on early Earth. *Geology*, **33**, 117–120.
- 2006. Effects of organic ligands on granite dissolution in batch experiments at pH 6. *American Journal of Science* **306**, 451–473.
- OMOTOSO, O., MCCARTY, D. K., HILLIER, S. and KLEEBERG, R. 2006. Some successful approaches to quantitative mineral analysis as revealed by the 3rd Reynolds Cup Contest. *Clay & Clay Minerals*, **54**, 748–760.
- PATE, J. S. and VERBOOM, W. H. 2009. Contemporary biogenic formation of clay pavements by eucalypts: further support for the phytotarium concept. *Annals of Botany*, **103**, 673–685.
- PETT-RIDGE, J. C., DERRY, L. A. and BARROWS, J. K. 2009. Ca/Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios as tracers of Ca and Sr cycling in the Rio Icacos watershed, Luquillo Mountains, Puerto Rico. *Chemical Geology*, **267**, 32–45.
- PIROZYNSKI, K. A. and MALLOCH, D. W. 1975. The origin of land plants: a matter of mycotropism. *Biosystems*, **6**, 153–165.
- POPP, B. N., ANDERSON, T. F. and SANDBERG, P. A. 1986. Brachiopods as indicators of original isotopic compositions in some Palaeozoic limestones. *Geological Society of America Bulletin*, **97**, 1262–1269.
- QUIRK, J., BEERLING, D. J., BANWART, S. A., KAKONYI, G., ROMERO-GONZALEZ, M. E. and LEAKE, J. R. 2012. Evolution of trees and mycorrhizal fungi intensifies silicate mineral weathering. *Biology Letters*, **8**, 1006–1011.
- ANDREWS, M. Y., LEAKE, J. R., BANWART, S. A. and BEERLING, D. J. 2014a. Ectomycorrhizal fungi and past high CO<sub>2</sub> atmospheres enhance mineral weathering through increased below-ground carbon-energy fluxes. *Biology Letters*, **10**, 20140375.
- LEAKE, J. R., BANWART, S. A., TAYLOR, L. L. and BEERLING, D. J. 2014b. Weathering by tree-root-associating fungi diminishes under simulated Cenozoic atmospheric CO<sub>2</sub> decline. *Biogeosciences*, **11**, 321–331.
- RAVEN, J. A. and EDWARDS, D. 2001. Roots: evolutionary origins and biogeochemical significance. *Journal of Experimental Botany*, **52**, 381–401.
- REMY, W., TAYLOR, T. N., HASS, H. and KERP, H. 1994. Four hundred-million-year-old vesicular arbuscular mycorrhizae. *Proceedings of the National Academy of Sciences*, **91**, 11841–11843.
- RETALLACK, G. J. 1985. Fossil soils as grounds for interpreting the advent of large plants and animals on land. *Philosophical Transactions of the Royal Society, London B*, **309**, 105–142.
- 1986. The fossil record of soils. 1–57. In WRIGHT, V. P. (ed.). *Paleosols: their recognition and interpretation*. Blackwell Scientific Publications, Oxford, 315 pp.
- 1988. Field recognition of paleosols. *Geological Society of America, Special Paper*, **216**, 1–20.
- 1997. Early forest soils and their role in Devonian global change. *Science*, **276**, 583.
- 2003. Soils and global change in the carbon cycle over geological time. *Treatise on Geochemistry*, **5** (5.18), 1–28.
- and HUANG, C. 2011. Ecology and evolution of Devonian trees in New York, USA. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **299**, 110–128.
- RUBINSTEIN, C. V., GERRIENNE, P., DE LA PUENTE, G. S., ASTINI, R. A. and STEEMANS, P. 2010. Early Middle Ordovician evidence for land plants in Argentina (eastern Gondwana). *New Phytologist*, **188**, 365–369.
- SANDBERG, C. A., ZIEGLER, W., DRESEN, R. and BUTLER, J. L. 1988. Late Frasnian mass extinction: conodont event stratigraphy, global changes, and possible causes. *Courier Forschungsinstitut Senckenberg*, **102**, 263–307.
- SARWAR, G. and FRIEDMAN, G. M. 1995. *Post-Devonian sediment cover over New York State: evidence from fluid-inclusion, organic maturation, clay diagenesis and stable isotope studies*. Lecture Notes in Earth Sciences, **58**, Springer, Berlin, 113 pp.
- SCHUßLER, A., SCHWARZOTT, D. and WALKER, C. 2001. A new fungal phylum, the Glomeromycota: phylogeny and evolution. *Mycological Research*, **105**, 1413–1421.
- SCHUMM, S. A. 1968. Speculations concerning paleohydrologic controls of terrestrial sedimentation. *Geological Society of America Bulletin*, **79**, 1573–1588.
- SCHWENDEMANN, A. B., DECOMBEIX, A.-L., TAYLOR, T. N., TAYLOR, E. L. and KRINGS, M. 2011. Morphological and functional stasis in mycorrhizal root nodules as exhibited by a Triassic conifer. *Proceedings of the National Academy of Sciences*, **108**, 13630–13634.
