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Earliest land plants created modern levels of atmospheric oxygen

Timothy M. Lenton[1]*, Tais W. Dahl[2], Stuart J. Daines[1], Benjamin J. W. Mills[1,3], Kazumi Ozaki[4], Matthew R. Saltzman[5], Philipp Porada[6]

[1]Earth System Science, College of Life and Environmental Sciences, University of Exeter, Exeter EX4 4QE, UK. [2]Natural History Museum of Denmark, Øster Voldgade 5-7, Copenhagen, Denmark. [3]School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK. [4]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, GA 30332-0340, USA. [5]School of Earth Sciences, The Ohio State University, Columbus, Ohio 43214, USA. [6] Department of Environmental Science and Analytical Chemistry, Stockholm University, Svante Arrhenius väg 8, SE-114 18 Stockholm, Sweden.

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The progressive oxygenation of the Earth's atmosphere was pivotal to the evolution of life, but the puzzle of when and how atmospheric oxygen (O_2) first approached modern levels (∼21%) remains unresolved. Redox proxy data indicate the deep oceans were oxygenated during 435-392 Ma, and the appearance of fossil charcoal indicates O_2>15-17% by 420-400 Ma. However, existing models have failed to predict oxygenation at this time. Here we show that the earliest plants, which colonized the land surface from ∼470 Ma onwards, were responsible for this mid-Paleozoic oxygenation event, through greatly increasing global organic carbon burial – the net long-term source of O_2. We use a trait-based ecophysiological model to predict that cryptogamic vegetation cover could have achieved ∼30% of today's global terrestrial net primary productivity by ∼445 Ma. Data from modern bryophytes suggests this plentiful early plant material had a much higher molar C:P ratio (∼2000) than marine biomass (∼100), such that a given weathering flux of phosphorus could support more organic carbon burial. Furthermore, recent experiments suggest that early plants selectively increased the flux of phosphorus (relative to alkalinity) weathered from rocks. Combining these effects in a model of long-term biogeochemical cycling, we reproduce a sustained +2‰ increase in the carbonate carbon isotope ($\delta^{13}C$) record by ∼445 Ma, and predict a corresponding rise in O_2 to present levels by 420-400 Ma, consistent with geochemical data. This oxygen rise represents a permanent shift in regulatory regime to one where fire-mediated negative feedbacks on organic carbon burial stabilise high O_2 levels.

oxygen | plants | Paleozoic | phosphorus | weathering

Introduction

After the well-defined 'Great Oxidation Event' 2.45-2.32 Ga, the trajectory of atmospheric oxygen is deeply uncertain (1, 2). Many recent studies, reviewed in (3-5), have argued for a Neoproterozoic oxygenation event (>550 Ma) – of uncertain cause – and have linked it to the rise of animals, but this has been questioned given a lack of change in iron-speciation ocean redox proxy data (6). Some models predict pO_2 ∼1 PAL (present atmospheric level) already in the early Paleozoic (7, 8), but this is at odds with data for widespread ocean anoxia (6, 9). The 'COPSE' model we adapt here (10) predicts early Paleozoic pO_2 ∼0.2-0.5 PAL consistent with redox proxy data, but like the other models (7, 8) it does not predict a rise in oxygen until the advent of forests starting ∼385 Ma, and continuing until ∼300 Ma. This is too late to explain marked changes in geochemical data that occur before ∼390 Ma (figure 1). The first appearance of fossil charcoal in the late Silurian (11) and its ongoing occurrence through the Devonian (12) (table S1), albeit rare and at low concentrations, indicates O_2>15-17% (by volume) of the atmosphere (13) (or O_2>∼0.7 PAL assuming a constant N_2 reservoir) already by ∼420-400 Ma. (Under ideal conditions of ultra-dry fuel and forced airflow, smoldering fires may be sustained at O_2>10%, but this is not believed to be possible under natural conditions (14)). The molybdenum isotope record (9) indicates a fundamental shift in the redox state of the deep ocean from widespread anoxia to widespread oxygenation sometime during 435-392 Ma (between the early Silurian and the mid-Devonian). This ocean oxygenation is also supported by a Silurian increase in the C/S ratio of shales (15), and a shift in iron-speciation data sometime during 435-387 Ma (6).

