The impacts of land plant evolution on Earth's climate and oxygenation state – An interdisciplinary review

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Invited research article

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ABSTRACT

The Paleozoic emergence of terrestrial plants has been linked to a stepwise increase in Earth's O_2 levels and a cooling of Earth's climate by drawdown of atmospheric CO_2. Vegetation affects the Earth's O_2 and CO_2 levels in multiple ways, including preferential organic carbon preservation by decay-resistant biopolymers (e.g. lignin) and changing the continental weathering regime that governs oceanic nutrient supply and marine biological production. Over shorter time scales (≤ 1 Myr), land plant evolution is hypothesized to have occasionally enhanced P weathering and fertilized the oceans, expanding marine anoxia and causing marine extinctions. Oceanic anoxia would eventually become limited by oceanic O_2 uptake as oxygen accumulates in the atmosphere and surface oceans when excess organic carbon is buried in marine sediments. Here, we review hypotheses and evidence for how the evolving terrestrial ecosystems impacted atmospheric and oceanic O_2 and CO_2 from the Ordovician and into the Carboniferous (485–298.9 Ma). Five major ecological stages in the terrestrial realm occurred during the prolonged time interval when land was colonized by plants, animals and fungi, marked by the evolution of 1) non-vascular plants, 2) vascular plants with lignified tissue, 3) plants with shallow roots, 4) arborescent and perennial vegetation with deep and complex root systems, and 5) seed plants. The prediction that land vegetation profoundly impacted the Earth system is justified, although it is still debated how the individual transitions affected the Earth's O_2 and CO_2 levels. The geological record preserves multiple lines of indirect evidence for environmental transitions that can help us to reconstruct and quantify global controls on Earth's oxygenation and climate state.

1. Introduction

In this review we look at terrestrial plants as a geobiological agent and their possible imprints on Earth's climate and oxygenation state during their emergence on the continents. Land plants affect our planet in a multitude of ways in particular through the hydrological cycle, Earth's surface energy budget, and the global biogeochemical cycles. Vegetation changes the water cycling, rainfall, runoff, and soil properties, harvesting nutrients for biological production that, in turn, drives carbon sequestration and storage in terrestrial deposits and marine sediments. At the crux of this is how plants modify the physical and chemical weathering processes of the land surface with lasting impacts on the global element cycles. The modifications by land plants are carried out in networks of interactions with the terrestrial fauna and fungi that co-evolved with the emergence of plants.

The mid-Paleozoic colonization of land offers a unique opportunity to study how the terrestrial biosphere affected the Earth's climate and oxygenation state in the past. A noteworthy hypothesis, known as the 'Devonian cooling hypothesis', posits that early afforestation enhanced atmospheric CO_2 removal via enhanced silicate weathering, which led Earth to transit from a hot greenhouse climate into a glaciated icehouse (Berner, 1993). This hypothesis is commonly accepted (e.g., Algeo and Scheckler, 1998; Morris et al., 2015), although recent studies challenge the temporal correlation between the Late Devonian spread of vascular plants with deep roots (~380–360 million years ago, Ma) and the main phase of the Late Paleozoic Ice Age (335–260 Ma) (Goddéris et al., 2017; Montañez and Poulsen, 2013).

A more recent hypothesis states that the Late Ordovician climatic cooling also resulted from colonization by non-vascular, rootless plants (Lenton et al., 2012). Both the Ordovician and Devonian transition have also been linked to rises of atmospheric oxygen (Berner, 2006; Edwards et al., 2017; Lenton et al., 2016). In addition, the evolution of early lignified plants with shallow roots in the Late Silurian to Early Devonian (427.4–393.3 Ma) also changed the terrestrial ecosystems and soil properties, as might the emergence of seed plants in drier upland environments. Each one of these events could have affected atmospheric

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CO_2 and O_2 levels on Earth, but the governing processes are poorly understood.

Although the interplay between the evolving terrestrial ecosystems and atmospheric composition continued long after the mid-Paleozoic (Ordovician–Devonian) and plant evolution modulated climate both during the Late Paleozoic Ice Age and during the Cretaceous rise of flowering plants (angiosperms) (Boyce and Lee, 2017; Montañez and Poulsen, 2013), we focus this review on the environmental impact of the early history of land plants. We highlight five major ecological transitions that distinguish the terrestrial ecosystem at different times (Le Hir et al., 2011), including 1) the invasion of rootless plants, 2) the invasion of vascular plants with lignified tissue, 3) the invasion of vascular plants with shallow roots, 4) the invasion of tall, perennial trees with deep root systems, and 5) the invasion of seed plants in drier upland environments.

This review aims to provide an all-round perspective on how the early terrestrial biota has transformed Earth's climate and oxygenation state. In Section 2 we review the history of early land plants and ancient soils (paleosols). In Section 3, the obstacles and biological innovations during terrestrialization are summarized. In Section 4, we discuss the various effects of terrestrial vegetation on Earth's global biogeochemical cycles with specific focus on consequences to atmospheric O_2 and CO_2 levels. Section 5 deals with hypotheses for long-term climate and O_2 regulation on Earth and how the evolving flora may have played into this. Section 6 summarizes key lines of evidence for mid-Paleozoic environmental transitions and discuss links between evolving terrestrial ecosystems and Earth's climate and oxygenation state. In Section 7, we conclude with an outlook for future research.

2. History of early land plants and terrestrial ecosystems

The timeline for terrestrialization by land plants builds on both fossil evidence and phylogenetic comparisons of extant plants (e.g., Kenrick et al., 2012; Kenrick and Crane, 1997; Qie et al., 2019). Fig. 1 depicts the phylogenetic relationship with first appearances of representative fossils and approximate age of branch points of the major land plant lineages. We have added steps in the floral evolution that represent major ecological transitions. Importantly, the paleontological and phylogenetic records paint a consistent picture that early land plants evolved in stages through the mid-Paleozoic (Ordovician–Devonian). The associated stepwise change in terrestrial ecosystems could also have impacted the carbon cycle in a punctuated manner.

2.1. Vegetation on land before the colonization of land plants (> 510 Ma)

Aquatic plants (algae) evolved ~1.9 billion years ago and appear in the fossil record > 1.5 billion years ago (Bengtson et al., 2017; Knoll, 2011; Sánchez-Baracaldo et al., 2017). There is evidence that Archaeplastida, the group that involves red algae, green algae and land plants, evolved in freshwater habitats on land and that red and green algae represent later colonizations of the oceans (Sánchez-Baracaldo et al., 2017). The abundance of algae relative to cyanobacteria in the marine realm are found to have increased around 650 Ma (Brocks et al., 2017). Land plants (embryophytes) comprise a distinct lineage of related plants that appear to have a single origin from aquatic charophycean green algae (Delwiche and Cooper, 2015; Morris et al., 2018). That said, land was not barren prior to the advent of land plants. Cyanobacteria-based microbial ecosystems would have existed on exposed soils > 2 billion years ago (Gutzmer and Beukes, 1998; Wellman and Strother, 2015). Lichens, the composite organism that arises from algae or cyanobacteria living among filaments of multiple fungi species, have also been held responsible for impacting terrestrial weathering processes and the global carbon cycle since ~850 Ma (Knauth and Kennedy, 2009). Recent phylogenomic data, however, show that fungal origins of extant lichenization postdate vascular plants suggesting modern lichens were not around in the Precambrian and early

Paleozoic (Nelsen et al., 2019). However, algae-fungal symbioses have emerged multiple times in Earth history and the fungal tree of life is still less well constrained than the plant tree of life (Gargas et al., 1995; Hibbett et al., 2007; Lutzoni et al., 2018). The fossil record of lichens is sparse with putative representatives in the Ediacaran and Early Devonian (Taylor et al., 1995; Yuan, 2005). Today, lichens account for 7% of Earth's net terrestrial productivity (Elbert et al., 2012). The absence of lichens and non-vascular plants in the early terrestrial ecosystems would likely have resulted in drier, shallower and less stable soil ecosystems with lower productivity.

Fossil soils (paleosols) are preserved throughout the geologic record (Driese and Mora, 2001; Mángano and Buatois, 2016; Retallack, 2003; Sheldon and Tabor, 2009). Soils are altered surficial rock or sediment, composed of mixtures of organic matter, minerals, fluids, and organisms that develop through chemical weathering and deposition of litter (Amundson, 2014). The earliest soils experienced limited hydrolytic alteration and contained little humic material and bio-essential elements (e.g. N, P), which would have posed a serious challenge to plant colonization. In addition, Precambrian paleosols differ from Silurian and younger paleosols by the lack of animal burrows (Driese and Mora, 2001).

2.2. Colonization by non-vascular, rootless land plants (~515–470 Ma)

Early land plants reproduced solely by spores (cryptogamic). Seed plants (spermatophytes) evolved later, and flowering plants (angiosperms) much later in the Cretaceous (Fig. 1). The origin of land plants (embryophytes) is estimated to have occurred in the middle Cambrian–Early Ordovician, 515.2–473.5 Ma, based on phylogenomic data encompassing the diversity of embryophytes and utilizing a Bayesian relaxed molecular clock analysis (Morris et al., 2018).

The earliest fossil evidence of land plants comes from spores and body fragments (Kenrick et al., 2012). Plant spores have an excellent fossil record because they are made of sporopollenin that are among the most decay-resistant substances ever evolved by plants (Kenrick et al., 2012). Further, spores are naturally produced and shed in large numbers during life. The spores will be transported by wind and water over vast distances into sedimentary deposits, where they have a high fossilization potential because of their refractory sporopollenin wall. Diagnostic spores of non-vascular land plants are found in mid-Ordovician (Dapingian, ca. 470 Ma) to early Silurian deposits, although other spores more ambiguously associated with land plants are known from the Cambrian (Rubinstein et al., 2010; Wellman and Strother, 2015). From the mid-Ordovician to the early Silurian, the record is dominated by fossil spores characteristic of bryophytes (e.g. non-vascular land plants), demonstrating that the terrestrial flora was already geo-graphically widespread (Fig. 2) and that there was remarkably little spatial or temporal variation in the composition of assemblages during this time (Kenrick et al., 2012; Wellman et al., 2013).

Late Ordovician paleosols of the Juniata Formation at Potters Mills in Virginia USA appear organic-lean as would be expected for a cover of evergreen, rootless plants of bryophyte-grade (Davies et al., 2010; Driese and Mora, 2001; Retallack, 2003; Retallack and Feakes, 1987). Early evidence for plant-animal interactions on land from this site has been refuted by observations that the Potters Mills was deposited in a marginal marine setting with animals burrows generated during drowning events (Davies et al., 2010). Given that Ordovician paleosols show no clear root traces, we would expect lower respiration rates in such soils that would have gained only organic matter from above ground litter (Driese and Mora, 2001). Nevertheless, one study has suggested high soil respiration rates comparable to modern savannah grassland soils based on the mole fraction of CO_2 in pedogenic goethite and CO_2 exchange fluxes between the soil and atmosphere (Yapp and Poths, 1994). Thus, Ordovician paleosols are rare and still poorly understood. A spatially-resolved model for the vegetation cover in the Ordovician climate shows that bryophytes and lichens potentially could
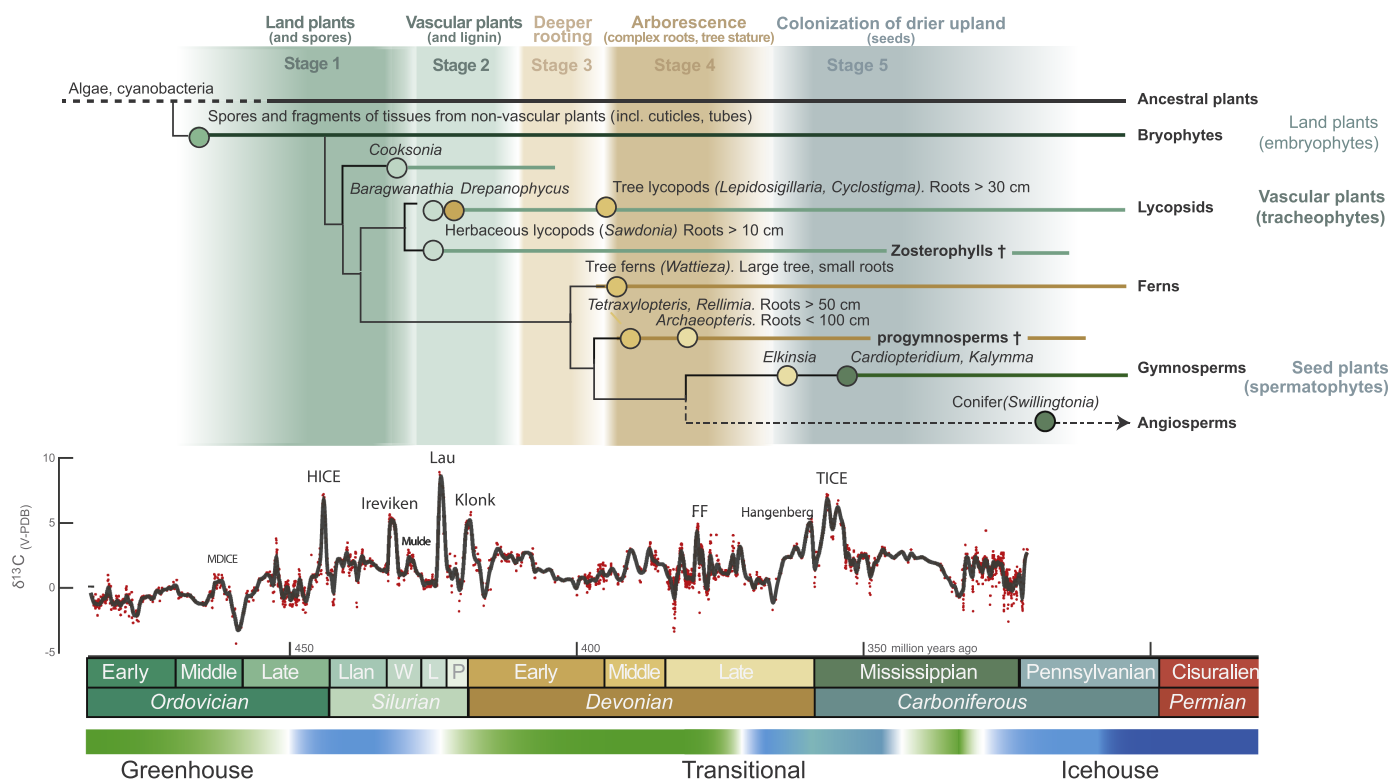
Fig. 1. Timeline of non-vascular to vascular plants 480–320 Ma. Five stages are highlighted, each with distinct terrestrial ecosystems that may have affected the Earth's climate and oxygenation state. Phylogenetic relationships of major land plant lineages are shown with approximate branch points *(according to references given in the text)*, providing the earliest date for the expected ecosystem change. Also, first appearances of selected fossils discussed in the text are plotted on the tree, providing minimum ages of the expected ecological shifts. The carbon isotope record from marine carbonates (δ13C) can be interpreted a proxy for the composition of the global oceanic carbon pool and, therefore, recording changes in the global carbon cycle (Saltzman and Thomas, 2012). It is debated whether the positive δ13C excursions may reflect abrupt changes driven by plant evolution. Ages are assigned after the Internal Commission on Stratigraphy, chart 2019/05. (http://www.stratigraphy.org/cheu.pdf).

have covered as much as 44% of land areas (relative to 74% today) and supported 24% of modern-day global net primary productivity (Porada et al., 2016). This potential extent of land vegetation is an overestimate, especially if lichens evolved later as they provide soil stability for bryophytes (Nelsen et al., 2019; Weber et al., 2016).

