First plants cooled the Ordovician

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The Late Ordovician period, ending 444 million years ago, was marked by the onset of glaciations. The expansion of non-vascular land plants accelerated chemical weathering and may have drawn down enough atmospheric carbon dioxide to trigger the growth of ice sheets.

Between 488 and 444 million years ago, during the Ordovician period, the climate cooled gradually[1], culminating in the abrupt onset of periods of temporary glaciation. These Late Ordovician glaciations are puzzling, because they occurred when atmospheric CO_2 concentrations, as estimated by geochemical models[2–4] and proxy data[5–7], were roughly 14–22 times present-day atmospheric levels (PAL). Yet complex climate models[8,9] suggest atmospheric CO_2 levels had to drop to about 8 PAL to trigger glaciations at this time. The uncertainty in the proxy estimates[5–7] allows for such a temporary reduction in atmospheric CO_2 levels during the Late Ordovician, but it is unclear which process (or processes) could have lowered these levels temporarily at the time.

The slow decline in CO_2 levels can be explained by invoking the drawdown of CO_2 by increased silicate weathering. The Taconic Orogeny led to extensive mountain building[10] — and weathering — along what is now the mid-Atlantic and northeastern coast of the United States. The eruption rate of basalt, a relatively weatherable rock type, was also elevated during the Ordovician, according to seawater $^{87}Sr/^{86}Sr$ records[11]. Finally, the movement of the continents through the intertropical convergence zone, where rainfall rates are exceptionally high, could also have enhanced weathering[12]. Together with basalt production, this process could have lowered CO_2 to approximately 12 PAL from the Middle Ordovician to Early Silurian period.

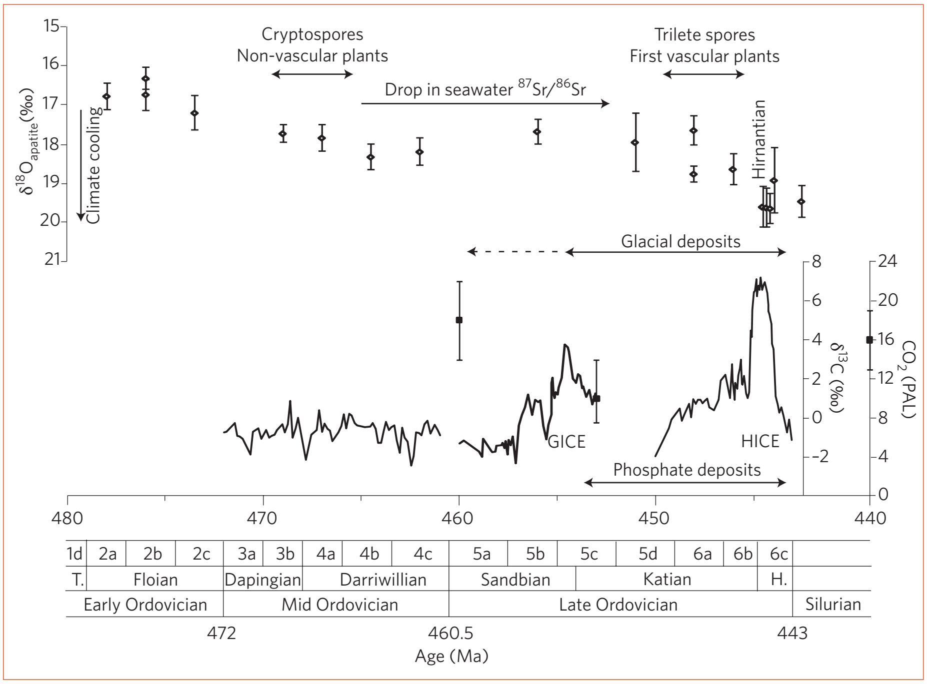

Figure 1 | Global changes during the Ordovician period. Appearances of non-vascular[18] and vascular[23] plants dot the timeline of climate change as recorded by conodont $\delta^{18}O$ values[1] (diamonds, left-hand scale). The appearance of non-vascular plants is followed by an increase in the abundance and weathering of volcanic rock, as recorded by seawater $^{87}Sr/^{86}Sr$ (ref. 11). The weathering seems to coincide with a drop in atmospheric CO_2 concentrations (solid squares, outer right-hand scale), though proxy-based estimates are scarce and highly uncertain[5–7]. Glacial deposits appear early in the Late Ordovician and increase in frequency as it progresses[13], and phosphate deposits appear then in marine settings[14]. Two carbon isotope excursions also mark the Late Ordovician: the Guttenberg and Hirnantian isotopic carbon excursions (GICE and HICE)[13]. T., Tremadogian age; H., Hirnantian age.