The persistent oxygenation of the ocean and appearance of charcoal can be explained by a rise in atmospheric oxygen occurring by ∼400 Ma. This could be due to a persistent increase in oxygen source – considered here – or a decrease in oxygen sink (16), leading to a reorganization of the Earth's surface redox balance at a higher steady-state level for atmospheric O_2. The major long-term source of oxygen to the atmosphere is the burial of organic carbon in sedimentary rocks (which represents the net flux of photosynthesis minus various pathways of respiration and oxidation). Increases in global organic carbon burial are recorded as positive shifts in the isotopic composition of carbonate rocks ($\delta^{13}C$). Consistent with a rise in oxygen, the carbon isotope record (17) (figure 1) indicates a fundamental shift in baseline from ≤0‰ prior to the Late Ordovician to ∼2‰ from ∼445 Ma onwards. Whilst there are many subsequent $\delta^{13}C$ fluctuations, including drops back to 0‰, e.g. at ∼400 Ma, the long-term mean $\delta^{13}C$ remains ∼2‰ throughout the rest of the Paleozoic, the Mesozoic, and the early Cenozoic (17), indicating a sustained increase in

Significance

The rise of atmospheric oxygen over Earth history has received much recent interdisciplinary attention. However, the puzzle of when and how atmospheric oxygen reached modern levels remains unresolved. Many recent studies have argued for a major oxygenation event - of uncertain cause - in the Neoproterozoic Era >541 million years ago (Ma), enabling the rise of animals. Previous modelling work has predicted a late Paleozoic oxygen rise (<380 Ma) due to the rise of forests. Here we show that neither scenario is correct. Instead the earliest plants, which colonized the land from 470 Ma onwards, first increased atmospheric oxygen to present levels by 400 Ma. This instigated fire-mediated feedbacks that have stabilised high oxygen levels ever since, shaping subsequent evolution.