2.3. Evolution of vascular plants and ground-hugging root plants (~430–410 Ma)

Vascular plants (tracheophytes) originated in the Late Ordovician-Early Silurian, 450.2–419.3 Ma, as dated by relaxed molecular clocks (Morris et al., 2018). The first fossil evidence comes from trilete spores in sediments of Sandbian age (458.4–453.0 Ma). which are predominantly produced by vascular plants today. This may push the origin of vascular plants a bit further back in time (Rubinstein and Vajda, 2019; Steemans et al., 2009; Wellman et al., 2015). In any case, vascular plants likely first became ecologically important in the late Middle to Late Silurian (433.4–419.2 Ma) where a dramatic increase in the diversity and abundance of trilete spores occurred (Wellman et al., 2013). At the same time, cryptospore dyads become an increasingly rare constituent in spore assemblages, suggesting a vascular vegetation cover started to dominate over non-vascular vegetation (Kenrick et al., 2012). The oldest body fossil of vascular plants might be, *Cooksonia,* found in Central Europe and Avalonia by Wenlock (433.4–427.4 Ma), and soon after it occurs at higher latitudes on Gondwana by Ludlow (427.4–423.0 Ma) (Edwards et al., 1983; Libertín et al., 2018; Morel et al., 1995; Wellman et al., 2013). Yet, some Cooksonia sporophytes were inadequately photosynthetic and had a bryophyte-like ecology (Boyce, 2008). Lignified tissue was produced by land plants of Silurian-

Early Devonian age (e.g. *Asteroxylon),* but likely not all early vascular plants (e.g. *Aglaophyton, Rhyniophytes)* deposited lignin in the conducting cells to produce true tracheids as seen in modern vascular plants (Boyce et al., 2003). Generally, the early record of vascular plants is dominated by wet lowland environments (Greb et al., 2006). Some *Cooksonia* were arguably poikilohydric, i.e. they lacked the ability to regulate water content within the cells relative to the ambient environment (Boyce and Lee, 2017).

Baragwanathia is a genus of extinct lycophytes (club mosses) that grew up to 1 m tall and with stems up to a few centimeters of thickness. It appears far the most advanced plant of its time. *Baragwanathia* fossils have been reported from Australia, Canada, Czech Republic and Podolia (Ukraine) in strata of Gorstian (427.4–425.6 Ma) to Emsian (407.6–393.3 Ma) age (Hueber, 1983; Kraft and Kvaček, 2017; Rickards, 2000; Tims and Chambers, 1984). One specimen from the Czech Republic has been found with marine species (bryozoans and brachiopods) attached to its lower part, suggesting that specimen grew in marine waters (Kraft and Kvaček, 2017). An alternative explanation is that it was transported into the shallow sea.

It is generally accepted that Middle and Late Silurian plants lacked true roots. Instead, they had stems that ran along the surface and just beneath the surface of the soil as runners and rhizomes furnished with thin unicellular root hairs (Kenrick and Crane, 1997). Some of the earliest evidence of roots comes from *Drepanophycus,* known from the Early Devonian (Lochkovian, 419.2–410.8 Ma), and their close relatives in the extinct zosterophylls (e.g. *Sawdonia*) of similar age. These 'ground-hugging' plants were among the first to develop small, simple root-like structures (Gensel et al., 2001; Raven and Edwards, 2001).

a) Late Devonian
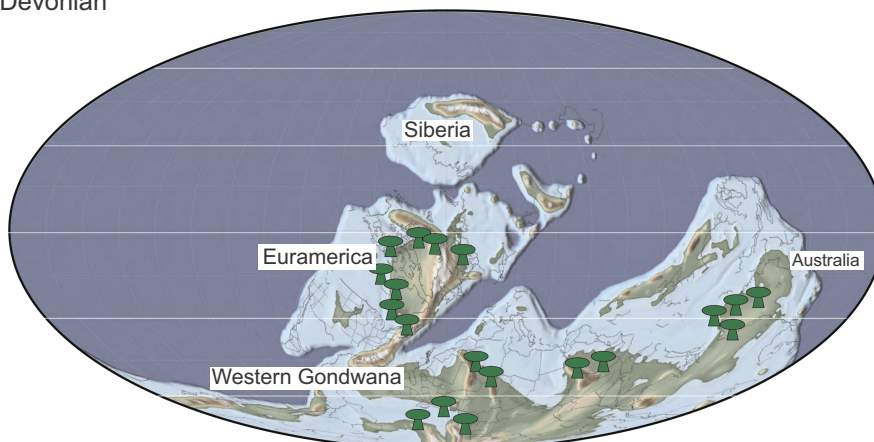
b) Late Silurian – Early Devonian
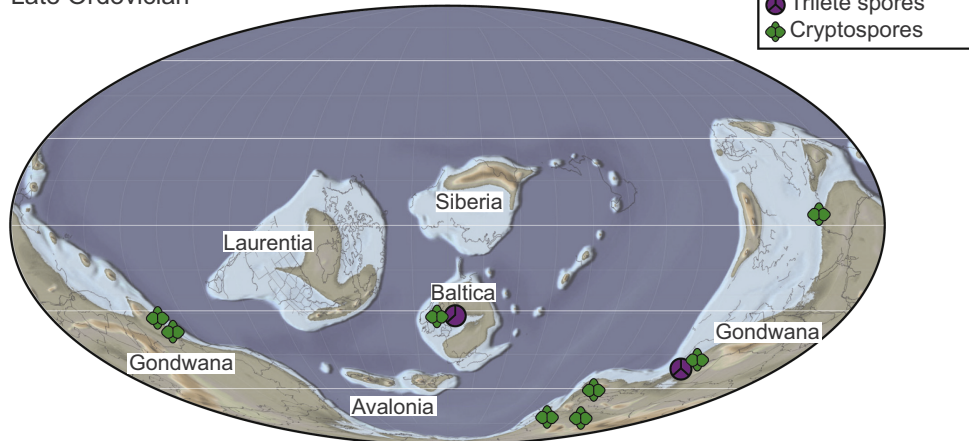
c) Mid – Late Ordovician

Fig. 2. Paleogeography and some known fossil sites during a) Late Devonian, b) Late Silurian - Early Devonian, and c) Middle-Late Ordovician. Paleomaps: Scotese, 2014. Phytogeography: a) *Archaeopteris and other progymosperms* (Streel, 2000), b) fossil spores including trilete spores from vascular plants during Wenlock (Wellman et al., 2013) and Lochkovian (Steemans et al., 2010), and c) Ordovician cryptospores and the first appearance of trilete spores in Sandbian (Baltica) and Katian (Saudi Arabia), after (Rubinstein and Vajda, 2019).

2.4. The emergence of vascular plants with deeper rooting systems (~410–390 Ma)

The earliest members of the vascular plant lineage were small, lacked 'true roots' and inhabited poorly developed soils (Gensel et al., 2001; Kenrick and Strullu-Derrien, 2014). The proportion of root mass to shoot mass is poorly constrained for early land plants. Exceptionally well-preserved fossils from the ~407 Ma Rhynie Chert Lagerstätten deposit in Scotland offer the best evidence of early roots and their interactions with mycorrhizal symbionts in rhizoid-based systems (Kenrick and Strullu-Derrien, 2014; Remy et al., 1994; Strullu-Derrien et al., 2019). The Rhynie Chert fossil assemblage comprises various herbaceous lycophytes that may have grown to heights of ~50 cm (*Asteroxylon mackiei*) with small roots up to 5 cm. Today, the majority of land plants have symbiotic relations to mycorrhizhal fungi (Taylor et al., 2009). Mycorrhizal symbionts assist P harvesting from soils in 90% of modern plant species in exchange for photosynthate (e.g. sugars) produced by the plant. Mycorrhizal fungi evolved in parallel with the early land plants and likely played an important role already during the earliest colonization of land (Field et al., 2015; Humphreys et al.,
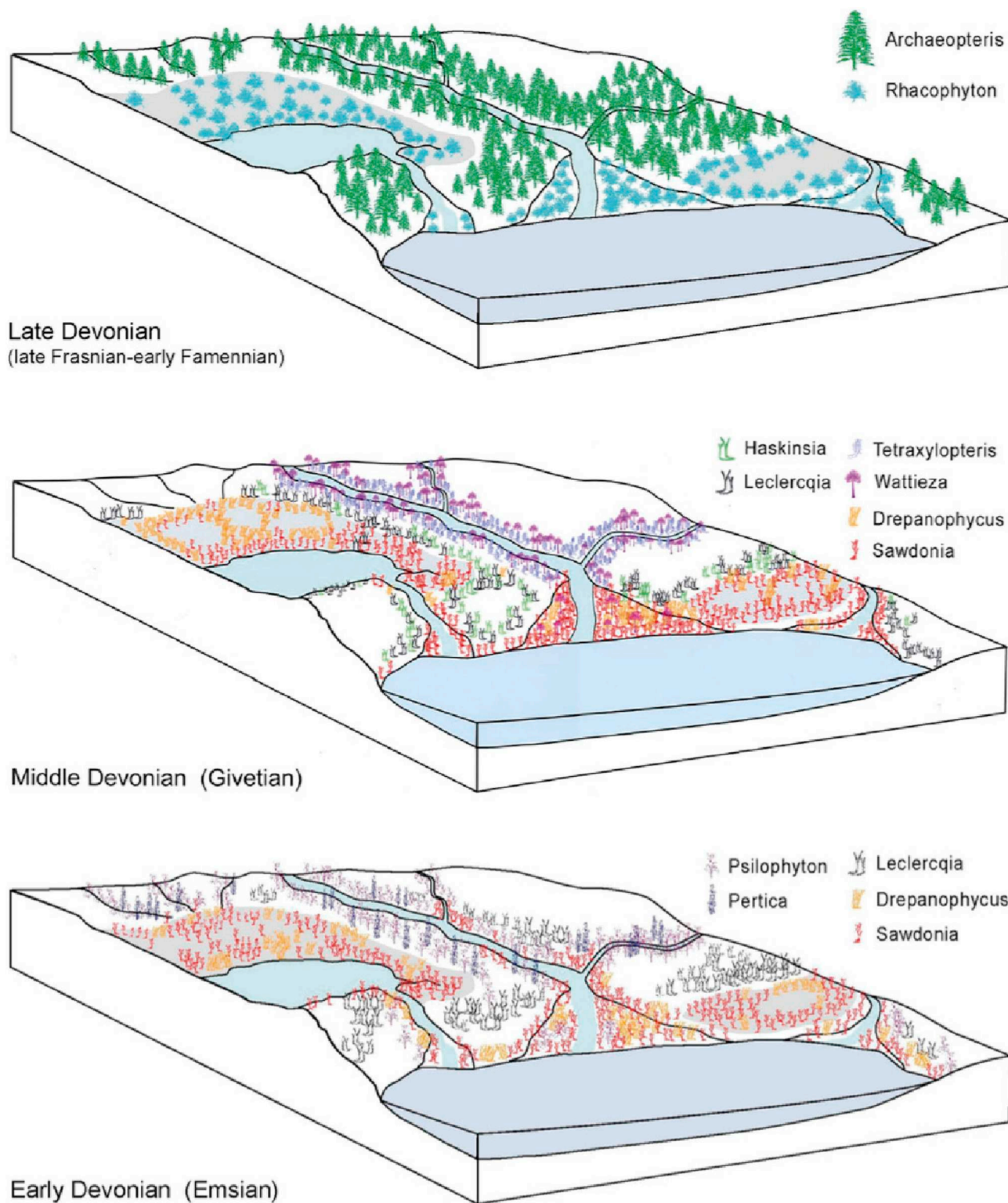
Fig. 3. Illustrative reconstruction of the ecological distribution of 10 vascular plant taxa in the Early, Middle and Late Devonian as inferred from carbon isotope data in fossil plant tissue (Wan et al., 2019). Reprinted from Palaeogeography, Palaeoclimatology, Palaeoecology, vol. 531, Wan et al., Environmental influences on the stable carbon isotopic composition of Devonian and Early Carboniferous land plants, 1–18, Copyright (2019), with permission from Elsevier.

2010; Pirozynski and Malloch, 1975; Smith and Read, 2009).

The most common plants in the Rhynie Chert are *Rhynia* that had no roots other than filamentous rhizoids (Strullu-Derrien et al., 2019). The zosterophyll, *Asteroxylon,* was closer related to *Drepanophycus* and did possess small root-like structures. Early Devonian vascular plants were dominantly ground-hugging, rhizomatous lycophytes (*Sawdonia,*

Drepanophycus, Leclercqia, Haskinsia) and shrubby trimerophytes (*Psilophyton, Pertica*), mostly with heights < 1 m (Algeo and Scheckler, 1998; Kenrick et al., 2012; Kenrick and Crane, 1997). However, evidence from paleosols suggest that some Emsian (407.6–393.3 Ma) vascular plants achieved substantial stature of 2–3 m height and nearly 1 m roots (Elick et al., 1998). The largest structures in Emsian terrestrial

deposits are trunks up to 8 m in size (*Prototaxites*) interpreted as giant fungi (Boyce et al., 2007). Early Devonian paleosols have abundant traces of true roots, including woody tap roots of a variety of land plants (Elick et al., 1998; Hotton et al., 2001).

A study of the water utilization efficiency in Devonian plants, based on carbon isotope fractionation in fossil plant tissue, has led to an illustrative reconstruction of the distribution of Devonian land plants (Fig. 3; Wan et al., 2019). The early Devonian flora is known as Eotracheophytic vegetation (Le Hir et al., 2011). Some plants may have withstood seasonal freezing or aridity (Wellman et al., 2000; Wellman and Gray, 2000). Tundra formations are perhaps the more appropriate modern analogue.

2.5. Colonization of arborescent trees with deep root systems (~390–370 Ma)

The colonization of land was a protracted process that cascaded through the Devonian. The maximum size of trees slowly increased, and root systems became deeper and more complex several tens of million years after the first primitive root plants had appeared (Algeo et al., 1995; Algeo and Scheckler, 1998; Wan et al., 2019). Root systems were essential to the development of an arborescent growth habit. The oldest fossil forests contains remnants of fern-like trees (*Archaeopteris*, *Wattiezia/Eospermatopteris*) at Plattekill Formation of the Hamilton Group near Cairo, New York, USA from the early mid Givetian, ~385 Ma, and at the famous and 2–3 My younger Riverside Quarry, at Gilboa, New York, USA (Driese et al., 1997; Mintz et al., 2010; Stein et al., 2007, 2012, 2020). Towering > 8 m with narrow unbranched roots akin to modern palm trees, this fern forest existed in a tropical-subtropical, coastal wetland. Indeed, much of the Middle Devonian flora was found in riparian and lake-margin settings (Greb et al., 2006). The Gilboa forest was dense and developed on a wetland coastal plain (Stein et al., 2012).

The appearance of *Archaeopteris* trees in the earliest Frasnian (382.7–372.2 Ma) represents a marked step forward in plant architecture and growth habit. These progymnosperms display a tree architecture akin to modern conifers with extended root systems and were abundantly woody (Algeo and Scheckler, 1998; Meyer-Berthaud et al., 1999). Archaeopterids achieved the greatest size with trunk diameters up to 1.5 m and estimated heights up to 30 m. The increase in size was facilitated in part by the development of a massive root system, although rarely deeper than 1 m (Meyer-Berthaud et al., 2013). *Archaeopteris* was perennial with some individuals living for at least 40–50 years (Cantrill and Poole, 2012). In contrast to earlier bushy and arborescent plants, it shed its leafy branch systems (e.g to cope with water stress during dry season) and likely produced deep litter mats that affected soil moisture, pH and humic content in soils (Algeo and Scheckler, 1998). Paleosols from Gilboa forest represent vertisols (high clay content) and inceptisols (no clay accumulation) with persistently high water tables (Mintz et al., 2010). Middle Devonian paleosols are the earliest known soils with clay-enriched subsurface horizons. The clay horizon in modern soils is formed in situ, which is greatly influenced by root holes (Retallack, 2003). *Archaeopteris* dominated forests until their extinction near the Devonian-Carboniferous boundary (the Hangenberg event, ~360 Ma) (Algeo et al., 2001).

2.6. Colonization of drier upland habitats by seed plants (380–340 Ma)

Early land plants had neither flowers nor seeds and reproduced by spores (pteridophytic reproduction). This life style might have restricted land plants to wet lowland habitats because sperm, produced from free-living gametophytes that grew from dispersed spores, swim to the egg-bearing archegonia of the same or other gametophytes (Algeo and Scheckler, 1998). Nevertheless, bryophytes with exactly that lifestyle can dominate modern desert soil crusts (Seppelt et al., 2016).

The evolution of seeds permitted plants to invade drier habitats, in

part because reproduction no longer depended on aqueous sperm dispersal (Algeo and Scheckler, 1998; Scott and Chaloner, 1983). The origin of seed plants is thought to involve a whole genome duplication event, dated by molecular clock analysis to 399–381 Ma (Clark and Donoghue, 2017; Jiao et al., 2011). The fossil record of seed plants begins in the Late Devonian and follows by a diversification in the Carboniferous, where tall trees filled ecological niches in floodplain and upland forests that were previously occupied by progymnosperms (Rothwell et al., 1989). Podsols/spodosols – typical of coniferous, boreal forests today – were rare, and the earliest known are Early-Mid Mississippian in age, 358.9–330.9 Ma (Taylor et al., 2009; Vanstone, 1991). However, conifers first appeared in the Pennsylvanian, 323.2–298.9 Ma, as did other seed plant clades such as ancestral forms of cycads (e.g. *Taeniopteris, Phasmatocycas*) and gingkos (e.g. *Trichopitys*) (Boyce and Lee, 2017). By the Permian, 298.9–251.9 Ma, deciduous forests were well established at higher latitudes with *Cordaites* and *Glossopteris* seed plants dominating the Northern and Southern hemispheres, respectively (Rees et al., 2002).