However, these geological mechanisms seem insufficient to lower CO_2 to 8 PAL and they do not explain the temporary abrupt glaciations[1], or other striking global changes, in the Late Ordovician (Fig. 1). In particular, the $\delta^{13}C$ record of carbonates contains two global positive excursions[13] that indicate pulses of high organic carbon burial rates in the ocean. Extensive shallow-water phosphate deposits[14] from the Late Ordovician suggest that the input of phosphorus to the ocean, where it is the ultimate limiting nutrient, was high. The resultant increase in productivity seems to have triggered regional ocean anoxia, as well as high rates of organic carbon burial, as evidenced by the deposition of black shales[15].

Here we suggest that this suite of Late Ordovician global changes was caused, at least in part, by the origination and expansion of the first land plants. All plants require rock-derived minerals — including phosphorus, potassium, calcium, magnesium and iron — for growth. Land plants have evolved a variety of systems and symbiotic relationships that accelerate the release of these essential nutrients from rocks[16]. This acceleration has been well characterized in vascular plants[17], which enhance the breakdown of nutrient-containing silicate minerals (silicate weathering) by factors of 2 to 10 (as is the case for calcium). The step change in silicate weathering rates caused by the radiation of vascular plants is widely thought to have caused the drawdown of atmospheric CO_2 between 400 and 360 Ma in the Devonian period that led to global cooling and polar glaciations[2].

Yet it is likely that land plants affected the global carbon cycle before the Devonian. Fossilized plant spores found in ~470 Ma sediments[18,19] indicate that non-vascular land plants were growing in damp environments on continental surfaces by the middle of the Ordovician (Fig. 1). Furthermore, phylogenies constructed using DNA sequences support the contention that the earliest plants were non-vascular[16,20]. Because non-vascular land plants lack deep rooting structures, existing models[3,4,17] assume that the early expansion of land plants had negligible effects on the existing weathering regime. But given their need to access rock-bound minerals, we suggest that these first colonizers actually caused a substantial change in chemical weathering, with a significant impact on the global carbon cycle and climate.

Weathering experiments

We set out to determine if non-vascular plants enhance chemical weathering using the moss *Physcomitrella patens* (also known as *Aphanoregma patens*). This modern moss has evolved considerably compared with its Ordovician ancestors, but is a representative non-vascular plant that can be used for experimentation.

To measure the effect of non-vascular-plant growth on silicate weathering, we compared the release of elements from granite and andesite in microcosms that were incubated with or without moss. Microcosms containing either granite or andesite were incubated with either a suspension containing macerated moss cultures or with suspensions from which the moss had been removed by filtration (control). Moss-containing and control microcosms were incubated in 16-hour light, 8-hour dark cycles at 25 °C for ~130 days. During this time 18.4 ± 14.9 mg and 13.4 ± 6.2 mg of biomass accumulated in the granite- and andesite-containing microcosms respectively; extensive mats of haploid protonema, gametophores and rhizoids formed (Supplementary Fig. S1). Sporophytes did not develop because of the high temperature, and hence the mosses did not complete their life cycle.

We determined the extent of calcium- and magnesium-silicate weathering in each treatment by measuring the total moles of elements released from rock during the incubation period using inductively coupled plasma-atomic emission spectroscopy. To measure the elements released from rock in the moss-containing microcosms, we determined the abundance of elements in the liquid (consisting of water and inoculation media) and the biomass. We used the abundance of elements present in the incubating media of the control (moss-free) microcosms to assess the amount of abiotic background weathering.

The presence of moss enhanced the chemical weathering of all measured elements from both granite and andesite (Fig. 2). Specifically, moss increased calcium weathering by factors of 1.4 ± 0.2 and 3.6 ± 0.9 from granite and andesite, respectively. Similarly, mosses increased magnesium weathering by a factor of 1.5 ± 0.2 and 5.4 ± 0.9 from granite and andesite, respectively. Given the relatively small amounts of biomass present in these microcosms, these data demonstrate that non-vascular plants considerably enhance silicate weathering over background abiotic levels, and do so by a factor comparable to that of vascular plants[17].