Reserved for Publication Footnotes

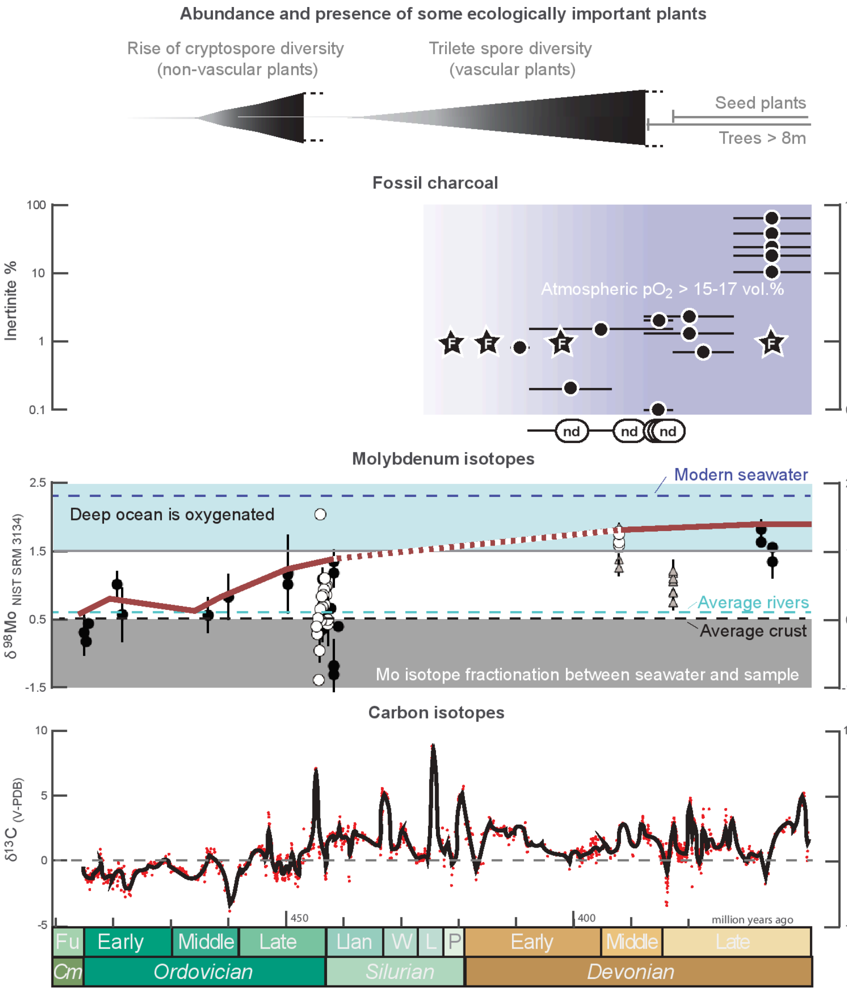

Fig. 1. . Global changes during the Ordovician, Silurian, and Devonian Periods. The rise of non-vascular plants (indicated by cryptospore diversity (32)) then vascular plants (indicated by trilete spore diversity (18)) overlaps with the first appearances of fossil charcoal (table S1); F = fossils, black dots = inertinite in coal, nd = none detected. Molybdenum isotope data (9) indicate oxygenation of the deep ocean, following an uncertain trajectory ~440-390 Ma; black circles = euxinic shales as defined by Fe-speciation, white circles = euxinic shales as defined by Mo-enrichment, grey triangles = ferruginous shales as defined by Fe-speciation, blue area = isotope offset from oceanic input that requires a substantial Mn-oxide sink in the deep oceans. The carbonate carbon isotope record (17) (red dots, black line is a smoothed spline fit) indicates elevated organic carbon burial ($\delta^{13}C$ ~2‰) ~445-410 Ma. Cm=Cambrian, Fu=Furongian, Llan=Llandovery, W=Wenlock, L=Ludlow, P=Pridoli.

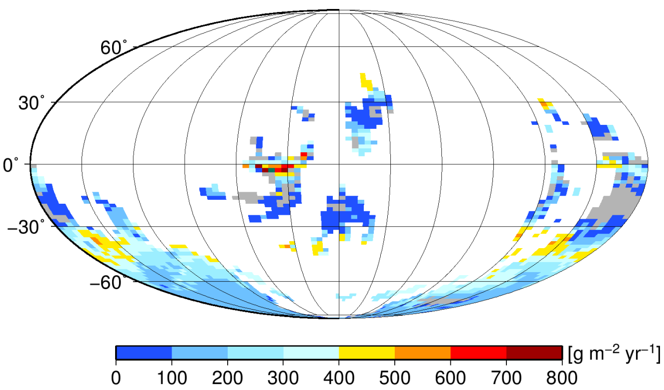

Fig. 2. Predicted Late Ordovician (445 Ma) net primary production (NPP). Result from ecophysiological model of cryptogamic vegetation cover driven by simulated Late Ordovician (445 Ma) climate, atmospheric CO_2 = 8 PAL, and atmospheric O_2 = 0.6 PAL (14 vol.%), with no ice sheet mask. Simulated global NPP = 18.7 GtC yr^{-1}.

global organic carbon burial. Such a permanent shift requires a unidirectional driver that kicked-in during the mid-Paleozoic. The evolution of land plants is the obvious candidate, with the first non-vascular plants (ancestors of extant mosses, liverworts and hornworts) colonizing the land in the Mid-Late Ordovician (~470-445 Ma), followed by the first vascular plants in the Silurian (~445-420 Ma) and early Devonian (~420-390 Ma) (figure 1) (18, 19).

Here we hypothesize that the evolution of these earliest land plants permanently increased organic carbon burial causing atmospheric oxygen to approach modern levels by ~400 Ma, and creating a new dynamically stable steady state for the oxygen cycle (where the major long-term O_2 sink from oxidative weathering of ancient organic carbon increased to counterbalance the increased O_2 source). In simple terms, on long timescales, the global organic carbon burial flux is determined by the supply flux of the ultimate limiting nutrient phosphorus from weathering and the (molar) ratio of carbon-to-phosphorus in material that is buried:

$$\text{P weathering flux} \times C_{organic}/P_{total} \text{ burial ratio} = C_{organic} \text{ burial flux}$$