3. Obstacles and drivers for the colonization of land

Today, the biological success of life on land is overwhelming. There are ~5 times more named species on land than in the oceans (Costello and Chaudhary, 2017). The land biota (mainly plants) contains ~100 fold more biomass than that present in the marine realm (Bar-On et al., 2018), and there is yet still more organic carbon in soils than in the standing crop of terrestrial plants (Berner et al., 1998). Clearly, the colonization of land was ultimately a major biological success. Along the way, several physical, chemical and biological obstacles were overcome by the evolution of new biological machinery and interactions. For example, the Silurian-Devonian radiation of land vegetation postdate the Neoproterozoic origin of important cell-cell signaling processes in complex multicellular organisms also utilized by multicellular land plants, and it also postdate the Cambrian-Ordovician radiations of marine animal ecosystems in which new networks of ecological interactions arose (Knoll, 2011; Bush and Bambach, 2011). Here, we highlight some of the main challenges that early land plants had to overcome to evolve and succeed on land.

3.1. Desiccation

First of all, the transition to land required protection against dehydration. Land plants control their water balance by evolution of stomata that enable plants to transform their epidermis (outer cells) into a permeable layer that could be either water-tight under dry conditions or highly permeable to CO_2 during favorable conditions. The earliest land plants were poikilohydric plants of a bryophyte grade without a water proofing cuticle and stomata that help resist desiccation (Boyce and Lee, 2017). Early land plants were likely ecologically restricted to moist environments, such as wetlands and riverbanks, and were still relatively small in stature until the Late Silurian-Early Devonian. Further, seed plants might have evolved a greater capacity to actively control water loss through their stomata suitable for survival in drier terrestrial environments (Brodribb and McAdam, 2011; Cai et al., 2017).

3.2. Soil formation

Land surface has been available for colonization from an early point in the history of multicellular life (Willis and McElwain, 2014). Land plants need soil, and soils slowly developed in concert with the evolving terrestrial biota of animals, plants and fungi (Kenrick et al., 2012). Today, soil animals play a crucial role in 'farming' soils (Bardgett and van der Putten, 2014; Blouin et al., 2013; Wardle, 2004). Detritivores and decomposers contribute to the breakdown of dead and decaying organic matter in terrestrial ecosystems, and they aerate and mix up the

soil with their movement, which is important for plant growth.

It is, therefore, striking that the body fossil record of terrestrial arthropods shows a transition from ocean to land independently in three distinct animal groups roughly at the same time (Kenrick et al., 2012). The earliest body fossils of millipedes and spiders are Late Silurian in age (Wenlock, 433.4–427.4 Ma), insects (hexapods) and centipedes are found in the Devonian (Davies et al., 2010; Kenrick et al., 2012; Mángano and Buatois, 2016). Trace fossils of large aquatic vertebrates with paired limbs (tetrapods) are found in the Eifelian, 393.3–387.7 Ma (Niedźwiedzki et al., 2010) and the earliest amphibian tetrapod body fossils (*Panderichthys, Tiktaalik, Ichthyostega*) are Late Devonian in age (Ahlberg and Milner, 1994). The size of terrestrial animals and plants evolved in concert with soils becoming deeper at this time (Algeo and Scheckler, 1998). The first terrestrial vertebrate fossils are Carboniferous in age (Carroll, 1992).

Mycorrhizal fungi and plants have co-evolved in many different ways, and these interactions would have developed in soils during the earliest colonization of land (Field et al., 2015; Humphreys et al., 2010; Pirozynski and Malloch, 1975; Smith and Read, 2009). The oldest fossil locality that could preserve mycorrhizal fungi is from the Early Devonian (Rhynie Chert), and it shows that simple rhizoid based terrestrial ecosystems were already diverse (Kenrick and Strullu-Derrien, 2014).

3.3. UV shield at the Earth's surface

Intense UV radiation can destroy nucleic acids, proteins and phenolics and make the surface environment inhospitable for life. The lack of UV shielding has been advocated as an obstacle for colonization of land by plants and animals because at a lower atmospheric O_2 levels than today, the column density of ozone in the atmosphere would have been lower and more UV light from the Sun reached Earth's surface. However, an efficient UV shield is estimated to arise at only 10% of the present atmospheric level (PAL) of O_2 (Berkner and Marshall, 1965), and atmospheric O_2 levels were most likely higher than this when plants colonized the continents (Bergman, 2004; Berner, 2006; Dahl et al., 2010, 2017, 2019; Edwards et al., 2017; Glasspool and Scott, 2010). Thus, an efficient UV shield is expected at mid-Paleozoic atmospheric O_2 levels, and life on land would not have gained any further UV protection once atmospheric O_2 increased further.

3.4. Stature

The transition from an aqueous to gaseous medium exposed land plants to new physical conditions that resulted in key physiological and structural changes, including the evolution of lignin, flavonoids, cutin, and plant hormones in vascular plants (Kenrick and Crane, 1997). Once vegetation had evolved, competitive pressures for space may have favoured axial sporophytes with an indeterminate growth habit (i.e. the *zosterophylls* and *trimerophytes*), resulting in an overall increase in height and biomass (Morris and Edwards, 2014).

By the Middle Devonian, 393.3–382.7 Ma, land plants developed several strategic innovations in growth. The evolution of secondary vascular tissues in some clades (namely the pseudosporochnalean *cladoxylopsids, lycopsids* and *archaeopteridalean* progymnosperms) allowed for arborescence (Berry and Fairon-Demaret, 2002; Meyer-Berthaud et al., 2010; Stein et al., 2007). Concurrently, with a greater need for nutrients, water and structural support, rooting systems evolved from simple rhizomatous axes that were shallow to subaerial in the Early Devonian, 419.2–393.3 Ma, to deeper and more complex root systems by the Middle Devonian (Algeo et al., 2001; Meyer-Berthaud et al., 2013).

The advent of forests probably generated selective pressures on terrestrial plants to evolve larger size. It is commonly hypothesized that early land plants also were competing for light, but every plant in the Paleozoic appears to have had a low hydraulic and photosynthetic potential and would have been well adapted to life in shaded

understory by modern standards. Rather, the evolution of larger trees was more likely driven by selection of those with greater dispersal of spores (or seeds), had greater leaf area and/or deeper root system suited to access nutrients from the soil and/or reach the water table (Boyce et al., 2017). In turn, the evolution of deeper roots to ~1 m depth might well have been a key factor in the success of the transition to above ground arborescence (Algeo et al., 1995; Algeo and Scheckler, 1998).

3.5. Reproduction

The earliest land plants developed sporophytes, new type of gametophytes with sexual organs, cuticle, and non-motile, airborne sporopollenin-walled spores and the photorespiratory glycolate oxidase pathway (Kenrick and Crane, 1997). Unlike animals that are only multicellular in the diploid phase of their life cycle, when they have two sets of chromosomes, plants have two multicellular generations in their life cycle: a multicellular haploid and a multicellular diploid stage. The diploid stage of the plant life cycle probably developed in a terrestrial setting (Delwiche and Cooper, 2015; Kenrick and Crane, 1997). Hence, several biological innovations took place and allowed early plants to overcome the obstacles associated with survival and reproduction in terrestrial environments.

4. How do land plants affect the global environment?

Today, vegetation has evolved to become an integrated part of the Earth system, affecting the climate and oxygenation state of the atmosphere and oceans by altering the mass and energy flow in Earth's surface environments. Plants convert sunlight, CO_2 and water into chemical energy and organic matter at a scale that profoundly influences the biological, chemical and physical conditions on our planet (Bonan, 2015). Fig. 4 summarizes the key processes by which plants affect Earth's climate and oxygenation state, including global energy balance, the hydrological cycle, physical and chemical weathering processes, soil formation, biomass storage and preservation.

4.1. Energy balance on Earth

Vegetation affects the energy balance on Earth surface via the greenhouse effect and Earth's albedo. Basically, the incoming short-wave radiation (1368 W/m^2 today) always balance the outgoing long-wave radiation. Solar insolation was 4% and 3% weaker than today in the mid-Ordovician and Late Devonian, respectively (Caldeira and Kasting, 1992). Everything else equal, a simple energy balance calculation suggests the fainter Sun would correspond to a cooling of the global mean surface temperature by -3 °C and -2 °C at these times, respectively.

By lowering equilibrium levels of atmospheric CO_2 through silicate weathering (described further below in Section 4.3), vegetation weakens the greenhouse effect and cools the planet. At the same time, vegetation also acts to warm the planet by reducing the planetary albedo relative to a non-vegetated planet with rock- and ice-covered surfaces. Today, the cooling effect of removing greenhouse gas CO_2 is on average greater than the albedo-warming, but it is worth noting that climate change induce non-linear regional differences, where some regions will actually warm up while most areas cool down (Betts, 2000). Although the mid-Paleozoic transition does not represent a transition from fully non-vegetated (high albedo) continents to fully vegetated (low albedo) continents, climate models for the Devonian suggest the albedo warming effect would have increased Earth's mean surface temperature by < 1–2 °C (Brugger et al., 2018; De Vleeschouwer et al., 2014). The paleotemperature records are uncertain, but do show a consistent decline by > 10 °C during the mid-Paleozoic (Section 5). If that represents the global mean, a decrease in greenhouse forcing is the most reasonable explanation.
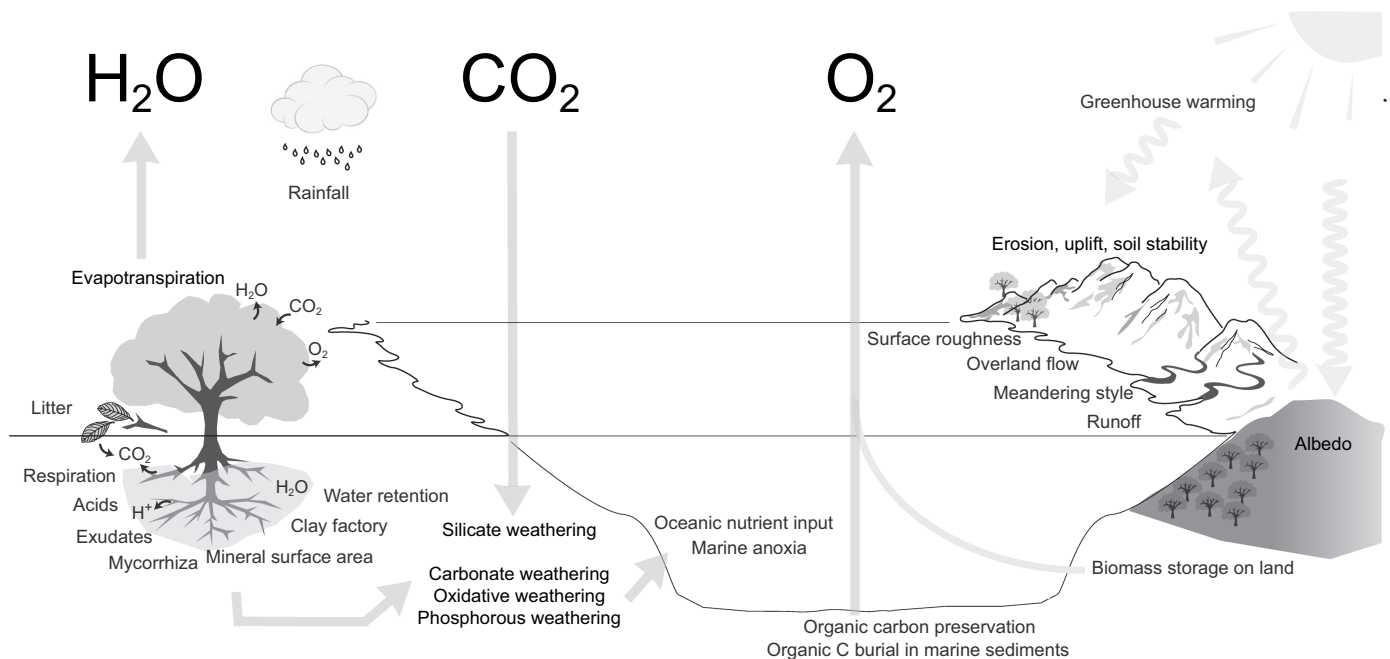
Fig. 4. Land plants affect the climate and oxygenation state of the Earth in multiple ways. Plants accelerate the hydrological cycle through evapotranspiration and stimulate rainfall. Plants also enhance chemical weathering processes and clay formation in soils, which ultimately represents long-terms sinks for atmospheric CO_2. Therefore, vegetation also affects the energy budget of the Earth, both via cooling through the greenhouse gasses (drawdown CO_2) albedo-warming through absorbing more short-wave radiation from the Sun. Terrestrial plants evolved recalcitrant biopolymers (e.g. lignin, sporopollenin) that enhance preservation of organic matter and biomass preservation on land (coal deposits), and enhance phosphorous weathering to the oceans due to the lower C/P ratio in terrestrial biomass. The terrestrial biota (plants, mycorrhizal fungi and animals) affect soil function and chemical weathering rates via soil respiration, release of acids (CO_2 and H^+), root exudates, production of clay minerals and mineral surface area that moisturize soils. The chemical weathering of P-bearing minerals is primary source of biolimiting nutrient P in the oceans that, in turn, affects the development of marine anoxia. Plants may also affect O_2 consumption through oxidative weathering of kerogen and pyrite. Large arrows (light grey) represent system effects, whereas the direct effect of plants on atmospheric gasses are shown with small black arrows.

4.2. Water cycling on Earth

By evapotranspiration, land plants pump water from the soil into the atmosphere and affect the global hydrological cycle. Today, this recycling of moisture constitutes approximately 2/3 of the precipitation on land (Boyce and Lee, 2017). As a consequence, large scale removal of tropical forests will probably decrease global precipitation (Lawrence and Vandecar, 2015). Conversely, we should expect that the evolution of land plants with deep roots increased global evapotranspiration, atmospheric moisture transport, and rainfall on the continental interiors (Ibarra et al., 2019). As vegetation alters the hydrological cycle and atmospheric heat transport, it will affect the climate system as a whole and also lead to differences at the regional scale (Le Hir et al., 2011; Boyce and Lee, 2017).

Terrestrial vegetation also has the potential to affect rainfall through its influence on cloud formation. For example, some spores, pollen and chemical compounds released from plants and fungi serve as condensation nuclei for clouds and promote precipitation (Boyce and Lee, 2017; Hassett et al., 2015; Le Hir et al., 2011; Steiner et al., 2015). Arguably, tall trees also decrease evaporation in a region by increasing the surface roughness and decreasing wind speed near the surface (Boyce and Lee, 2017; Le Hir et al., 2011).

4.3. Physical weathering, erosion and landscaping

Physical weathering - the mechanical destruction of rocks - occurs across a wide range of length scales by exfoliation (uplift and reduction of pressure), freeze-thaw processes, glacial grinding, rivers cutting through the landscape inducing rockfalls, wave thrashing and by roots advancing into crustal rocks. Physical weathering can be very efficient in producing fine-grained mineral fractions with a large surface area. Roots may also increase the surface area by fracturing existing rock.

Observations from the geological record show that fine-grained mud is rare in alluvium deposited before the evolution of land plants, but common from the Silurian onwards (Fig. 5) (McMahon and Davies, 2018). The proportion of mudrock increases steadily from the Silurian to the Carboniferous concurrently with the emergence of deeper root systems (Fig. 5C).

Both non-vascular and vascular land plants stabilize soils (Pawlik et al., 2016). Land plants also increase the production of fine-grained mineral fractions including secondary clay precipitates (see Section 3.4). In continental depositional systems these fines are captured from suspension and deposited when water moves around plant parts. The fines are also directly bound to plants (McMahon and Davies, 2018). Together, these processes arising from the evolution of land plants increase surface area of crustal rocks and prolong the exposure of mineral surface to weathering fluids.