Effects of plant colonization

To determine the potential effects of enhanced weathering by the first plants on the Ordovician Earth system, we used an adapted version of the COPSE model[4] (Supplementary Methods). In our baseline version, which does not take non-vascular-plant weathering into account, the CO_2 concentration was ~16 PAL and global temperature was 21.4 °C 460 Myr ago, the start of the Late Ordovician (Fig. 3, red dotted line). These are consistent with proxy estimates[5] for the background levels of atmospheric CO_2 of ~14–22 PAL, and the lack of evidence for glaciations up to that point. When we simulated non-vascular-plant colonization of 15% of the currently vegetated land surface between 475 and 460 Myr ago — amplifying silicate weathering by a factor of ~5 (a global average amplification factor of 1.75) — the model predicted a CO_2 drop to 8.4 PAL and global cooling of 4.4 to 17.0 °C by 460 Myr ago (Fig. 3, blue dashed line). This is consistent with the requirement of CO_2 concentrations ~8 PAL for the start of glaciations, as suggested by more complex climate models[8,9].

In our sensitivity analyses (see Supplementary Information) we varied uncertain parameters, which altered initial model conditions such that the atmospheric CO_2 concentrations ranged from 14 to 21 PAL 460 Myr ago. Application of the same colonization scenario for non-vascular plants then lowered CO_2 to about 7 to 10 PAL (Supplementary Fig. S2, Supplementary Table S1), broadly consistent with values necessary to trigger glaciation. Alternatively, varying the extent of colonization by non-vascular plants between 5–45%, or their amplification of silicate weathering over a range of ~1.6–6.7 (global average amplification factor of 1.085–1.85), lowered CO_2 to ~5–13 PAL (Supplementary Fig. S3, Supplementary Table S2). These sensitivity analyses all resulted in a significant decrease in global mean temperature, in the range 1.4–7.2 °C. In our simulations, atmospheric CO_2 concentrations and temperature remained low during the Late Ordovician (Fig. 3), consistent with the reported sustained cold interval of over 10 Myr[1,13,14] (Fig. 1).

However, if we used an earlier date for the colonization of the land by plants[19], in this case, about 490 Myr ago, the model produced Early to Middle Ordovician cooling (Supplementary Fig. S4a). This simulation better matches the temperature trend inferred from oxygen isotopes of conodonts[1] (Fig. 1). However, evidence for early colonization by land plants is contested[18]. Alternatively, if colonization started later or took longer, CO_2 drawdown and cooling were correspondingly delayed (Supplementary Fig. S4b,c). Taking all the sensitivity analyses into account, the model demonstrates that the enhancement of silicate weathering by the first land plants is likely to have reduced atmospheric CO_2

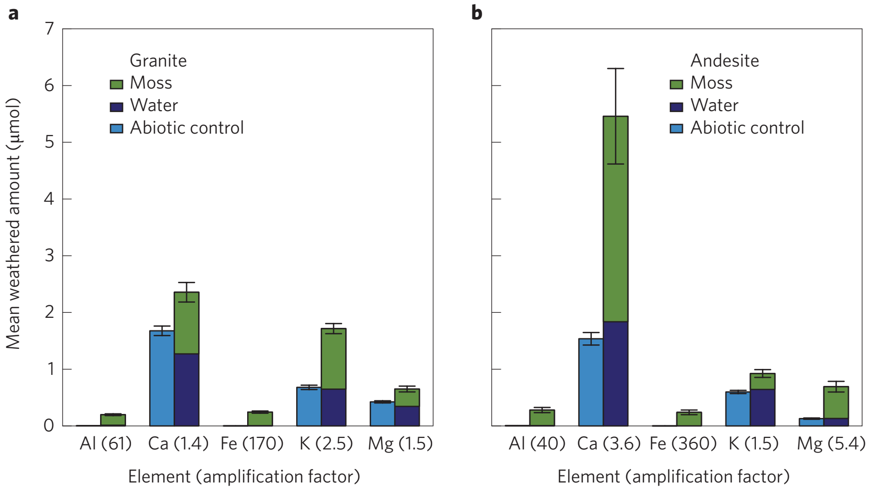

Figure 2 | Moss enhances the weathering of Al, Ca, Fe, K and Mg from silicates. Summary of results from all weathering experiments on different substrates: **a**, granite (control $n = 77$; moss $n = 72$) and **b**, andesite (control $n = 37$; moss $n = 41$). The amount weathered in micromoles (mean of all microcosms of each substrate) are shown, with abiotic and total biotic (moss + water) data in separate columns. The weathering 'amplification factor' due to the presence of moss = total biotic weathering/abiotic weathering. Error bars represent ~95% confidence intervals applied using the Student's *t*-test.

concentrations and global temperature towards or below the threshold for glaciations. However, increasing silicate weathering alone could not generate large, positive spikes in the $\delta^{13}C$ record, or create short-lived cooling events, notably the Hirnantian glaciation around 445 Myr ago (Fig. 1).