Land plants typically have a much higher molar C/P ratio (~1000) than marine organic matter (~100) due to carbon-rich but phosphorus-poor structural compounds such as sporopollenin, lignin and, in their fungal mycorrhizal symbionts, chitin. Therefore they can support an increased organic carbon burial flux for the same P weathering flux. The P weathering flux is partly tied to bulk silicate weathering, e.g. due to the dissolution of apatite inclusions in silicate rocks, and the silicate weathering flux of alkalinity is in turn set by negative feedback in the long-term carbon cycle, so is ultimately controlled by the degassing input of CO_2 on timescales ≥1 Myr (7, 10). However, plants and their associated mycorrhizal fungi can increase phosphorus weathering

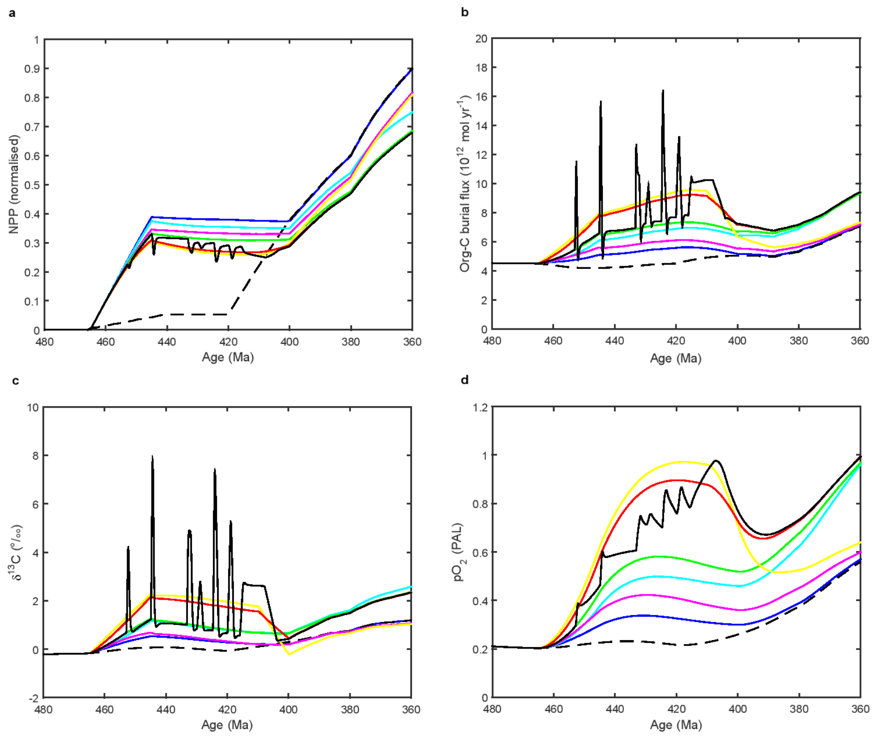

Fig. 3. Predictions of mid-Paleozoic global carbon cycle change due to early plants from the updated COPSE model: **a.** Net primary production (NPP); **b.** Organic carbon burial (both terrestrial and marine derived material); **c.** Carbonate carbon isotope record ($\delta^{13}C$); **d.** Atmospheric O_2. Note that fossil charcoal 420-400 Ma indicates O_2 > 0.66-0.77 PAL. (Further results of the same model runs are in figures S3 and S5.) Black dashed = original baseline model run. Blue = early plant colonization (C/P=1000). Cyan = early plant colonization + C/P=2000. Magenta = early plant colonization + biotic effects on silicate weathering (C/P=1000). Green = early plant colonization + C/P=2000 + biotic effects on silicate weathering. Yellow = early plant colonization + biotic effects on silicate weathering + 50% increase in P weathering. Red = early plant colonization + C/P=2000 + biotic effects on silicate weathering + 25% increase in P weathering. Black = early plant colonization + C/P=2000 + biotic effects on silicate weathering + spikes of P weathering.

(20-22), and this could be sustained on longer timescales if they preferentially weather phosphorus relative to alkalinity.