The impact of vegetation on global denudation rates due to chemical, biological, and physical processes has been elusive (Brantley et al., 2011; Dosseto et al., 2014; Istanbulluoglu, 2005; Istanbulluoglu and Bras, 2006; Roering et al., 2010). The sedimentary rock volume in North America shows systematic trends correlated to orogenesis (Fig. 6) and no systematic trend through the mid-Paleozoic that could be solely assigned to the evolving terrestrial biota (Husson and Peters, 2018). Specifically, there is a steady, 3–fold increase in sedimentary rock volume in Laurentia coinciding with the exhumation of the Taconics orogeny (Swanson-Hysell and Macdonald, 2017). The increase in overall erosion rate, inferred from sedimentary rock volume, predate the rise of mud retention on land that has been ascribed to the spread of land plants (McMahon and Davies, 2018). Therefore, we conclude from paleorecords that early land plants did not permanently change global erosion rate (e.g. by stabilizing soils), but the record does not exclude any shorter-term impact of plants on erosion regimes.

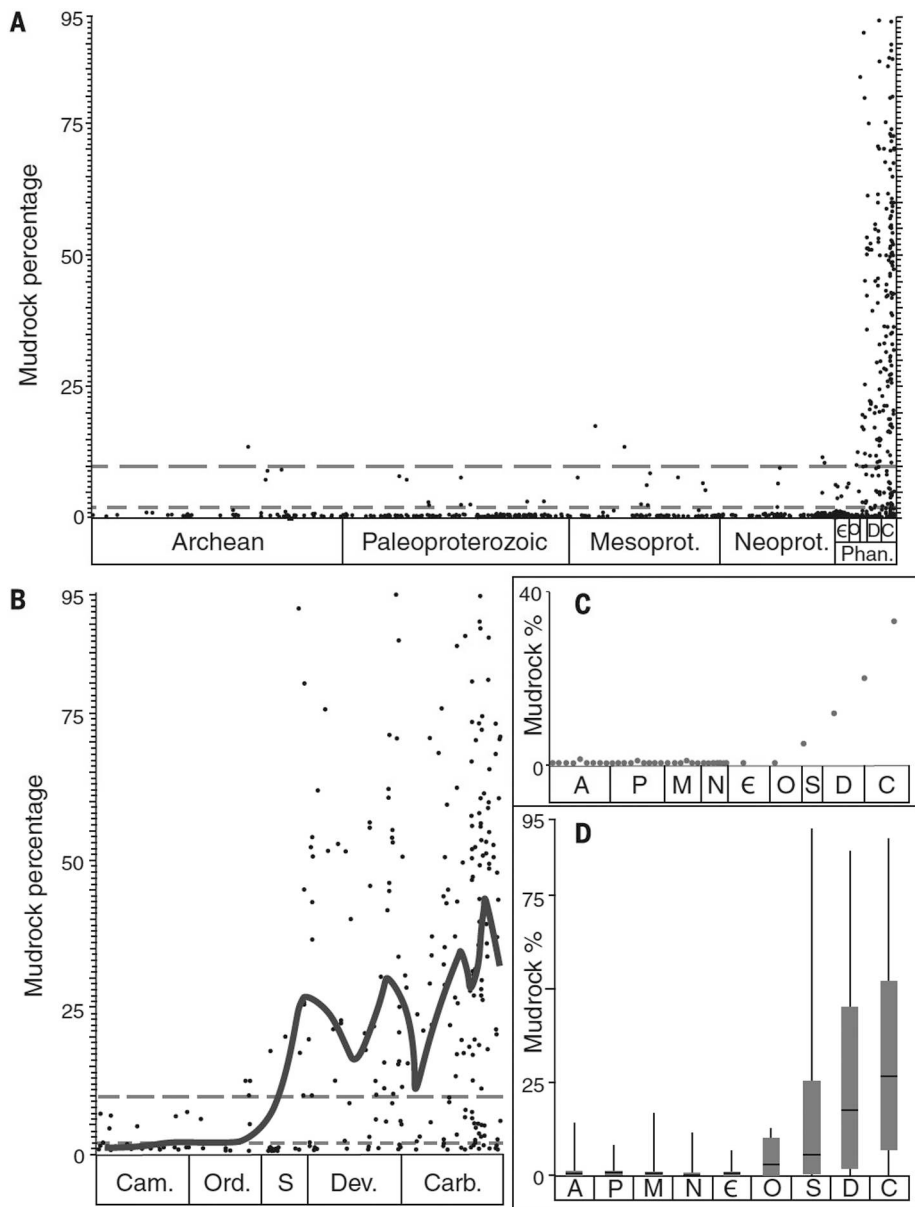Vegetation also shapes landscapes. Although, there is no landscape

Fig. 5. The proportion of mudrock (defined as rocks composed of dominantly detrital and weathered sedimentary grains < 0.063 mm) in alluvial successions through geological time. A) Each individual point represents one of 594 alluvial stratigraphic units. In Archean strata the mudrock accounts for 0–14% (median, 1.0%) whereas Carboniferous strata contain 0–90% (median 26.2%). B) Enlarged plot with LOESS regression line (smoothing parameter = 0.9). C) Proportion of mudrock corrected for sampling intensity in each geological period. D) Median, range, upper quartile and lower quartile of mudrock proportion for each interval. From (McMahon and Davies, 2018).
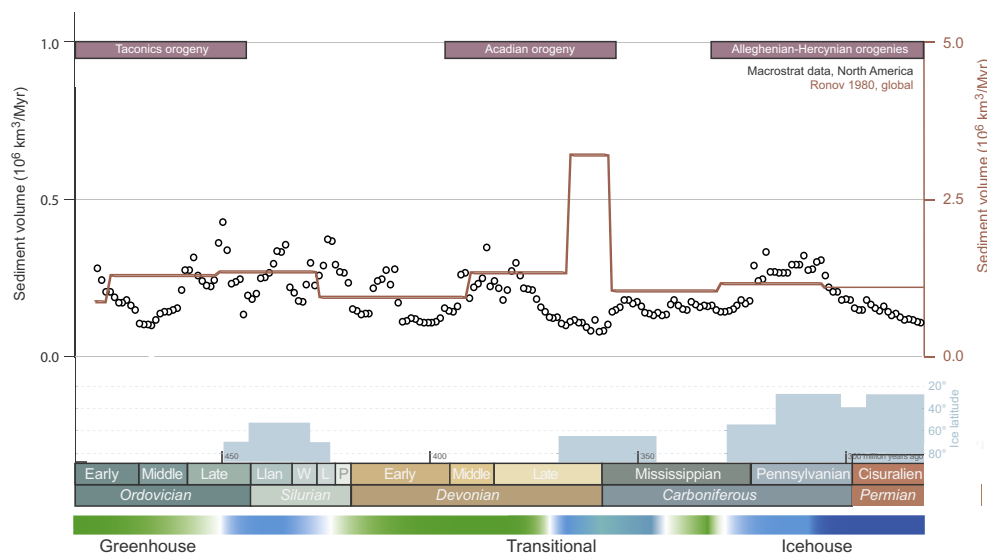

Fig. 6. Global sediment volumes for the mid-Paleozoic is derived from the North American Macrostrat database (Husson and Peters, 2018). The Taconic Orogeny in North America exhumed mafic and ultramafic lithologies ca. 465 Ma, coinciding with shifts in the strontium and neodymium isotope composition of seawater at this time (Swanson-Hysell and Macdonald, 2017).

uniquely created by life, vegetation influences the precipitation pattern and, thus, the height, width and symmetry of mountain ranges (Dietrich and Perron, 2006). Also, the path for water transport during runoff from the continents into the oceans will depend on the terrestrial ecosystem. Reconstructions of ancient channel systems suggest that Cambrian and Ordovician rivers were dominantly wide sand beds and aeolian tracts. Meandering rivers first appeared in the geological record near the Silurian-Devonian boundary when the flora was dominated by ground-hugging, rhizomatous plants with shallow roots. Multi-channel systems appear in the Early Pennsylvanian (Gibling et al., 2014; Gibling and Davies, 2012). The latter has been linked to the evolution of trees with deeper roots because vegetation affects meandering style and bank stability.

4.4. Chemical weathering (dissolution of rock)

Chemical weathering refers to the processes by which crustal minerals dissolve via reactions in aqueous solutions. Although distinct reactions occur for individual minerals, we distinguish between weathering of 1) carbonates, 2) silicate minerals and 3) sedimentary organic matter and pyrite.

For silicate minerals, the chemical reaction can be exemplified by an end-member elemental composition, such as wollastonite $CaSiO_3$ (Sarmiento and Gruber, 2006):

$$CaSiO_3 + 2\,CO_2 + 3\,H_2O \rightarrow Ca^{2+} + 2\,HCO_3^- + Si(OH)_4$$
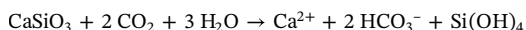
More weathering reactions for selected common minerals can be found in Hartmann et al., 2013. The dissolution of silicate minerals release cations (e.g. Ca^{2+}) to the soil solution by reaction with carbonic acid derived from atmospheric CO_2 in the presence of water. The cations and bicarbonate anions are transported in solution and ultimately results in the precipitation of carbonate minerals (in the oceans). In the soil the silicate minerals essentially transform into secondary clay minerals (Eberl et al., 1984). Chemical weathering may occur as a congruent or an incongruent reaction, depending on the mineral being weathered. Congruent weathering dissolves the mineral completely, whereas incongruent weathering produces dissolved species and new solids that are more stable in the weathering environment. The residual solids are the minerals that constitute soil.

4.4.1. Biotic influence on weathering in soils

The terrestrial biota affects chemical weathering processes and alter soil formation (pedogenesis) in many ways. Soils are mixtures of organic matter, minerals, fluids, and organisms that develop through chemical weathering and deposition of litter. By delivering energy and organic matter for decomposition, and altering the solution chemistry of weathering fluids, land plants affect the chemical dissolution of silicate minerals, the neoformation of clays, as well as the reaction kinetics (Eberl et al., 1984). In turn, these processes are affected by spatial and temporal changes in the evolving hydrological cycle and physical weathering regime. The principle processes affecting chemical weathering are illustrated in Fig. 4 and discussed further in below.

1) **Soil acidification.** Plants deliver organic matter to soils, which drives soil respiration and increase soil pCO_2 and decreasing pH in the soil solution. Organic matter is both delivered from above by dead plant tissue, through litter fall (e.g. deciduous progymnosperms and seed plants) and via shallow rhizoids and/or deep root systems below ground to the mycorrhizal symbionts and soil microbiota.

2) **Reactive species.** Root plants and their mycorrhizal symbionts also release root exudates into the soil solution to harvest bioessential nutrients. This capacity has evolved in step with the evolution of mycorrhizal fungi and the soil microbiota. Even the earliest bryophytes (thalloid liverworts) appear to have had AMF symbionts (Humphreys et al., 2010). Arbuscular Mycorrhizal Fungi assist the

plant with mobilization and transport of nutrients, especially P, to the plant by emitting reactive species, such as H^+, to the soil solution. Today, some angiosperms (flowering plants) are often associated with ectomycorrhizal fungi (EMF) that actively mobilize organic acids and siderophores to accelerate mineral dissolution without necessarily changing soil pH. This capacity, however, did not evolve until the Cretaceous (Taylor et al., 2009). Overall, the microbiota is mining the crust in exchange for carbohydrates in a mutualistic symbiotic relationship with land plants (Quirk et al., 2012).

3) **Water exchange.** Evapotranspiration in vegetation increases the flow of cations and nutrients between soil and plants. The recirculation of water can result in longer water-rock contact time promoting weathering (Taylor et al., 2009). Evapotranspiration also increases rainfall on a regional scale (see Section 3.2), leading to higher weathering rates in areas that are not limited by mineral supply (Ibarra et al., 2019).

4) **Water content.** Plants enhance the organic load in soils, and roots change the porosity necessary to trap moisture in soils. As animal-plant-fungal interactions evolved on land, soils became deeper and richer in organic matter, thereby changing where and how weathering reactions occur. Animals also play a key role in modifying these soil properties. Earthworms, which constitute the largest portion of animal biomass in soil today, process large volumes of organic matter in soil influencing soil structure (Bardgett and van der Putten, 2014; Blouin et al., 2013; Wardle, 2004). Plants influence soil development and the abundance of organic matter in particular, resulting in increased water-holding capacity and altered weathering processes (Crocker and Major, 1955; Kramer and Boyer, 1995).

5) **Clay mineralogy**. Plants also influence soil properties through clay mineralogy that, in turn, influence plant growth. Primary clay minerals form slowly in mildly acidic solutions as the solvents migrate through the weathering rock after leaching through upper weathered layers. The four most important groups of clay minerals, include smectites, illites, chlorites and kaolinites. All types of clay minerals have been reported in soils. Each group has distinct cation exchange properties, surface areas and abilities to expand in water, host organic compounds, and catalyze reactions on the mineral's surfaces. Today, smectite dominates in vertisols (clayey soils), kaolinite is the dominant component in oxisols (lateritic soils). Podsols/spodosols (e.g. in boreal forest) contain illite and smectite (Ito and Wagai, 2017). Soils with illite and chlorite are well suited for agricultural use, due to the capacity to hold plant nutrients. Small amounts of smectite stimulate growth, but large amounts are detrimental because they are impenetrable and have too great a water-holding capacity. Although the impact is spatially variant and depend on the lithology of the rocks undergoing weathering (e.g felsic or mafic), the terrestrial biota would have influenced "the clay factory", soil water content, and organic carbon pools on land in a manner that still remains to be quantified.

Marine clastic deposits reveal an increasing proportion of smectite and kaolinite from the Mississippian and Pennsylvanian onwards, at the expense of illite and chlorite (Weaver, 1967). Today, smectite and kaolinite formation are produced in large amounts under moderate to strong soil leaching in temperate and tropical climate, respectively. Arguably, the invasion of seed plants did not only expand the area where plant-assisted weathering occurs, it could also have intensified weathering processes resulting in finer-grained and compositionally more mature soils (Algeo et al., 1995; Algeo and Scheckler, 1998; Velde, 1985).

6) **Oxygen availability in the weathering zone.** The terrestrial biota also affects O_2 availability in the soil and weathering fluids. Due to the low O_2 solubility in water relative to air, atmospheric oxygen
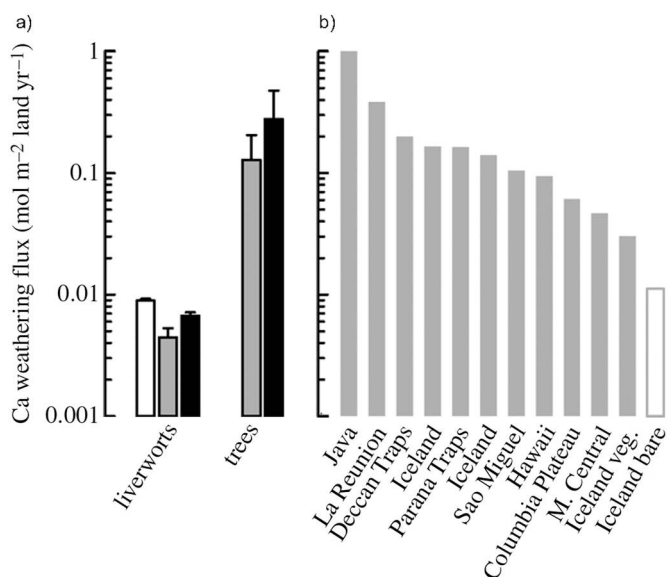
Fig. 7. a) The calcium-silicate weathering flux associated with liverworts and trees grown under similar observational conditions. b) The Ca weathering flux from major basaltic catchments with various vegetation cover. 'Iceland veg' and 'Iceland bare' refer to a vegetated site with small trees and a neighboring unvegetated site in Iceland, respectively (Quirk et al., 2015).

exchange is faster in dry and aerated soils, whereas anoxic conditions develop in waterlogged soils (e.g. peat). The loading of organic matter and formation of thicker clay horizons could affect water retention in soils and limit the exchange of O_2 between the atmosphere and the weathering zone: In turn, this would affect the solubility of redox-sensitive elements such as iron and change the properties of terrestrial 'clay factories' as well as the oxidative weathering processes in soils (Brantley et al., 2013).