- SHELDON, N. H. and TABOR, N. J. 2009. Quantitative paleoenvironmental and paleoclimatic reconstruction using paleosols. *Earth-Science Reviews*, **95**, 1–52.
- SIMON, L., BOUSQUET, J., LEVESQUE, R. C. and LALONDE, M. 1993. Origin and diversification of endomycorrhizal fungi and coincidence with vascular land plants. *Nature*, **363**, 67–69.
- SMECK, N. E. 1985. Phosphorus dynamics in soils and landscapes. *Geoderma*, **36**, 185–199.
- SMITH, S. E. and READ, D. J. 2008. *Mycorrhizal symbiosis*. Third edition. Academic Press, Amsterdam, London, 800 pp.
- STEIN, W. E., MANNOLINI, F., HERNICK, L. V., LANDING, E. and BERRY, C. M. 2007. Giant cladoxypsid trees resolve the enigma of the Earth's earliest forest stumps at Gilboa. *Nature*, **446**, 904–907.
- BERRY, C. M., HERNICK, L. V. and MANNOLINI, F. 2012. Surprisingly complex community discovered in the mid-Devonian fossil forest at Gilboa. *Nature*, **483**, 78–81.
- STOCKEY, R. A., ROTHWELL, G. W., ADDY, H. D. and CURRAH, R. S. 2001. Mycorrhizal association of the extinct conifer *Metasequoia milleri*. *Mycological Research*, **105**, 202–205.
- STRULLU-DERRIEN, C. and STRULLU, D.-G. 2007. Mycorrhization of fossil and living plants. *Comptes Rendus Palevol*, **6**, 483–494.
- KENRICK, P., PRESSEL, S., DUCKETT, J. G., RIOULT, J.-P. and STRULLU, D.-G. 2014. Fungal associations in *Horneophyton ligneri* from the Rhynie Chert (c. 407 million years ago) closely resemble those in extant lower land plants: novel insights into ancestral plant–fungus symbioses. *New Phytologist*, **203**, 964–979.
- TAYLOR, T. N., KLAVINS, S. D., KRINGS, M., TAYLOR, E. L., KERP, H. and HASS, H. 2004. Fungi from the

- Rhynie Chert: a view from the dark side. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, **94**, 457–473.
- TAYLOR, L. L., LEAKE, J. R., QUIRK, J., HARDY, K., BANWART, S. A. and BEERLING, D. J. 2009. Biological weathering and the long-term carbon cycle: integrating mycorrhizal evolution and function into the current paradigm. *Geobiology*, **7**, 171–191.
- TOSCA, N. J., JOHNSTON, D. T., MUSHEGIAN, A., ROTHMAN, D. H., SUMMONS, R. E. and KNOLL, A. H. 2010. Clay mineralogy, organic carbon burial, and redox evolution in Proterozoic oceans. *Geochimica et Cosmochimica Acta*, **74**, 1579–1592.
- TURNER, B. L., LAMBERS, H., CONDRON, L. M., CRAMER, M. D., LEAKE, J. R., RICHARDSON, A. E. and SMITH, S. E. 2013. Soil microbial biomass and the fate of phosphorus during long-term ecosystem development. *Plant & Soil*, **367**, 225–234.
- VERBOOM, W. H., PATE, J. S. and ASPANDIAR, M. 2010. Neoformation of clay in lateral root catchments of mallee eucalypts: a chemical perspective. *Annals of Botany*, **105**, 23–36.
- WALKER, T. W. and SYERS, J. K. 1976. The fate of Phosphorus during pedogenesis. *Geoderma*, **15**, 1–19.
- WANG, B. and QIU, Y. L. 2006. Phylogenetic distribution and evolution of mycorrhizas in land plants. *Mycorrhiza*, **16**, 299–363.
- WARDLE, D. A., WALKER, L. R. and BARDGETT, R. D. 2004. Ecosystem properties and forest decline in contrasting long-term chronosequences. *Science*, **305**, 509–513.
- WEAVER, C. E. 1989. *Clays, muds, and shales*. Developments in Sedimentology, **44**, Elsevier, Amsterdam, 820 pp.
- WOODROW, D. L. and SEVON, W. D. 1985. *The Catskill Delta*. Geological Society of America Special Paper, **201**, 246 pp.
- WRIGHT, V. P. 1992. Paleosol recognition: a guide to early diagenesis in terrestrial settings. Chapter 12. 591–620. In WOLF, K. H. and CHILINGARIAN, G. V. (eds). *Diagenesis, III*. Developments in Sedimentology, **47**, Elsevier, Amsterdam.
- YANAI, R. D., BLUM, J. D., HAMBURG, S. P., ARTHUR, M. A., NEZAT, C. A. and SICCAMI, T. G. 2005. New insights into calcium depletion in Northeastern Forests. *Journal of Forestry*, **103**, 14–20.
- ZEHETNER, F., LAIR, G. J., GRAF, M. and GERZABEK, M. H. 2009. Rates of biogeochemical phosphorus and copper redistribution in young floodplain soils. *Biogeosciences*, **6**, 2949–2956.