In existing models, the evolution of trees starting ~385 Ma is assumed to have led to the burial of high C/P organic material in coal swamps (7, 8, 10), potentially augmented by increased phosphorus weathering rates (10). The Carboniferous-Permian peak in coal production has often been attributed to the evolution of lignin synthesis and a lag before the evolution of fungal degradation of lignin (23), but recent work has questioned this (24). Earlier plants possessed lignified 'woody' tissue (25), with precursor structures existing in marine algae before the transition to land (26), and lignin-degrading fungi potentially present before the Carboniferous (24). Carboniferous coals are not dominated by lignin, instead their accumulation was controlled by a combination of climate and tectonics supporting the creation and sedimentary preservation of peat bogs (24, 27). Given that earlier plants developed peatlands (28), and had rock weathering capabilities (20, 21), they could also have affected the global carbon cycle (18, 20).

Results and discussion

To test our hypothesis we revised the COPSE biogeochemical model (10) to better capture the early rise of plants and examine under what conditions it could explain the geochemical data (persistent rise to $\delta^{13}C$ ~2‰ and the appearance of charcoal). The original baseline model (10) predicts early Paleozoic O_2 ~0.23 PAL at a reference time of 445 Ma, supported by an organic carbon burial flux of ~4×10^{12} mol yr^{-1} (about half the present day value) with $\delta^{13}C$ = 0.03‰. In this stable state, oxidative weathering of ancient organic carbon is correspondingly reduced and its sensitivity to changes in O_2 provides a key negative feedback stabilizing O_2. Key assumptions going into altering the forcing of the model are the global extent and associated productivity of early plants, the C/P ratio of plant material that was buried, and their effect (if any) on phosphorus weathering. To help parameterize these factors we drew on a mixture of experiments, existing data, and more detailed spatial modelling.

We used a trait-based spatial model of cryptogamic vegetation (i.e. bryophyte and lichen) cover (29, 30) driven by Late Ordovician climate simulations (31) at different atmospheric CO_2 levels to predict the potential global net primary productivity (NPP) of the early plant biosphere (32). At atmospheric CO_2 = 8 PAL, consistent with Late Ordovician glaciations (20), predicted global NPP is ~19 GtC yr^{-1} (figure 2), ~30% of today. Predicted NPP is sensitive to variations in CO_2 and climate (figure S1), ice sheet cover (figure S2), and O_2 (table S2), but is consistently higher than the 4.3 GtC yr^{-1} (7% of today) estimated elsewhere (33). In the original COPSE model (10), predicted NPP only reaches ~5% of today's value in the Late Ordovician and Silurian, but when we assume a stronger late Ordovician phase of land colonization by non-vascular plants (following (20), see SI), then COPSE predicts global NPP 30-40% of today (figure 3a), consistent with the detailed spatial model. In COPSE, this advent of early land plants alone, with no assumed effect on weathering fluxes, and assumed C/P=1000, increases total organic carbon burial by ~25%, $\delta^{13}C$ by 0.5‰, and atmospheric O_2 by 0.11 PAL (figure 3, blue).

We undertook a literature review of molar C/P ratios in extant bryophytes (table S3) to test whether C/P=1000 is a reasonable assumption for early plants. This gives a range of C/P=800-4300 with a mean of C/P ~1900. Furthermore, early Devonian coaly shales indicate extensive peatlands 410-400 Ma and have C/N of 44-119 (28), comparable to that in modern peatlands where N/P and C/P ratios tend to increase with depth to C/P >3000 (34). Taken together these data suggest that assuming C/P=1000 for early plants is conservative. If instead we assume that buried early plant matter had C/P=2000, then given their productivity, even with no effect on weathering fluxes, this increases global organic carbon burial by ~50%, $\delta^{13}C$ by 1.1‰ and atmospheric O_2 by 0.27 PAL (figure 3, cyan).

Early plants could also have had a significant effect on weathering fluxes (20), as they and their fungal mycorrhizal symbionts evolved means of accessing rock-bound nutrients, notably phosphorus. Experimental work (20) has shown that a modern non-vascular plant, the moss *Physcomitrella patens* amplifies the weathering of Ca ions 1.4-3.6 fold and Mg ions 1.5-5.4 fold from silicate rocks (granite-andesite), and amplifies the weathering of phosphorus from granite ~24(15-43) fold (see Materials and Methods). Subsequent experiments (21) with the modern liverwort *Marchantia paleacea* found a 2.5-7 fold amplification of Ca weathering and a 9-13 fold amplification of P weathering from basalt. Both studies thus indicate preferential weathering of P relative to Ca and Mg (and corresponding alkalinity). The presence of these rock weathering capabilities in two early-diverging lineages (mosses and liverworts) suggests it is an ancestral trait. It has been argued (21, 33) that such large measured local effects would not have scaled up to significant global effects, because of low global NPP (33) and a limited depth of influence in the soil (21). However, we estimate much higher global NPP (figure 2) and weathering potential (32). We also note that extensive shallow water phosphate deposits in the Late Ordovician (35) indicate a marked increase in phosphorus input to the ocean (20).