4.4.2. Silicate weathering flux

In both controlled experiments and field studies, living plants increase the absolute silicate weathering rate relative to abiotic controls on shorter (human) time scale (Fig. 7); see review by Taylor et al., 2009. Plants and their mycorrhizal symbionts, enhance Ca weathering fluxes 3–7 fold over plant-free controls (Quirk et al., 2015). Trees enhance weathering rates per unit land area more than rootless plants do (Quirk et al., 2012, 2015), although rootless plants may also enhance silicate weathering relative to abiotic weathering (Lenton et al., 2012, 2016). A higher weathering rate is also observed in vegetated areas on Iceland relative to a neighboring unvegetated catchment area (Moulton and Berner, 1998). Therefore, the weathering flux of cations into continental runoff initially accelerates as plants invade new land areas. Over longer time scales, however, the weathering flux from a catchment area will reach a new steady state, limited by either the supply of 1) fresh mineral surfaces, 2) supply of weathering fluids or 3) the reactivity of the weathering fluids.

Biologically enhanced weathering affects weathering fluxes especially in areas, where weathering is not limited by mineral supply (Arens and Kleidon, 2011). In these areas, the dissolution rate of silicate minerals governed by other limitations, such as water and CO_2 availability. Topography influences the limiting factor for chemical weathering with elevated areas generally supplied by more fresh rock from erosion (Maher and Chamberlain, 2014). Also, the accumulation of a thick regolith in tropical flat areas may limit the downwards circulation of water and shift the weathering regime from one, where the kinetics of the dissolution reactions matter to a situation where the accessibility of fresh minerals to flowing waters becomes the limiting factor (Goddéris et al., 2008). Thus, the controls on global weathering rates are complex and require spatially resolved global models that take both geological and biological factors into account.

The largest biological intensification of global weathering (i.e. increase in weatherability, see Section 5) may well have occurred with the colonization of seed plants. This transition conceivably deepened and moisturized soils in drier upland areas and, thus, may have intensified the silicate weathering flux in mountainous areas, where weathering rates were not already mineral-supply limited (Algeo and Scheckler, 1998). Conversely, earlier sporophytes could not have enhanced weathering much if their habitat were mainly confined to wet lowlands limited by fresh mineral supply. These regional differences should have had important consequences for Earth's climate evolution, discussed further in Sections 5 and 6.

4.4.3. Phosphorous weathering flux

Continental weathering also dictates marine biological productivity, because the principle supply of the bio-limiting nutrient phosphorous (P) to the oceans comes from rivers (Froelich et al., 1982). The dissolved P input flux to the oceans has been assumed proportional to their marine burial flux, with 2/12 from silicate weathering, 5/12 from carbonate weathering and 5/12 from oxidative weathering (Bergman, 2004; Cappellen and Ingall, 1996; Lenton et al., 2018). In controlled growth experiments, plants and their mycorrhizal symbionts can selectively weather P from the soils with an amplification factor of 9–13 fold over plant-free controls (Quirk et al., 2015).

Bursts of selective P weathering sustained over < 1 Myr have been advocated as drivers for Silurian and Devonian carbon isotope events (Lenton et al., 2016). Recent studies, however, demonstrate that not all perturbations to the carbon cycle at this time are associated with cooling and expanded anoxia (see Section 6), but some events in the geological record do fit with such a global terrestrial-marine teleconnection, where marine anoxia associated with marine biotic extinctions occur at times when terrestrial flora and weathering processes increased the P weathering and oceanic nutrient supply (Algeo et al., 1995; Algeo and Scheckler, 1998; Qie et al., 2019).

4.4.4. Carbonate weathering

Today, carbonates cover ~10% of the land surface and dissolve much more readily than silicates (Gaillardet et al., 2018). Carbonate weathering has received little attention in part because it is not a significant contributor to changes in atmospheric CO_2 over long time scales, when weathering occurs via reactions with carbonic acid or organic acids (> 0.5–1.0 Myr) (Berner and Berner, 2012). However, carbonate weathering with nitric or sulfuric acids is a source of CO_2 to the atmosphere and oceans. The effect depends on the uplift and exposure of organic- and sulfide-rich sediments that undergo weathering (Spence and Telmer, 2005). We can only speculate that CO_2 release from sulfide-promoted carbonate weathering was higher in the aftermath of widespread deposition of sulfide-rich sediments in the early Paleozoic (Dahl et al., 2010), as these sediments were uplifted and weathered; e.g. maybe even linked to the apparent Mid-Late Devonian ocean warming and the Acadian orogeny (Fig. 10). The dissolution of carbonate depends on temperature and soil pCO_2, showing a bell-shape function of temperature with maximum dissolution between 10 and 15 °C. We expect the emergence of land plants affected carbonate weathering rates through their effects on soil respiration and soil temperature, although this has still not yet been implemented in Earth-system hindcast models (e.g., Arndt et al., 2011; Berner, 2006; Lenton et al., 2018).

4.4.5. Oxidative weathering

Oxidative weathering is the oxidation or oxidative dissolution of reducing minerals and organic carbon in soils. For instance, the oxidative weathering reaction involving pyrite is:

$$4 \, FeS_2 + 15 \, O_2 + 8 \, H_2O \rightarrow 2 \, Fe_2O_3 + 8 \, H_2SO_4$$
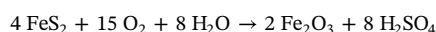
Oxidative weathering of pyrite and sedimentary organic carbon in

soils depends on transport of O_2 into soils, primarily by way of diffusion. The diffusion rate depends on the physical properties of the soil, such as porosity and moisture content. Plants change these properties in many ways. For instance, plant-induced changes to the "clay factory" affect grain size, porosity and water retention. Plants also stimulate oxygen consumption by soil respiration in the top soil (Kanzaki and Kump, 2017; Kump, 2014). Hereby, plants alter the extent and duration of contact between minerals and O_2 in soils that should lead to less oxidative weathering.

It is debated how oxidative weathering has influenced atmospheric O_2 levels through time. In this respect, it is central to understand how the long-term O_2 sinks depends on the atmospheric O_2 levels. Ever since the Great Oxidation Event at 2.4 Ga, reduced sulfur in crustal rocks have been completely oxidized upon weathering, which means that pyrite oxidation has not varied in response to Paleozoic atmospheric O_2 levels (Johnson et al., 2014). In contrast, oxidation of sedimentary organic carbon is sensitive to O_2 at probable Paleozoic O_2 levels (Daines et al., 2017), making this a prime candidate for atmospheric O_2 control as are the long-term O_2 sources: organic carbon and pyrite burial (see Section 5.2).

Finally, we stress that the different chemical weathering processes may pose limitations on one another. This is evidenced by recent work on nested reaction fronts (Brantley et al., 2013, 2017). For instance, the extent to which a weathering reaction results in increased porosity, aiding diffusion, is essential for the whole suite of weathering processes. It is therefore also probable that changing atmospheric O_2 levels could have indirectly affected atmospheric CO_2 through interactions between oxidative and silicate weathering processes in which the terrestrial biota may have played a role.

4.5. Wild fire

Land plants are essential for wildfire. At high atmospheric O_2 level, > 17 atm%, and low moisture content, terrestrial biomass from plants ignite and burn. Fire consumes O_2 and wild fire frequency increases at higher O_2 levels, leading to a rapid and strong feedback on phosphorous weathering and atmospheric O_2 (see Section 5) (Kump, 1988; Lenton and Watson, 2000). This leads to an upper limit on atmospheric O_2 around ~30 atm% even in a wet climate. Wildfire immediately decomposes organic matter and alters soil properties by adding dead organic matter and nutrients to the soils. This leads to a short-lived increase in soil temperature, moisture content and soil respiration, but over longer time scales the soil fertility decreases, due to nutrient release and loss to runoff during rainfall after the fire (Neary et al., 2008).

4.6. Biomass accumulation and preservation

The emergence of the terrestrial biota promoted both biomass storage on land and in marine sediments.

In the marine realm, the global burial flux of marine organic carbon is ultimately limited by the oceanic P flux, which limits marine production and organic carbon export from the photic zone to the sediments. The marine organic matter is buried with a relatively constant C/P molar ratio of ~200, reflecting the canonical 'Redfield ratio' of living biomass (C/P ~ 106) and degradation during diagenesis. The appearance of land plants led to the production of phosphorous-poor structural compounds, including sporopollenin, lignin and chitin (in their fungal mycorrhizal symbionts). This would have given the land biota a higher C/P ratio (~1900) and allowed more organic carbon production and burial on Earth for a certain rate of P mining and weathering from the crust (Lenton et al., 2016). Today, terrestrial organic carbon accounts for ~1/3 of organic matter in marine sediments (Burdige, 2007). The continental flux of particulate organic carbon is perfectly correlated to the erosion rate in modern catchment areas, and not to terrestrial biological productivity (France-Lanord and Derry,

1997; Galy et al., 2007, 2015). Hence, tectonics exerts first order control on the global burial of the terrestrial organic matter, and the effect of land plants on global organic carbon burial would be to source more P for marine biological production, promoting organic export to sediments and organic burial in marine deposits.

Marine sediments generally display a wide range of total organic carbon content (TOC). This challenges statistical interpretations if the known record suffers from sampling bias (Sperling and Stockey, 2018). Nevertheless, the available database of nearly 10,000 measurements in Phanerozoic shales shows a systematic increase in the median TOC content from ~1 wt% in the Silurian (444–419 Ma) to ~5 wt% in the latest Devonian (370–355 Ma), consistent with the expected greater production and preservation potential of decay-resistant organic compounds produced at this time. An increase in the proportion of smectite in marine mudrocks has been linked to rhizosphere developments and the emergence of seed plants in marine sediments (Algeo et al., 1995). Yet, the proportion of smectite clays in marine sediments first increases in the Late Mississippian, ~330 Ma, when there is no further rise in marine TOC (Sperling and Stockey, 2018; Weaver, 1967). Hence, it is unclear whether these records result from the same or distinct ecological transitions.

The Carboniferous (358.9–298.9 Ma) is so named for its widespread coal deposits. Indeed, a markedly increase in coal accumulation on land took place in the Pennsylvanian (323.3–298.9 Ma), but coal deposits span essentially the entire history of lignified vascular plants with the first coals in the Lower Devonian involving plants that were very scantly lignified (Nelsen et al., 2016). There is no evidence of earlier (bryophyte-derived) peat. Peat moss itself appears to have diversified in the Neogene (Shaw et al., 2010). The evolution of the biopolymer lignin used by vascular plants in some cell walls associated with biomechanical support was likely important for coal to form in the first place. In addition, the evolution of land plants further inland may have allowed organic matter to accumulate on land.

The Pennsylvanian coal peak has been causally linked to the unique confluence of climate and tectonics (Nelsen et al., 2016). Coal accumulates in areas where productivity/litter fall exceeds the rate of decay. Terrestrial productivity is high in wet tropics and decay is reduced in anoxic environments that develop in stagnant water-logged substrate. In the Pennsylvanian and Permian, the changing tectonic configuration led to extensive low-latitude foreland basins ideally suited for coal formation (Nelsen et al., 2016).

5. Land plants and the regulation of Earth's climate and oxygenation state

Did the colonization of the Earth's surface by land plants affect the global environment? In order to answer this question, we turn our attention to the current understanding of the global biogeochemical cycles of carbon, phosphorous and oxygen that control the Earth's climate and oxygenation state. How does the state and function of the land surface regulate the global biogeochemical cycles, and what room is there for plants to modify these cycles?

5.1. Climate regulation

Over the past 4.5 billion years, the Sun's luminosity has increased 25–30% (Bahcall et al., 2001; Gough, 1981), yet the Earth's climate has been clement and allowed liquid water at the surface, interrupted only by temporary global glaciations. The prevailing theory is that greenhouse warming has compensated for the fainter Sun (Caldeira and Kasting, 1992; Kasting, 1993; Walker et al., 1981). Earth's long-term climate stability is remarkable in the sense that the necessary atmospheric CO_2 levels were ~ 40,000 ppmv (parts per million in units of volume air) in the early Archean and has declined two orders of magnitude to the modern level (Catling, 2014). By the same principles, a higher atmospheric CO_2 level would be expected to compensate for the
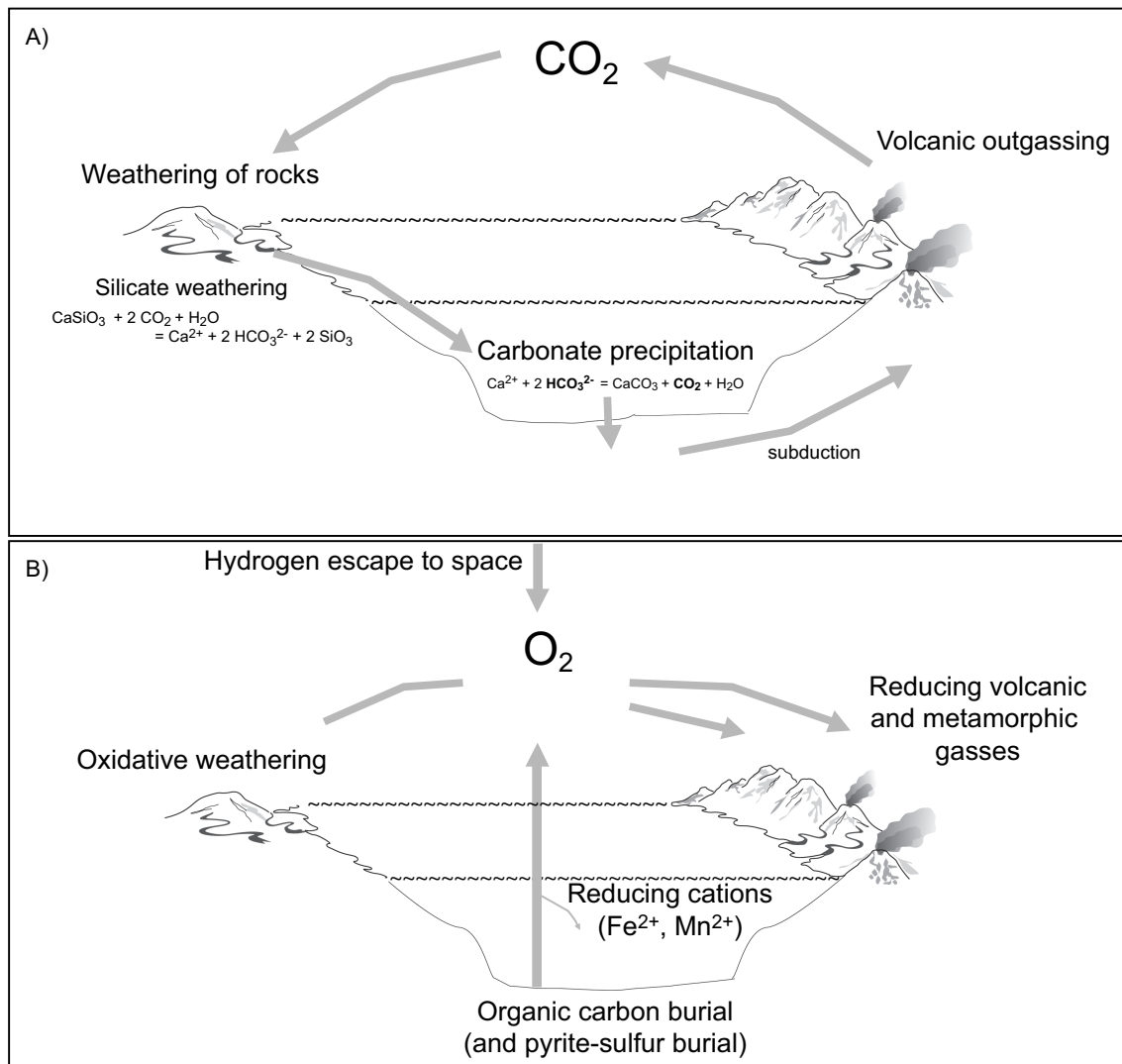
Fig. 8. Climate (CO_2) and oxygenation (O_2) regulation on Earth. a) The atmospheric CO_2 level is determined by the balance between its long-term volcanic sources and its sinks. Silicate weathering consumes CO_2 and delivers alkalinity (e.g. HCO_3^-) to the oceans, where it precipitates as carbonate (e.g. $CaCO_3$). b) The atmospheric O_2 level is controlled by the balance between sources and sinks, where organic carbon, pyrite burial and H_2 escape to space represent the major source fluxes and oxidative reactions with reducing fluids emanating from Earth's interior (modified after Catling, 2014).