Phosphorus weathering

To explain these positive spikes in the $\delta^{13}C$ record and short-lived cooling events, we propose that the colonization of land by plants enhanced the weathering of phosphorus from the land surface. This would have transiently increased the flux of phosphorus to the oceans, where it would have fuelled new production and organic carbon burial. Phosphorus is essential for plant growth and reproduction, and constitutes ~0.1% of the dry weight of mosses (Supplementary Methods). Crucially, phosphorus has no significant gaseous form. Hence there must have been strong selection pressure for effective phosphorus weathering, which vascular plants achieve by secreting organic acids, using their rooting systems and associated mycorrhizal fungi.

We therefore determined if our non-vascular-plant analogue secreted organic acids into the growth medium (Supplementary Methods). We identified malic, citric, glyceric and succinic acids in purified exudates (Supplementary Fig. S5), indicating that non-vascular and vascular plants secrete the same acids into the rhizosphere. We also determined whether our moss analogue enhanced the release of phosphorus from granite, and found that phosphorus weathering was amplified by a factor of ~60 compared with the controls that lack moss (see Supplementary Methods). This value is likely to be a large underestimate because the moss used in these experiments was grown without fungal symbionts, whereas earliest land plants are likely to have evolved symbiotic associations with fungi similar to those that form mycorrhizae today.

Enhancement of phosphorus weathering by a factor of ~60, even if restricted to a few per cent of the land surface, could have more than doubled the global flux of phosphorus to the ocean. However, once the first plants began to exhaust the supply of easily accessible phosphorus in available rocks, and they became effective at recycling phosphorus from organic sources as soils formed, phosphorus flux to the oceans would have decreased. This would have resulted in a transient spike of increased phosphorus flux to the ocean, analogous to what happens during the colonization of modern lava flows (for example, on the Hawaiian islands). Initially, phosphorus weathering and leakage to the ocean were high, but after several million years the ecosystem exhausted its substrate and shifted to internal recycling of phosphorus with little leakage[21]. Each time plants evolved to colonize new regions of the land surface, or innovations allowed plants to further exploit previously colonized areas, a pulse of phosphorus weathering and supply to the ocean would have occurred, as has been argued for the Late Devonian[22].

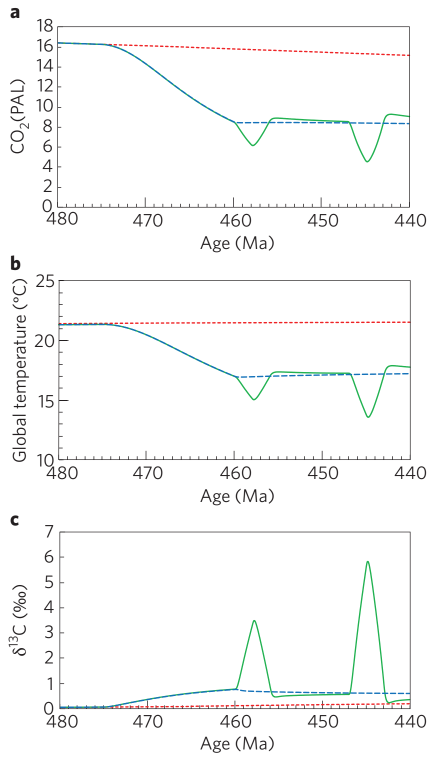

Figure 3 | Model results. Predicted Ordovician variations in **a**, atmospheric CO_2, **b**, global temperature, and **c**, $\delta^{13}C$ of marine carbonates, for: baseline model with Ordovician geological forcing and changing solar luminosity only (red dotted line), including enhancement of silicate weathering by non-vascular plants (blue dashed line), and adding transient enhancement of phosphorus weathering by early plants (green solid line).