If we include in COPSE an effect of early plants on silicate weathering following (20), assuming C/P=1000, this increases organic carbon burial by ~35%, $\delta^{13}C$ by 0.7‰, and O_2 by 0.18 PAL (figure 3, magenta). The effect on O_2 is constrained because atmospheric CO_2 and temperature are reduced (20) such that the silicate weathering flux (and associated phosphorus flux) continues to match the degassing flux of CO_2 (figure S3). However, increases in carbonate weathering (enhanced by plants) and oxidative weathering (due to the rise in O_2) increase the overall phosphorus weathering flux, roughly doubling the O_2 rise due to terrestrial production of high C/P material alone. Assuming that buried early plant matter had a higher C/P=2000 causes larger increases in total organic carbon burial ~60%, $\delta^{13}C$ +1.2‰, and atmospheric O_2 +0.35 PAL (figure 3, green).

However, to reproduce the observed $\delta^{13}C$ +2‰ excursion requires the inclusion of some selective weathering of phosphorus by early plants. Assuming that early plants caused a sustained 50% increase in phosphorus weathering relative to bulk rock dissolution, with C/P=1000, increases total organic carbon burial by ~95%, $\delta^{13}C$ by 2.2‰ and O_2 by 0.74 PAL (to 0.97 PAL at 417 Ma) (figure 3, yellow). Assuming a sustained 25% increase in phosphorus weathering relative to bulk rock and C/P=2000, increases organic carbon burial by ~90%, $\delta^{13}C$ by 2.1‰ and O_2 by 0.67 PAL (figure 3, red). Alternatively, a series of P weathering spikes designed to reproduce the observed sequence of positive $\delta^{13}C$ excursions (figure 1), combined with C/P=2000, produces a series of spikes in organic carbon burial and a peak increase of O_2 of 0.72 PAL at 407 Ma (figure 3, black). We hypothesize that these assumed weathering spikes could reflect phases of plant colonization (20, 36) followed by the establishment of phosphorus recycling ecosystems (20). However, direct evidence linking a phase of land colonization to enhanced weathering and a positive $\delta^{13}C$ excursion has only thus far been established for the Silurian-Devonian boundary excursion (36). Therefore alternative hypotheses for short-lived positive $\delta^{13}C$ excursions should also be considered.

Regarding the simulated long-term ~2‰ rise in $\delta^{13}C$ this is smaller than would be expected from standard application of the simplified formula: $\delta^{13}C(\text{ocean}) = \delta^{13}C(\text{river}) + f_{\text{org}}\bullet\varepsilon$, where f_{org} is the fraction of carbon buried as organic matter, ε is the fractionation between carbonates and organic matter, and both ε and $\delta^{13}C(\text{river})$ are usually assumed to be constant. In our COPSE simulations there is a fully interactive isotope mass balance and these terms are not constant. The approximate doubling of organic carbon burial (with roughly constant carbonate burial) represents an increase from $f_{\text{org}} = 0.18$ to $f_{\text{org}} = 0.31$. However, the increase in burial of isotopically-light organic carbon is counteracted by an increase in the oxidative weathering of isotopically-light organic carbon, which lowers the $\delta^{13}C$ of riverine input to the ocean from ca. -5‰ to ca. -7.5‰. This in turn is partially counteracted by an increase in fractionation between carbonates and organic matter from $\varepsilon \sim 27$‰ to $\varepsilon \sim 30$‰, due to increasing O_2 (somewhat counteracted by declining CO_2).