3–4% fainter mid-Paleozoic Sun (Berner, 1993). Although, the mid-Paleozoic atmospheric CO_2 level would need to have been higher than today, it may not be by very much. State-of-the-art climate models predict that a doubling of CO_2 leads to 3.0 ± 1.5 °C increase in global mean temperature today (Pachauri et al., 2015), whereas an inverse modeling approach to available proxy records reveals a climate sensitivity of $5.6^{+1.3}_{-1.2}$ °C for a doubling of CO_2 over the past 100 Myr (Krissansen-Totton and Catling, 2017). Thus, everything else equal, the same mean temperature as today could be achieved if the mid-Paleozoic atmosphere contained only ~800 ppmv (2 x CO_2 PAL). In the absence of land plants, atmospheric CO_2 levels is predicted higher than this.

To appreciate this, it is essential to understand how land plants affect the silicate weathering feedback at play in the global carbon cycle (Fig. 8A). Importantly, the absolute CO_2 consumption rate via silicate weathering must balance the geological CO_2 input flux from volcanic outgassing and oxidation of sedimentary organic carbon in order to achieve a steady state atmospheric CO_2 level. A small long-term imbalance of only 5% between these fluxes is enough to cause runaway greenhouse or icehouse conditions within < 10 Myr (Berner and Caldeira, 1997; D'Antonio et al., 2019). The mass balance for the ocean-atmospheric CO_2 reservoir can be written as follows:

$$\frac{dCO_2}{dt} = F_{vol} - F_{silw} + F_{ocw} - F_{ocb}$$

Here CO_2 is the combined ocean-atmospheric reservoir of CO_2, F_{vol} is volcanic outgassing, F_{silw} is the silicate weathering equivalent CO_2 flux, F_{ocw} is CO_2 production by oxidative weathering of sedimentary organic carbon and F_{ocb} is the burial of sedimentary organic carbon (SOC). In the simplest case of steady state, where the reservoirs of atmospheric CO_2 and SOC are constant, silicate weathering balances volcanic outgassing, i.e.

$$\left.\begin{array}{r}\frac{dCO_2}{dt} = 0 \\ F_{ocw} = F_{ocb}\end{array}\right\} \Rightarrow F_{vol} = F_{silw}$$

As a result, any biological enhancement of weathering cannot forever increase the silicate weathering flux to the ocean and absolute CO_2 consumption rate. Rather, plants can modify the feedback and change the atmospheric CO_2 level, at which the global silicate weathering flux comes to balance the volcanic source (Fig. 8A).

Indeed, global mass balance models such as GEOCARB, GEOCAR-BSULF (Berner, 1987, 2006) and COPSE (Bergman, 2004; Lenton et al., 2018) have been designed to explore the potential effects of the
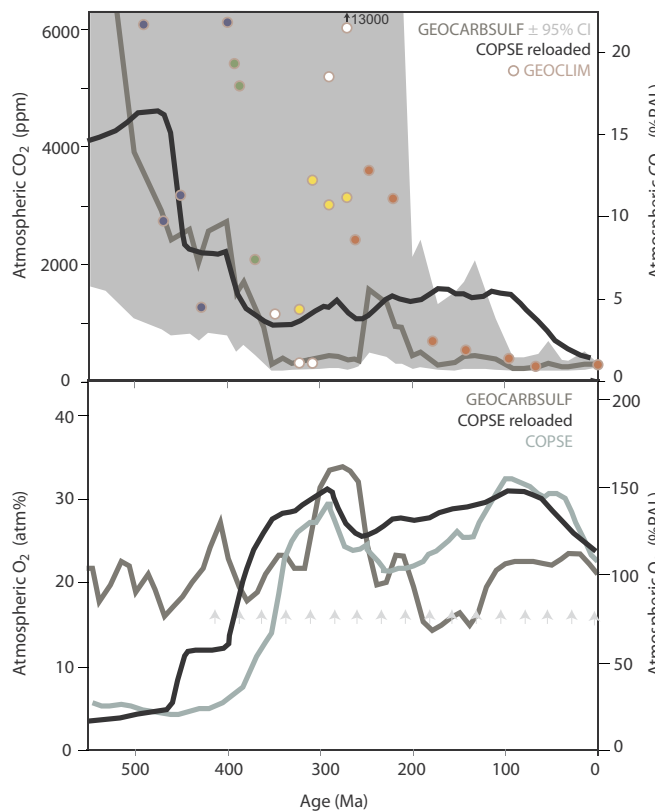
Fig. 9. Plausible atmospheric CO_2 and O_2 trajectories for the Phanerozoic (540–0 Ma). a) Atmospheric CO_2 levels according the GEOCARBSULF model (dark grey curve) with 95% confidence interval (grey shaded area) (Royer et al., 2014), COPSE reloaded model (black curve)(Lenton et al., 2018), and GEOCLIM GCM model runs for distinct climate scenario (red circles) are show with data for Early Paleozoic (blue circles; Nardin et al., 2011), the Devonian (green circles; Le Hir et al., 2011), Late Paleozoic (yellow circles, Goddéris et al., 2017) and Mesozoic-Cenozoic (orange circles; Donnadieu et al., 2006). To illustrate the dramatic consequences for CO_2, GEOCLIM models with a different style of weathering, affected by soil shielding, are also shown (white circles Goddéris et al., 2017) . b) Atmospheric pO_2 according to GEOCARBSULF (Berner, 2006), COPSE (Bergman, 2004), and COPSE reloaded (Lenton et al., 2018). Abbreviations: ppm = parts per million. %PAL – percentage of Present-day Atmospheric Level. atm% – percentage of atmospheric partial pressure. CI – confidence interval. The presence of charcoal since 420 Ma indicate atmospheric O_2 levels above 17 atm% (75% PAL) (Glasspool and Scott, 2010). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

evolution of plants on the climate. The models support the possibility of a ~ 10-fold decline in atmospheric CO_2 levels in response to the evolution of land plants (Fig. 9).

5.1.1. The silicate weathering thermostat

The atmospheric CO_2 level and greenhouse forcing on Earth reflects the balance between the volcanic sources and carbonate sinks via silicate weathering reactions (Fig. 8A). The weathering of silicate minerals releases cations (e.g. Ca^{2+}, Mg^{2+}) into soil solutions. These solutions are eventually transferred via rivers and streams into the oceans, where the cations bind to HCO_3^- to form carbonates. Because silicate weathering depends on temperature, runoff and soil CO_2, the result is a stabilizing feedback on atmospheric CO_2 and climate. The feedback was first parameterized in the seminal work of (Walker et al., 1981), and has here been modified to include a factor, ω, which represents the susceptibility of land to undergo weathering (now defined as 'weatherability' according to Kump et al., 2000):

$$F_{silw} \approx F_{silw,0} \cdot \omega \cdot (pCO_2)^n \cdot exp.(\Delta T/T_e)$$

Here, the exponent $n = 0.3$ is the sensitivity of silicate dissolution rates to CO_2 based on empirical data (laboratory experiments). The temperature dependence is an exponential function with $T_e = 13.7$ K that covers both the sensitivity of mineral dissolution rates to temperature and the sensitivity of global runoff to mean global temperature based on a general circulation model. ΔT is defined as the temperature offset from present day global average temperature (288 K). The constant $F_{silw,0}$ corresponds to the modern reference silicate weathering rate at modern CO_2 level and mean temperature, and ω is defined as a dimensionless weatherability factor.

This formulation is used in the GEOCARB, GEOCARBSULF (Berner, 1987, 2006) and COPSE models (Bergman, 2004; Lenton et al., 2018). Recognizing that geographical changes of the land surface will modify the silicate weathering rate, it has been assumed that global silicate weathering rate can be adequately described as the product of a feedback function, $f(T, CO_2)$ for the Earth system that only depends on temperature and CO_2 and a time-varying land surface function $g(t)$, which is similar to ω. In COPSE silicate weathering rate F_{silw} takes the following general form:

$$F_{silw}(t) = F_{silw,0} \cdot g(t) \cdot f(T, CO_2)$$
$$g(t) = U(t) \cdot PG(t) \cdot A(t)$$
$$f(T, CO_2) = f_T(T) \cdot f_{run}(T) \cdot f_{biota}(CO_2)$$
$$f_T = e^{k \cdot \Delta T}$$
$$f_{run} = (1 + 0.038 \cdot \Delta T)^{0.65}$$
$$f_{biota} = pCO_2^{0.5}$$

Here, $F_{silw, 0}$ is the modern reference global silicate weathering rate. $g(t)$ is the product of the time dependent uplift rate (U), the global effect of paleogeography on runoff and weathering (PG) and the land surface area (A), all normalized to the modern day values. The temperature function f_T is essentially the same as in Walker et al., 1981, although the temperature dependence of runoff has been modified to include the effect of dilution of dissolved loads at high runoff rates (Berner, 1994), because soil depth scales with runoff and deep soils have limited mineral supply for weathering (Bluth and Kump, 1994; Hilley et al., 2010; Riebe et al., 2001; Stallard and Edmond, 1983). That means, the exponent accounts for the increased depletion of weatherable minerals in soils at higher temperature.

Importantly, the CO_2 dependence of silicate weathering has been embedded in f_{biota}, which is a function for the biotic enhancement of weathering. In COPSE the effect of CO_2 on silicate weathering is assumed mediated by plants. Before the advent of vascular plants, the biotic factor was assumed to be $f_{biota} = pCO_2^{0.5}$ (adopted from GEOCARBII, Berner, 1994), which represents semi-open soil weathering systems where the CO_2 loss from the soil is partly compensated by CO_2 supply via diffusion from the atmosphere. The square-root dependence of silicate weathering on CO_2 has dramatic consequences for the calculated CO_2 level in the models, and was originally not founded on physical processes. Recent models based on first principles and inverse modeling of the necessary strength of the feedback suggest the exponent has a lower value than 0.5 (Krissansen-Totton and Catling, 2017; Arens, 2013). In the equations above, this would translate to higher CO_2 levels before the evolution of land plants than previously predicted in order to balance volcanic outgassing.

5.1.2. Global biotic effects on atmospheric CO_2

Land plants can affect both the weatherability of the land surface, $g(t)$, and the silicate weathering feedback function, $f(CO_2, T)$ (Bergman, 2004; Berner, 1994; Berner et al., 1998; Kump et al., 2000, Volk, 1989). In GEOCARB and COPSE, vegetation enhance weatherability by a factor of ~4–7 based on field studies and control weathering experiments that compare vegetated and non-vegetated areas today (Moulton, 2000; Moulton and Berner, 1998; Taylor et al., 2009). These studies are usually limited to one location. Laboratory experiments for individual

plants compare weathering rates during the colonization phase, i.e. on short time scales and for predefined substrates (Lenton et al., 2012; Quirk et al., 2015). An alternative is 'sandbox' experiments for decadal studies (Balogh-Brunstad et al., 2008). In all cases, the experiments do not capture the weathering enhancement at steady state for the ecosystem, which are molded by interactions in the soil. Moreover, scaling up from watersheds to the global scale is challenged by geographical variations in ecosystems and tectonic settings (e.g., Ferrier et al., 2016).

The parameterization of plants in the silicate weathering feedback function is focused on the relationship between plant growth and environmental factors. Here, it is inherently assumed that chemical weathering is controlled by plant growth and that plant growth is controlled by atmospheric temperature, CO_2 and O_2. In COPSE, the silicate weathering sensitivity to CO_2 is an amalgam of the non-vascular CO_2 sensitivity ($\sim pCO_2^{0.5}$) and the effect of vegetation on weathering (Lenton et al., 2018). The silicate weathering rate is assumed to scale as:

$$f_{biota} = [1-\min(V \cdot W, 1)] \cdot k_{be} \cdot pCO_2^{0.5} + V \cdot W$$

where V is normalized vegetation biomass and W is the normalized effect of vascular plants on weathering relative to non-vascular plants, and has evolved from 0 to 1 through time (i.e. $W = 1$ for the present). Importantly, k_{be} is a constant that describes the global biotic enhancement of weathering from non-vascular to vascular weathering regimes (e.g. 4-fold for $k_{be} = 0.25$). To represent the colonization of land by arborescent vascular plants, the weight of vascular plant weathering ($V \cdot W$) increases from 0 towards 1. Thus, f_{biota} increases from 0 to 1 and enhances weathering rates, causing an imbalance in the model that draws down CO_2 levels. Furthermore, because the vegetation biomass (V) responds to changes in the environment, such as temperature and CO_2 (and to a lesser extent O_2), the f_{biota} function results in a stabilizing feedback for climate. The global impact of vegetation on climate in COPSE is, thus, to act as a stabilizing feedback to atmospheric CO_2 perturbations. This feedback has increased in strength over time and brought down atmospheric CO_2 levels (Fig. 9).

In summary, existing Earth system models suggest that the emergence of land plants primarily cooled the Earth by drawing down CO_2 from the atmosphere through enhanced efficiency of silicate weathering.

5.2. O_2 regulation on Earth

It is generally accepted that land plants influence both the short-term and long-term O_2 sources and sinks on Earth.

Oxygen production through oxygenic photosynthesis in cyanobacteria, algae and land plants is kept in almost perfect balance with oxic respiration. A small offset from balance amounts to about 1 part in 1000 where excess organic matter is buried in the crust. This burial of organic matter (as well as pyrite) in sediments represents the primary long-term source of atmospheric O_2. Hydrogen escape to space represents a minor source of O_2, but it can be ignored for the Phanerozoic (Catling, 2014). Over the course of Earth history, life has affected the global biogeochemical cycles resulting in a net oxidation of Earth's oceans and atmosphere (Lenton et al., 2016; Lyons et al., 2014).

Earth's long-term O_2 cycle is considered tightly coupled to the marine carbon and phosphorous cycles (Cappellen and Ingall, 1996; Kump, 1988; Lenton and Watson, 2000). Continental weathering is the primary source of the bio-limiting nutrient phosphate (PO_4^{3-}) to the oceans. Therefore, continental weathering can fertilize the oceans, increasing global marine productivity and the flux of organic matter to the deeper, aphotic part of the oceans. This will deplete O_2 from the water column via aerobic respiration and promote organic carbon burial in marine sediments. Therefore, continental weathering can both expand ocean anoxia (via marine O_2 consumption), and over million-year time scales sustain increasing atmospheric pO_2 (Lenton et al., 2016). These relationships represent both shorter-term and longer-term

teleconnections between terrestrial and marine ecosystems, where vegetation on land set the stage for marine animal extinctions and proliferations (Section 6).

Although two distinct parametric Earth system models (COPSE and GEOCARBSULF) predict different Phanerozoic O_2 trajectories (Fig. 9), both models suggest that the colonization of land by vascular plants led to a major rise of atmospheric pO_2 (Bergman, 2004; Berner, 2006; Lenton et al., 2011, 2018). The COPSE model predicts a stepwise increase ($25 \rightarrow 100\%PAL$ O_2) whereas the GEOCARBSULF model suggests atmospheric pO_2 returned to initial levels ($100 \rightarrow 150 \rightarrow 100\%$ PAL). Both models fit the carbon, sulfur and strontium isotope evolution of Phanerozoic seawater, but the COPSE model better fit new lines of evidence from Mo isotopes and other ocean redox proxies for increasingly oxygenated oceans (Dahl et al., 2010; Sperling et al., 2015; Stolper and Keller, 2018; Wallace et al., 2017).

Importantly, the two models differ substantially in how global organic carbon burial and oxidative weathering are controlled over long-time scales – and therefore also in how land plants can have influenced Earth's oxygenation.

In GEOCARBSULF, O_2 is regulated *indirectly* in the sense that O_2 production (organic carbon burial) and destruction (weathering) does not depend on O_2 itself. Rather, O_2 is controlled by 'rapid recycling' of young recently buried organic carbon through uplift and oxidative weathering. If excess organic carbon burial is sustained for a long period of time, O_2 rises and the reservoir of young organic carbon increases. Because oxidative weathering depends on the size of this young organic carbon reservoir excess organic carbon weathering follows and brings atmospheric O_2 levels back down (with a response time of ~ 10 Myr). Therefore, in the GEOCARBSULF world, increased organic carbon burial by any cause will only lead to a *temporary* increase in O_2. The buildup of a terrestrial organic carbon reservoir (e.g. coal) is a driver for a temporary increase in atmospheric pO_2. In the GEOCARBSULF model, land plants mainly contribute to Earth's long-term steady state O_2 level through enhanced organic carbon preservation.

In contrast, COPSE tracks the bio-limiting nutrient, phosphorous. Enhanced P weathering by plants allows a *transient* rise in global productivity and organic carbon burial. COPSE also predicts a permanent shift to higher O_2 levels due to higher C/P ratio of bryophytes and vascular plants compared to their marine ancestors, resulting in more organic carbon burial at the global scale for the same P weathering rate (Kump, 1988; Lenton et al., 2016). Also, preferential weathering of P by pre-vascular plants together might have contributed to atmospheric O_2 rise already in the Ordovician and Silurian. Overall, these fertilization effects might well have led to more biological production on Earth.