To simulate transient selective enhancement of phosphorus weathering, we introduced a new forcing parameter into the COPSE model (Supplementary Methods), and varied it to reproduce the two Late Ordovician peaks in the carbonate carbon isotope ($\delta^{13}C$) record (Fig. 3, green solid line): the Guttenberg (GICE; $\delta^{13}C$ +4‰, ~455 Myr ago) and Hirnantian (HICE; $\delta^{13}C$ +6‰, ~445 Myr ago) isotope excursions[13] (Fig. 1). Both events involved pulses of organic carbon burial that further lowered atmospheric CO_2 and temperature (Fig. 3, green solid line). We found that a temporary doubling of global phosphorus weathering by the first land plants (well within the range of our experiments) could have caused the GICE. Our model predicts the GICE was accompanied by a temporary CO_2 drop to 6.2 PAL and a 2.0 °C cooling to average temperatures of 15.0 °C, comparable to today. Reproduction of the HICE requires a transient tripling of phosphorus weathering, causing CO_2 to drop to 4.5 PAL and a 3.4 °C cooling to 13.6 °C. This might have been due to the evolution of the first vascular plants[23], colonizing new habitats and thus causing a second pulse of phosphorus weathering.

Sensitivity analyses produce atmospheric CO_2 concentrations in a range of 3.5–9.8 PAL for the GICE and 2.5–7.2 PAL for the HICE (Supplementary Tables S1 and S2), and corresponding temperature ranges of 12.0–18.0 °C and 10.7–16.2 °C, respectively. These predicted atmospheric CO_2 and temperature ranges are consistent with glaciations starting during the GICE and become most pronounced in the Hirnantian[1]. After each event, our simulations suggest atmospheric CO_2 concentrations and temperature rebounded temporarily above the steady-state level determined by silicate weathering. The rebound could help explain the Boda warming event between the $\delta^{13}C$ excursions, as well as the observed warming after the Hirnantian glaciation. Our enhanced phosphorus weathering scenario is also consistent with phosphate-rich deposits formed during the Late Ordovician[14]: Our simulations show an increase in phosphorus burial that closely tracks the phosphorus input because phosphate only has a 10^4–10^5year residence time in the ocean.

Finally, as iron can limit productivity of the remote oceans, we also determined the effects of moss on iron release from granite and andesite. Moss increased iron weathering by factors of 170 ± 20 for granite and 360 ± 100 for andesite (Fig. 2). Today, approximately 0.5% of the total weathered iron (~800 Tg yr^{-1}) that enters the global river system reaches the deep ocean in reactive (that is, bioavailable) form[24]. Thus, despite potential changes in redox and chelation states with a transition from abiotic to biotic chemical weathering, land colonization would have significantly enhanced the iron flux to the open ocean. This in turn would have increased new production and organic carbon burial, and contributed further to the positive $\delta^{13}C$ excursions.

Biological and geological drivers

We demonstrate that the evolution of the first land plants, through their effects on silicate weathering and fluxes to the ocean, could explain Ordovician global changes, culminating in one of only two glacial episodes in the Paleozoic era. Geological factors may also have contributed to CO_2 drawdown and long-term cooling, but cannot at present explain the short-lived Hirnantian glaciation or other global biogeochemical changes in the Late Ordovician. These environmental changes are associated with a marine mass extinction[25] that defines the end of the Ordovician Period. Thus, the evolution of the first land plants could have indirectly contributed to killing off many of their compatriots in the ocean. More precise dates on the timing of the evolution of the first land plants and better estimates of the extent of these early floras, as well as more detailed quantification of silicate weathering on a range of rock types, will increase the accuracy of our models.

An ongoing puzzle is why CO_2 levels and temperature increased later in the Silurian. Here we must appeal to a geological mechanism[12]: the movement of continents away from the intertropical convergence zone. We suggest that future work consider both biological and geological influences on weathering through this pivotal interval of early land colonization.

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Acknowledgements

We thank the Earth and Life Systems Alliance (ELSA) for funding this research. T.M.L. is also supported by NERC (NE/I005978/1). L.D. and N.P. are also supported by an EVO500 grant from the ER AdG program. P. Bota provided assistance with GC-MS.

Author Contributions

T.M.L. and L.D. designed the study. M.C. conducted the microcosm experiments with input from N.P. and L.D. M.C., M.J., L.D. and T.M.L. conducted geochemical analyses. N.P. and L.D. identified acids in moss exudates. T.M.L. did the modelling and sensitivity analyses. T.M.L. and L.D. wrote the paper with input from M.J., M.C. and N.P.

Additional information

Supplementary information accompanies this paper on www.nature.com/naturegeoscience.