Sensitivity analyses (see SI) indicate that our results are robust. Varying the uplift and degassing forcing of the model within plausible bounds only causes ±0.08 PAL variation in O_2 about the initial state (figure S4), although it does cause the effect of the same early plant forcing scenario to range over +0.4-1.0 PAL O_2 (table S4). Including an additional negative feedback on O_2, from increased marine organic C/P burial ratios under anoxic waters (37), increases its initial early Paleozoic level to 0.54 PAL and reduces the effect of the same biological forcing scenarios on O_2 by ~10-30%, giving a maximum increase of +0.63 PAL (table S5). However, because the initial O_2 is now higher, the final O_2 is also higher in all cases, and even scenarios without selective weathering of phosphorus could explain the appearance of charcoal (O_2 >~0.7 PAL).

Our model makes additional predictions that can be tested against geochemical data, notably it predicts a decline in pyrite sulfur burial and associated drop in $\delta^{34}S$ and increase in seawater [SO_4] and C/S burial ratio with the rise of the earliest plants (figure S5). This is broadly consistent with the sulfur isotope ($\delta^{34}S$) record (38-40), which shows a marked decline through the Silurian-early Devonian from ~30‰ to ~18‰, although available data also suggest an earlier late Ordovician-early Silurian rise from ~25‰ to ~30‰, which the present model does not capture. The model is consistent with proxy reconstructions of seawater [SO_4], which suggest an Ordovician-Silurian rise from ~6 mM to ~10 mM (41), and with a Silurian increase in the molar C/S ratio of shales from ~5 to ~16 (15).

Other processes not yet included in the model warrant future consideration, for example the effect of increasing atmospheric mass on climate (42), and the effect of weathering forcing scenarios on δ^7Li and $^{87}Sr/^{86}Sr$, which enable additional tests against data.

Conclusion

Our model can only reproduce Paleozoic geochemical data if the rise of the earliest land plants caused a major oxygenation event of the Earth's atmosphere and oceans by ~400 Ma. We attribute this mid-Paleozoic oxygenation event to a persistent global increase in organic carbon burial supported by the high C/P ratio of early land plant material, augmented by a plant-driven increase in P weathering flux relative to the weathering flux of alkalinity. The $\delta^{13}C$ record suggests this increase in organic carbon burial was essentially permanent, producing a new dynamically stable state for atmospheric O_2. In this new steady state, oxidative weathering was increased (becoming less sensitive to variations in O_2) and new fire-mediated negative feedbacks on O_2 were instigated that have played a key role in stabilising atmospheric O_2 concentration up to the present day (22, 43). For the earliest land plants to be responsible for such a major mid-Paleozoic oxygenation event requires that they were much more productive and globally extensive than has been previously assumed (7, 10, 33). This hypothesis makes testable predictions with regard to effects on other biogeochemical cycles, notably sulfur. If it stands up to further scrutiny, then we can infer that the earliest land plants created a stable oxygen-rich atmosphere that was necessary for the subsequent evolution of large, mobile, intelligent animals with a high respiratory oxygen demand – including ourselves.

Materials and Methods:

Data compilation: The early charcoal record (table S1) was compiled from the literature (11, 12, 28, 44-72), utilizing existing compilations (12, 44-47) and checking them where possible against the original sources. This involved some reconciling of disparate results between existing compilations and revision of some erroneous quoted values. Where recalculations were warranted, inertinite percentages were calculated on a mineral-matter-free (mmf) basis, following (45, 47).

The molybdenum isotope record from marine shales was updated from (9) with data from (73, 74). Uncertainties shown in figure 1 represent 2 standard deviation of the mean (analytical precision) plus the propagated uncertainty from matching in-house reference materials to the universal standard NIST SRM 3136 where seawater display $\delta^{98/95}Mo = 2.3‰$ (see (75, 76)). The redox state of the host shales was determined using either Fe-speciation or Mo-enrichment proxies. Euxinic shales are defined (77) by the Fe-speciation proxy when FeHR/FeT > 0.38 and FeP/FeHR > 0.7 (black circles in figure 1). Euxinic shales are defined (78, 79) by the Mo enrichment proxy when Mo > 25 ppm (white circles in figure 1). Ferruginous shales (77) are defined by the Fe speciation proxy when FeHR/FeT > 0.38 and FeP/FeHR < 0.7.