One controlling feedback for O_2 in COPSE is prescribed O_2 dependent oxidative weathering of the crust. This results in more O_2 consumption after a period of excess organic matter burial. Nevertheless, a permanent O_2 rise is destined due to more biomass production and organic matter loading in crustal reservoirs. Further, the COPSE model has an "O_2 roof", due to a wildfire feedback. At high O_2 levels, fire frequency dramatically increases, which is thought to limit P weathering and delivery to the oceans (see Section 4) (Kump, 1988; Lenton and Watson, 2000). Hence, in the COPSE world, land plants influence O_2 levels through phosphate weathering, C/P ratio of biomass, organic carbon preservation, which in turn is modulated by fire frequency.

6. Evidence for mid-Paleozoic transitions in the Earth system

The colonization of land by plants encompasses five transitions that all may have affected the Earth system in distinct ways. The main predicted consequences of plant colonization are:

I. Atmospheric CO_2 decline and climatic cooling (permanent transition)
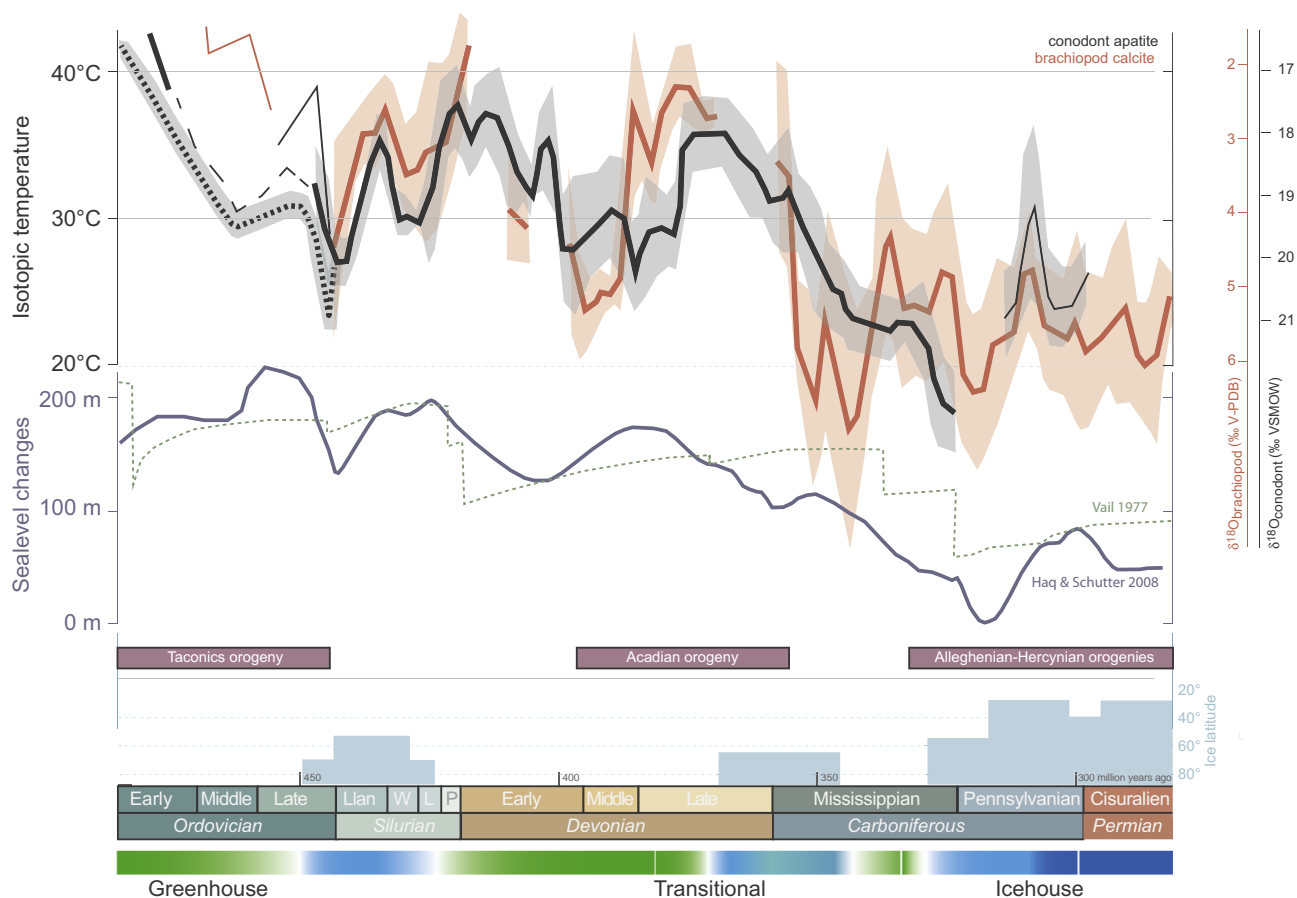II. Atmospheric O_2 rise and ocean oxygenation (potentially permanent transition)

Fig. 10. Paleotemperature of seawater inferred from $\delta^{18}O$ in conodont apatite and calcitic brachiopods assuming a constant $\delta^{18}O$ value in seawater of $-1‰$ (Grossman, 2012). Global sea-level change relative to present day (Haq and Schutter, 2008; Miller et al., 2005). The extent of glacial deposits are shown for comparison (after Foster et al., 2017).

III. Ocean fertilization and anoxia (temporary perturbations, ~1 Myr)

6.1. Evidence for climatic changes in the mid-Paleozoic

Originally, the Devonian cooling hypothesis proposed that a ~ 10-fold drop in atmospheric CO_2 took place in the mid-Paleozoic and caused climate cooling that initiated the Late Paleozoic Ice Age (Berner, 1990, 1991, 1993). Since then, it has become clear that the Ordovician cooling episode was prolonged and that plants with high C/P evolved earlier (Lenton et al., 2012; Trotter et al., 2008) and, thus, we need to consider how all stages in the evolution of terrestrial ecosystems contributed to the Paleozoic transitions.

6.1.1. Evidence for mid-Paleozoic cooling (paleo-temperature records)

The oxygen isotope composition of biogenic apatite and calcite reflect changes in seawater temperature and $\delta^{18}O$ (Grossman, 2012; Joachimski et al., 2004). Fig. 10 shows the best-fitted $\delta^{18}O$ curves and error envelopes based on data from shallow tropical/subtropical conodonts (black) and brachiopods (red), assuming seawater $\delta^{18}O$ was constant at $-1‰$. These curves are consistent with clumped isotope thermometry that can simultaneously constrain seawater $\delta^{18}O$ and temperature (Came et al., 2007; Henkes et al., 2018). The resulting temperature curve should reflect the temperature in shallow tropical/subtropical seawater, where the conodonts and brachiopods lived. These records demonstrate evidence for remarkably high surface temperatures up to ~40 °C in the Cambrian and early Ordovician oceans (520–465 Ma) followed by cooling from the Early-Mid Ordovician (> 467 Ma) onwards (Finnegan et al., 2011; Rasmussen et al., 2016; Trotter et al., 2008; Wotte et al., 2019). Climatic cooling followed in

several steps with glacial advances occurring mainly in the Late Ordovician and in the Pennsylvanian at times when the 'isotopic temperature' declined (although not below a certain temperature threshold).

The onset of the Ordovician cooling phase broadly coincides with the exhumation of the Taconic volcanic arcs in tropical regions, which arguably contributed to lower CO_2 through silicate weathering (Swanson-Hysell and Macdonald, 2017). Earth system models have been established that allow high-latitude glaciations with a modest decline in atmospheric CO_2 levels to ~2400 ppm (~8 PAL), consistent with available paleo-CO_2 proxy data (Lenton et al., 2012; Porada et al., 2016).

Glacial deposits occur also in the early Silurian (~440 Ma after the Hirnantian glacial maximum; Díaz-Martínez and Grahn, 2007), but seawater appears to have been warmer from the Late Silurian to the mid-Devonian (420–380 Ma) (Fig. 10).

Nevertheless, the reconstructed seawater $\delta^{18}O$ curve carries considerable uncertainty (< 2‰), which could considerably change the magnitude of the temperature drop. It is also possible that diagenesis has synchronously affected both the conodont and brachiopod records, although there is no evidence in support of this (Grossman, 2012). Lastly, we must not forget that the recorded temperature may reflect a change in the latitudinal temperature gradient instead of the actual mean temperature. That said, there is compelling evidence for an overall cooling throughout the mid-Paleozoic.

6.1.2. Eustasy

The history of sea-level change can be estimated from the flooding history of continental margins and cratons. The inferred sea level record

for the mid-Paleozoic (Fig. 10) exhibits changes on various time scales that correlate with the oxygen isotope record and reflect changes in ice-volume and tectonics (Haq and Schutter, 2008; Miller et al., 2005). Over the longest time scales ($> 10^7$ yr), the reconstructed sea level curve shows a gradual rise through the Cambrian reaching a peak in the Late Ordovician presumably as a result of new ocean ridges generated during the breakup of supercontinent Rodinia (Haq and Schutter, 2008; Miller et al., 2005). Hereafter, sea level declined by about 200 m from the Ordovician into the Permian superimposed by some substantial oscillations. This long-term sea-level drop broadly correlate with the cooling trend and have been attributed to declining atmospheric CO_2 levels (Miller et al., 2005).

6.1.3. CO₂ paleo-barometers

The Devonian cooling hypothesis soon gained support from geological evidence suggesting high atmospheric CO_2 levels prior to the rise of vascular plants (McElwain and Chaloner, 1996; Mora et al., 1996; Yapp and Poths, 1992, p. 1992). The early paleo-CO_2 barometers were based on carbon isotope data from paleosols as well as stomatal proxies in plant fossils, each interpreted with an independent set of assumptions. Both records indicated high atmospheric CO_2 levels in the Ordovician and early Devonian (~445–410 Ma). The latest compilation of paleo-CO_2 estimates can be found in Foster et al., 2017. We do urge caution with these records, since the mid-Paleozoic pCO_2 record carries very large uncertainties as we describe below (Fig. 9).

6.1.3.1. Paleosols.
Both the carbon in pedogenic carbonate and the carbon trapped in pedogenic goethite are derived from the admixture of atmospheric CO_2 and soil-respired carbon (Yapp, 1987). Air and soil-respired CO_2 sources have markedly distinct carbon isotopic signatures (ca. $-7‰$ and $-25‰$, respectively). Yapp and Poths (1992) discovered that the $\delta^{13}C$ and CO_2 content in pedogenic goethite varied systematically with depth in a Late Ordovician (~440 Ma) paleosol in a manner that could be ascribed to a two-component mixing curve of CO_2 derived from these two reservoirs. From this curve, the CO_2 content in the mineral was calculated for the scenario where the goethite had precipitated in the presence of atmospheric CO_2 only. Knowing the partition coefficient of CO_2 in goethite from laboratory experiment, they derived an atmospheric CO_2 level of 4800 ppm (Yapp and Poths, 1992). The calculation depends on the carbon isotope composition of the atmosphere ($-6.5‰$), the carbon isotope fractionation during CO_2 uptake into goethite (5‰), the temperature (24 ± 4 °C) and pH of the pedogenic fluids from which goethite precipitated (Yapp, 1987). Ignoring the pH effect, we propagated the errors of their data and temperature range to find that the Late Ordovician atmospheric CO_2 level was 4800 ± 1900 ppm (10–22 PAL, 1 SD). This result implies a remarkably high CO_2 levels at some point during the Hirnantian when the Earth was variably glaciated (Ghienne et al., 2014). Recent climate models suggest that 8–12 PAL CO_2 is still compatible with polar ice sheets at this time (Pohl et al., 2016).

The Silurian to Pennsylvanian (410–330 Ma) $\delta^{13}C$ record from pedogenic carbonate shows a systematic decline (from $-5‰$ to $-7‰$), while atmospheric $\delta^{13}C$ arguably increased (Mora et al., 1996). This trend was used to argue for a smaller atmospheric contribution into pedogenetic carbonate, consistent with theoretical predictions for a 10-fold decline in atmospheric CO_2 (Berner, 1991). However, the pedogenic carbonate CO_2 proxy carries large uncertainty, since the CO_2 level inside soils varies dramatically, for example there is $> 8‰$ geographical variability in Neogene soils grown at the same atmospheric CO_2 level (Rugenstein et al., 2016). As soils developed and could receive more organic litter, the proportion of CO_2 derived from soil respiration might have also increased and contributed to the $\delta^{13}C$ decline in pedogenic carbonate. Therefore, it is risky to infer atmospheric pCO_2 estimate until the paleosol record encompasses the spatial variability.

6.1.3.2. Stomatal proxies.
The stomatal density (SD) and ratio of stomatal to epidermis cells (stomatal index, SI) are inversely correlated to ambient CO_2 levels in 40% and 36% of controlled experimental studies, respectively. Notably, the correlation is more often observed in experiments carried out at sub-ambient CO_2 levels (Royer, 2001). The stomatal proxies for paleoatmospheric CO_2 levels have also been "calibrated" in the past based on atmospheric CO_2 levels inferred in other ways; e.g. the GEOCARB models. Yet, this logic becomes circular for the mid-Paleozoic, where there are no robust calibration points for atmospheric CO_2. Nevertheless, Early Devonian plant fossils (*Sawdonia* and *Aglaophyton* major) are found with 10–100 fold lower SD and SI values compared to their nearest living equivalent (NLE) (McElwain and Chaloner, 1996). To survive with only ~4 stomata per mm^2, McElwain and Chaloner inferred high CO_2 levels of 3600 ppm (12 PAL) in the Early Devonian atmosphere (~410 Ma).

The paleo-CO_2 estimates based on stomatal proxies and pedogenic carbonate suggest a decline in the Devonian (410–360 Ma) to ~300–500 ppm for the Carboniferous (360–298 Ma) (Foster et al., 2017). There is no difference between the Mississippian and the Pennsylvanian CO_2 levels or surface seawater temperatures (see below), despite coal deposition was ~7 fold more widespread in the second half of the Carboniferous (Nelsen et al., 2016). This indicates that coal deposition was likely never the main driver of atmospheric CO_2 decline. That said, other terrestrial or marine organic carbon deposits might have drawn down atmospheric CO_2 (e.g. D'Antonio et al., 2019).

6.1.4. Glaciations

Initially, the Late Paleozoic Ice Age was a key piece of evidence in support of the Devonian Cooling Hypothesis. The transition from greenhouse to permanent ice house conditions on Earth was thought to occur in the Late Devonian (~360 Ma) in the wake of deeply rooted plants (e.g. *Archaeopteris*) colonizing well-drained upland soils (Berner et al., 1998). However, the interpretation of the Late Devonian glacial deposits is now different. Indeed, there are short-lived glaciated events near the Devonian-Carboniferous boundary and in the earliest Mississippian that were initiated in alpine regions on Western Gondwana, and developed extended ice volumes (Brezinski et al., 2010). Yet, the main phase of the Late Paleozoic Ice Age occurred significantly later from the Pennsylvanian to the Early Permian (330–275 Ma) (Isbell et al., 2003; Montañez and Poulsen, 2013). The Late Paleozoic Ice Age has both been linked to the Carboniferous-Permian invasions of drier upland areas by seed plants (Algeo et al., 1995; Algeo and Scheckler, 1998), and the Hercynian orogeny, which increased physical weathering and removed a thick soil cover that could have previously limited silicate weathering (Goddéris et al., 2017).

Polar glaciations occurred already in the Late Ordovician and this has challenged the Devonian cooling hypothesis and questioned the high CO_2 estimates in the Late Ordovician. Although, still debated, recent climate models for the Late Ordovician have shown that continental ice sheets could actually persist even in a relatively warm climate at elevated atmospheric CO_2 levels, 3000–3600 ppm (10–16 PAL; Pohl et al., 2016). Further, the COPSE model has been revised to suggest a two-step cooling and concomitant CO_2 drawdown compatible with the glacial record (Lenton et al., 2016).