The carbon isotope record (17) was fitted with a smoothed spline function in Matlab; spline = csaps(age, $\delta^{13}C$, rho), where $\rho = 0.99$ (close to data, but the curve in figure 1 does not go through each data point).

The C/P ratio of extant bryophytes (table S3) was compiled from data in the literature (34, 80-88). Where only values of mg P/g biomass were available, a value of mg C/g biomass = 430 was assumed based on the mean value across 6 bryophyte species from (89). Results for molar C/P ratios are given to 2 significant figures, given the uncertainty in the input data, except where authors themselves provide more precise values.

Ecophysiological model of cryptogamic vegetation: We used a trait-based spatial model of cryptogamic vegetation (i.e. bryophyte and lichen) cover to estimate the potential global net primary productivity (NPP) of the early non-vascular plant biosphere (29, 30). The Late Ordovician (445 Ma, Hirnantian Stage) setup of the model is fully described elsewhere (32). The model is driven by existing Late Ordovician climate simulations (31), conducted at a range of different atmospheric CO_2 and O_2 concentrations. Initially, we assume atmospheric $O_2 = 0.6$ PAL ($\sim$14 vol.%) at 445 Ma, which is consistent with those COPSE model simulations (figure 3d) that go on to produce O_2 levels consistent with the fossil charcoal record. We also initially assume atmospheric $CO_2 = 8$ PAL, which is a widely quoted value consistent with the occurrence of Hirnantian glaciations at 445 Ma (20), and is consistent with those COPSE model simulations that assume an effect of early plants on silicate weathering following (20). We explored the sensitivity of predicted global NPP to variations in atmospheric CO_2 and corresponding climate state (figure S1), to constraining vegetation cover with extensive Late Ordovician ice sheet cover (figure S2), and to varying O_2 in combination with CO_2 (table S2). The relatively high global NPP results obtained are consistent with present day cryptogamic covers providing $\sim$7% of global NPP, despite making up only 1% of terrestrial vegetation by mass (90), and being restricted to relatively resource-poor habitats, whilst also operating in an atmosphere with a low CO_2/O_2 ratio.

Experimental P weathering calculation: In our previously reported (20) weathering experiments with granite, the mean amounts of phosphate weathered into aqueous solution were: control microcosms = 0.0137 μmol P, biotic microcosms = 0.0726 μmol P. The mean moss biomass in the biotic microcosms was 14.390 mg, which assuming 0.43 gC/g biomass and C/P = 2000 (table S3) suggests 0.26 μmol P in biomass, or for C/P = 1000-4000, 0.13-0.52 μmol P in biomass. This gives a biotic P weathering amplification factor $\sim$24 (range 15-43), whereas previously we suggested up to 60 (20). Clearly these estimates are dominated by the unmeasured P content of biomass. However, the P weathering amplification factor has to be >5.3 (the ratio of dissolved phosphate entering solution in microcosms with moss to those without), which is already considerably greater than the amplification factors for Ca = 1.4 and Mg = 1.5 from granite, indicating selective weathering of P.

COPSE model: We used the COPSE model (10, 20) to study the effects of the early rise of land plants on the coupled biogeochemical cycles of C, O, N, P and S, including the $\delta^{13}C$ record. The model is described in full in (10) and the version used here incorporates the changes in model structure described in (20). The model has several forcing parameters, including solar luminosity, the geological factors degassing (*D*), and uplift (*U*), and the biological forcing factors evolution/colonization (*E*), enhancement of weathering (*W*), selective phosphorus weathering (*F*), and changes to the C/P burial ratio of terrestrially-derived material (*CP*). The geologic and biologic forcing factors are all normalized to 1 at the present day, except C/P = 1000 at present day. Our overall modelling strategy was to try and reproduce key changes in the $\delta^{13}C$ record with plausible biological and geological forcing scenarios, constrained where possible by available data. We focused initially on altering the biological forcing scenario whilst using the original geological forcing scenario. Then in a sensitivity analysis we considered uncertainty in geologic forcing (91), and alternative initial conditions (altering the feedback structure of the model). The forcing scenarios and sensitivity analyses are detailed in the SI Materials and Methods.

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