6.2. Evidence for mid-Paleozoic oxygenation

Over Earth history, atmospheric O_2 levels have increased in concert with overall larger organic carbon burial pool in the crust (Berner, 1987; Berner and Canfield, 1989). Further, model simulations using the GEOCARBSULF framework predicted a massive increase in organic carbon burial and atmospheric O_2 during the Permian-Carboniferous (Berner, 2006). Supporting evidence came from the carbon isotope record of marine carbonates and increase in global sedimentation rates (Berner, 1987, 2000; Berner and Canfield, 1989). At that time the $\delta^{13}C$ record showed a large shift (0 to $+6‰$) to permanently high values for

the last third of the Paleozoic, ~360–250 Ma (Berner, 1987) implying sustained high organic carbon burial rates at the global scale and massive atmospheric O_2 increase. This record has now been updated (Fig. 1) and the interval with high $\delta^{13}C$ values is much shorter (~360–350 Ma; Chen et al., 2018), implying a smaller rise of O_2 from organic carbon burial than first thought.

6.2.1. Constraints on atmospheric oxygenation

Several attempts have been made to infer past atmospheric O_2 levels from gas inclusions in geological materials, including amber and evaporites (Berner and Landis, 1988; Blamey and Brand, 2019). The interpretation of these data has been ambiguous due to concerns regarding preservation and risk of contamination. Two lines of indirect evidence for high (> 75%PAL) or ultrahigh (> 125%PAL) atmospheric O_2 levels since the Late 420 Ma and in the Permo-Carboniferous have gained a lot of attention: gigantism and wildfire.

6.2.1.1. Gigantism. The peak of the GEOCARB-predicted Permo-carboniferous atmospheric O_2 rise coincides with the time when gigantism prevailed among insects and other arthropods (Berner, 2000; Dudley, 1998). This is compelling because insect body size scales positively with ambient O_2 levels in some controlled growth experiments. Nevertheless, the maximum body size of these arthropods may not have been O_2 limited at all. The physiological design and the plasticity of oxygen uptake mechanisms greatly influences the O_2 supply into the animal body. Further, the absence of large flying predators at this time (i.e. birds) imply that gigantic insect would have had no competitors in this niche. Hence, there are alternative explanations for gigantism at this time, irrespective of the atmospheric O_2 level (Clapham and Karr, 2012; Dudley, 1998; Schachat et al., 2018).

6.2.1.2. Wildfire, charcoal, inertinite. Perhaps the strongest argument for high atmospheric O_2 levels in the past 420 Myr is the evidence for wildfire, preserved in the fossil record of charcoal. One maceral group (inertinite) is almost exclusively considered the by-product of wildfire (Glasspool and Scott, 2010). Flames can be sustained at a high atmospheric O_2/N_2 ratio corresponding to an atmospheric O_2 pressure of 15 atm% or 75%PAL, or higher depending on moisture content of the fuel (Belcher and McElwain, 2008). All terrestrial vegetation is potential fuel and ignition would have occurred by lightning. The earliest charcoal represents material from a vascular rhyniophyte-grade plant that was mainly charred for a short period of time at relatively low temperature (< 400 °C). The charcoal record is essentially continuous since the Late Silurian ~420 Ma (Ludlow) suggesting atmospheric O_2 levels have been in the 'fire window' ever since (Glasspool et al., 2004; Glasspool and Scott, 2010; Lenton et al., 2016).

Glasspool and Scott (2010) suggested that the fraction of inertinite in charcoal (inertinite%) can be used in a statistical manner to derive atmospheric pO_2 levels. To do so, they calibrated this proxy with atmospheric pO_2 constraints from the GEOCARB model and derived Phanerozoic atmospheric pO_2 variations between 15 and 30 atm% (75–150%PAL). Substantial scatter in inertinite% (10–80%) implies that other factors than atmospheric O_2 influence this proxy. Hence, it remains a challenge to eliminate biases in this record.

6.2.1.3. Agile predatory fish. The Silurian–Devonian emergence of large predatory fish (> 1 m) has been linked to rising atmospheric O_2 levels above ~40%PAL (Choo et al., 2014; Dahl et al., 2010; Dahl and Hammarlund, 2011). Fish are among the most sensitive marine animals towards low O_2 concentrations in seawater, and active swimmers stop growing and metabolizing at lower O_2 levels. Specifically, the O_2 demand for active swimmers increases more steeply with body size than does O_2 uptake through the gill area (Dahl and Hammarlund, 2011). Therefore, the presence of large agile predators may also put a lower limit on atmospheric O_2 levels. Nevertheless, the physiological design of the oxygen uptake mechanism matters greatly, and large fish might alternatively have survived at low ambient O_2 levels if they had slightly thinner gills with shorter O_2 diffusion distance and thus faster O_2 uptake (Dahl and Hammarlund, 2011).

6.2.2. Oceanic oxygenation

The mid-Paleozoic transition also involved major change to the oxygenation state of the oceans. This is clear from the abundance of organic-rich shales in the Cambrian-Silurian (Berry and Wilde, 1978; Leggett, 1980), the ratio of pyrite to organic carbon in shales (Berner and Raiswell, 1983), models for the marine sulfur isotopic record (Berner and Raiswell, 1983; Gill et al., 2007; Halevy et al., 2012), as well as ocean redox proxies sensitive to either the immediately overlying bottom waters in the shallow ocean (Sperling et al., 2015; Wallace et al., 2017), the deep ocean (Stolper and Keller, 2018) or at the globally-integrated scale (Dahl et al., 2010; Kendall et al., 2017).

It is predicted that atmospheric O_2 levels have to exceed > 50%PAL in order to oxygenate the deep oceans at the modern oceanic O_2 consumption and P availability (Canfield, 1998). Based on this transition, geochemical proxies have been developed to constrain when the deep oceans transited into a fully oxygenated state. The molybdenum isotope record from euxinic shales suggests a substantially oxygenated deep ocean from the mid-Devonian onwards (Dahl et al., 2010; Kendall et al., 2017). The molybdenum isotope composition of seawater is particularly sensitive to burial of Mn-oxides that occur slowly and over vast areas in the abyssal ocean. The Mo isotope signal is well-mixed in the oceans due to the oceanic long residence time of Mo relative to ocean mixing time (~400 kyr vs. 1 kyr). This characteristic of a "global tracer" allows the isotope signal from the oxygenated deep ocean to also be recorded in shallow settings on the continental shelves, including euxinic mudrocks. One major challenge for this proxy is, however, that continental shelf sediments rarely record seawater directly, but carries a negative $\delta^{98}Mo$ offset relative to contemporaneous seawater. Nevertheless, the record suggests more oxygenated ocean conditions in the mid-Devonian (~390 Ma) compared to the Late Ordovician/earliest Silurian (~440 Ma). This trend has been linked to emergence of land plants with higher C/P ratio than marine biomass in support of the COPSE model (Dahl et al., 2010; Lenton et al., 2016).

Ongoing efforts seeking to establish other methods to extract global-scale information on ocean oxygenation focus on independent redox-sensitive elements, such as uranium, vanadium, rhenium and thallium isotopes. The long-term records are still under construction, but some of these systems have already demonstrated shorter periods of expanding marine anoxia and recovery (Bowman et al., 2019; White et al., 2018; Zhang et al., 2020; Cheng et al., 2020).

6.3. Evidence for oceanic fertilization and anoxia in the mid-Paleozoic

The colonization of land by plants could well have enhanced weathering and oceanic P input. This concept was originally proposed as explanation for the two episodes of marine extinctions near the Frasnian-Famennian (F−F) boundary, where anoxia developed in relatively shallow water roughly at the same time as forests spread on the continents (Algeo et al., 1995; Algeo and Scheckler, 1998).

The FF-boundary still constitutes the prime example of a terrestrial-marine teleconnection, where evolving vegetation on land set the stage for a biotic crisis in the ocean (Algeo and Scheckler, 1998). Several other events have been investigated with the same hypothesis in mind, including the Late Ordovician 'HICE' event (Hammarlund et al., 2012), the Late Silurian 'Lau' event (Bowman et al., 2019), the end-Devonian 'Hangenberg' event (Zhang et al., 2020) and the Early Mississippian 'TICE' event (Cheng et al., 2020). All of these are associated with positive carbon isotope excursion that might indicate enhanced organic carbon burial (Fig. 1). Yet, it slowly becomes clear that each of the events have unique biogeochemical affinities, as we will briefly discuss below.

The Late Ordovician extinction crises (~445–440 Ma) hit in two strikes during the onset of the Hirnantian glaciation and during subsequent transgression (e.g., Hammarlund et al., 2012). The first phase coincides with ~5 °C cooling recorded in conodonts from tropical seawater (Finnegan et al., 2011). The driving mechanism for cooling is debated, and enhanced organic carbon burial associated with ocean fertilization and/or enhanced silicate weathering promoted by nonvascular land plants are candidate hypotheses (Hammarlund et al., 2012; Lenton et al., 2012). A recent lithium isotope study suggests silicate weathering actually declined and instead ascribe the driver for cooling and CO_2 decline to lower rates of volcanic outgassing (Pogge von Strandmann et al., 2017). In this scheme, land plants may have played only a subordinate role on animal extinctions at this time.

The Late Silurian Lau-Kozlowskii event (~424–423 Ma) marks an extinction event followed by a large positive carbon isotope excursion (Fig. 1). New thallium isotope data demonstrates that the Lau extinction event was associated with an expansion of marine anoxia (Bowman et al., 2019). At this time, there is a sudden appearance of trilete spores in Baltica indicative of vascular plants (Wellman et al., 2013). There is no evidence for extensive black shale deposition or organic carbon burial during the extinction horizon, and the positive carbon isotope excursion occurred in the aftermath of the biotic crisis and oceanic anoxic event. Therefore, the carbon isotope excursion was likely driven by other factors, e.g. changes in ocean circulation, carbonate weathering and/or carbonate precipitation in the oceans (Farkaš et al., 2016).

The Frasnian-Famennian extinction events (~376–371 Ma) may have been caused by invasion of new flora. Oxygen isotopes in conodonts suggest a rapid cooling occurred in two strikes where surface seawater at low latitudes suddenly decreased (-3 °C and -6 °C) during the lower and upper Kellwasser events, respectively (Huang et al., 2018). At both occasions there is evidence for enhanced marine organic carbon burial and black shale deposition in shallower settings over wide areas in North America and southern Europe (Buggisch, 1991; Song et al., 2017; White et al., 2018). The expansion of anoxic water masses is clear during the upper Kellwasser event and is also recorded in the uranium isotope composition of marine carbonates, except for a short period during the peak of the extinction (White et al., 2018). The simultaneous oceanic cooling and expanding ocean anoxia at the global scale is diagnostic of enhanced marine O_2 consumption, which readily points to enhanced P input to the ocean. Temporally, the Frasnian-Famennian events overlaps with the peak abundance of progymnosperm forests and predate by a few million years the first fossil appearance of seed plants, e.g. *Elkinsia*, (Rothwell et al., 1989; Algeo and Scheckler, 1998; Myrow et al., 2014; Wan et al., 2019). In all cases, we still lack a process-based understanding that would link land plant evolution to enhanced P delivery to the oceans at this time.

The Late Famennian Hangenberg event (~360 Ma) resembles another major extinction event, which has a positive carbon isotope excursion recorded globally (Kaiser et al., 2016; Kaiser et al., 2011). Further, there is evidence for cooling and a dramatic ~100 m sea level drop. There is also evidence for expansive anoxic water masses at this time (Marynowski and Filipiak, 2007; Zhang et al., 2020), and the event coincides closely with the first appearance of seed plants that have been argued to enhance weathering in drier upland areas (Rothwell et al., 1989; Algeo and Scheckler, 1998; Wan et al., 2019). A simple parametric Earth system model fits roughly the overall isotope trajectories observed in one setting (Zhang et al., 2020), but more data from other parts of the ocean is necessary to decipher the timing of cooling, organic carbon burial and marine anoxia.

The Early Mississippian TICE event (~354–352 Ma) represents a + 5–7‰ positive carbon isotope excursion recorded in carbonates worldwide (Saltzman et al., 2004; Yao et al., 2015). The event coincides with onset of a longer-term cooling period (Fig. 10). Expansive marine anoxia and greater organic carbon burial has also been reported during the event (Cheng et al., 2020). Overall, the TICE event could have been triggered by enhanced P input from the continents that would have fueled marine productivity and organic export to deeper waters, resulting in expansive marine anoxia and organic matter burial in sediments. Moreover, it overlaps with the appearance of new seed plants on the continents (*Genselia, Rhodeopteridium*) (Wan et al., 2019). Hence, the event may have been linked to land plant evolution, and it also correlates with the Antler orogenic event (Saltzman et al., 2000).

7. Conclusion and outlook

Previous research has emphasized the role of early Ordovician bryophytes and/or late Devonian forests in climatic cooling and atmospheric oxygen rise during the mid-Paleozoic. Here, we advocate for an integrated view on the whole Paleozoic transition (Le Hir et al., 2011), by recognizing the evolutionary stages that brought the terrestrial ecosystems from simple cryptogamic covers to forested continental interiors by the spread of seed plants.

There is compelling evidence that surface temperatures declined, sea level increased, and the oceans became slowly more oxygenated during the mid-Paleozoic. Land plants are thought to have intensified CO_2 removal via silicate weathering, but we lack a mechanistic understanding of how the individual terrestrial ecosystems affected the Earth system. In our view the mid-Paleozoic colonization of land involved five major ecological transitions that each may have altered Earth's climate and oxygenation state:

1. The Ordovician colonization of non-vascular plants (~ 515–470 Ma)

Early embryophytes could potentially have covered a large part of the land surface, but had small impacts on soil carbon, water balance, and mud retention. Nevertheless, these plants could have influenced oceanic P input driving atmospheric oxygenation. Current isotope records suggest the Late Ordovician cooling were triggered by geologic drivers, thereby allocating a secondary role of early non-vascular plants on climate regulation, but there is still no consensus on this matter.

2. The Silurian rise of ground-hugging vascular plants (430–410 Ma)

The abundance of trilete spores characteristic of vascular plants suggest lignified plants became ecologically important at this time. Yet, there is no evidence of long-term cooling trend throughout the Silurian. In fact, the paleotemperature record suggests the Silurian-Devonian was warmer than the Ordovician. Nevertheless, the Silurian record reveals a series of shorter (< 1 Myr) cooling events that each may represent evolution and spread of vascular plants.

3. The rise of vascular plants with shallow root systems (~410–390 Ma)

Vascular plants evolved simple and shallow root systems and the first coal deposits are from this time (Nelsen et al., 2016). The rock record reveals the impacts of shallow roots on river bank stability, through emerging meandering rivers with increased alluvial mud retention. Shallow root systems changed the carbon input to soils by bringing litter and respiration underground. How these shallow ecosystems affected soil formation and atmospheric CO_2 and O_2 are presently unresolved.

4. Colonization of arborescent trees with deep root systems (~390–370 Ma)

The emergence of trees (progymnosperms) with deep branching roots and rootlets has been linked to climatic cooling by enhanced weathering. This could have been a driver of Frasnian-Fammenian oceanic anoxic events, although this still warrants a better understanding of the evolving weathering processes on land (Algeo et al.,

1995; Algeo and Scheckler, 1998). Perhaps, the emergence of deep root systems enhanced the overall weathering rate compared to earlier shallow vegetation (Fig. 7). Yet, it is not clear that deep root system could have forever increased the silicate weathering efficiency, especially not if vegetation was restricted to shallow wetlands, where silicate weathering was mainly limited in mineral-supply. Also, the paleorecords suggest the long-term cooling (presumably CO_2 drawdown) and glaciation occurred well into the Carboniferous long after the emergence of *Archaeopteris* forests and during the subsequent early evolution of seed plants.

5. The rise of seed plants in the latest Devonian and Carboniferous (~355–320 Ma)

It has been argued that the emergence of seed plants led to invasion of areas that were previously too dry for sporophytes. The geographical extent of terrestrial vegetation is still poorly constrained during the mid-Paleozoic transitions, and better constraints from the fossil record and climate-ecosystem models are needed. Land plants on steep hill slopes are thought to stabilize soils and limit erosion. However, the record of North American sedimentary rock volume indicates that erosion is primarily linked to orogenesis (~x4) and that plants play a minor role on long-term erosion rates.

In this review, we have outlined a series of factors by which the evolving terrestrial ecosystems contributed to the regulation of atmospheric oxygen and Earth's climate. Future research must address how each of these ecological transitions affected the Earth system by using an integrated framework that bridges process-driven models with observations in the rock record. This should help us identify why some transitions led to cooling and oxygenation – and others did not.

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Author contributions

TWD designed the research; Both authors contributed to the discussions and wrote the paper.

Data and materials availability

Where not tabulated or stated in the text, data were measured from graphics by pasting the image into Adobe Illustrator and overlaying guidelines to obtain exact measurements of data point positions.

Declaration of competing interest

The authors declare that they have no competing interests.

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