

## CENTENARY SYMPOSIUM SPECIAL FEATURE

# Ecosystem CO<sub>2</sub> starvation and terrestrial silicate weathering: mechanisms and global-scale quantification during the late Miocene

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## Summary

1. The relative constancy of the lower limit on Earth's atmospheric CO<sub>2</sub> concentration ([CO<sub>2</sub>]<sub>a</sub>) during major tectonic episodes over the final 24 million years (Ma) of the Cenozoic is surprising because they are expected to draw-down [CO<sub>2</sub>]<sub>a</sub> by enhancing chemical weathering and carbonate deposition on the seafloor. That [CO<sub>2</sub>]<sub>a</sub> did not drop to extremely low values suggests the existence of feedback mechanisms that slow silicate weathering as [CO<sub>2</sub>]<sub>a</sub> declines. One proposed mechanism is a negative feedback mediated through CO<sub>2</sub> starvation of land plants in active orogenic regions compromising the efficiency of the primary carboxylating enzyme in C<sub>3</sub> plants (Rubisco) and diminishing productivity and terrestrial weathering.

2. The CO<sub>2</sub> starvation hypothesis is developed further by identifying four key related mechanisms: decreasing net primary production leading to (i) decreasing below-ground C allocation, reducing the surface area of contact between minerals and roots and mycorrhizal fungi and (ii) reduced demand for soil nutrients decreasing the active exudation of protons and organic acids by fine roots and mycorrhizas; (iii) lower carbon cost-for-nutrient benefits of arbuscular mycorrhizas (AM) favouring AM over ectomycorrhizal root–fungal symbioses, which are less effective at mineral weathering, and (iv) conversion of forest to C<sub>3</sub> and C<sub>4</sub> grassland arresting Ca leaching from soils.

3. We evaluated the global importance of mechanisms 1 and 2 in silicate weathering under a changing late Miocene [CO<sub>2</sub>]<sub>a</sub> and climate using a process-based model describing the effects of plants and mycorrhizal fungi on the biological proton cycle and soil chemistry. The model captures what we believe are the key processes controlling the pH of the mycorrhizosphere and includes numerical routines for calculating weathering rates on basalt and granite using simple yet rigorous equilibrium chemistry and rate laws.

4. Our simulations indicate a reduction in the capacity of the terrestrial biosphere to weather continental silicate rocks by a factor of four in response to successively decreasing [CO<sub>2</sub>]<sub>a</sub> values (400, 280, 180 and 100 p.p.m.) and associated late Miocene (11.6–5.3 Ma) cooling. Marked reductions in terrestrial weathering could effectively limit biologically mediated long-term carbon sequestration in marine sediments.

5. These results support the idea of terrestrial vegetation acting as a negative feedback mechanism that counteracts substantial declines in [CO<sub>2</sub>]<sub>a</sub> linked to increased production of fresh weatherable minerals in warm, low-latitude, active orogenic regions.

**Key-words:** biological weathering, Miocene, modelling, mycorrhiza, plant–climate interactions

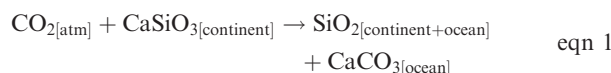
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## Introduction

Paraphrasing Oscar Wilde, the gifted but controversial Oxford botanist and geneticist C. D. Darlington (1903–1981) scathingly described ecology during the 1950s as being the ‘the pursuit of the incomprehensible by the incompetent’ (Harman 2004). Darlington had evidently not yet absorbed the emerging legacy of Sir Arthur Tansley, the father of British ecology and one of the founders of the *Journal of Ecology* (Godwin 1957). Tansley (1935) pioneered an enlightened approach to ecology by conceptualizing the ecosystem as a set of interacting components, whereby plants, climate, soils and animals function as a system and emphasizing investigation of processes that link them. Consequently, over the past five decades, ecosystems have become increasingly recognized as playing a central role in Earth’s environmental history, through their effects on the major cycles of elements, the fate of sediments, and atmospheric and ocean chemistry (Knoll 2003; Berner 2004; Beerling 2007).

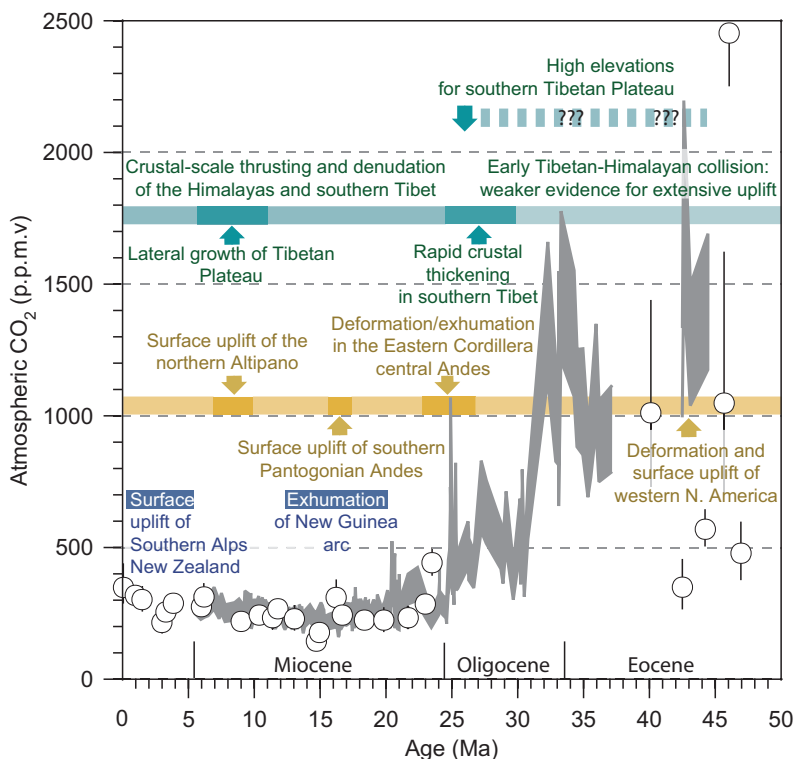
Our contribution to the Centenary celebration of the *Journal of Ecology* develops this theme by investigating the interplay between the terrestrial biosphere, climate and the geosphere in the context of Earth’s atmospheric CO<sub>2</sub> history over the past 24 million years (Ma) (Pagani *et al.* 2009; Beerling & Royer 2011) (Fig. 1). We adopt a process-based approach to terrestrial ecosystem functioning, and its chemical interaction with the regolith (weathering), by investigating its hypothesized role in regulating Earth’s lower limit of atmospheric concentration ([CO<sub>2</sub>]<sub>a</sub>) during major orogenic events (Pagani *et al.* 2009) (Fig. 1).

Our paper is organized into three parts. First, we provide an overview of the proposed linkage between silicate weathering by terrestrial ecosystems, climate and [CO<sub>2</sub>]<sub>a</sub> during the late Cenozoic (Pagani *et al.* 2009). Second, we critically review the ecological literature to identify mechanisms by which changing [CO<sub>2</sub>]<sub>a</sub> influences terrestrial plants, their symbiotic fungal partners and soil carbon cycle processes that contribute to the chemical weathering of Ca- and Mg-rich silicate minerals. Silicate mineral weathering is important because on a timescale of millions of years, it acts as the long-term sink of [CO<sub>2</sub>]<sub>a</sub> (Berner 2004). The overall process by which silicate weathering transfers Ca<sup>2+</sup> ions into the oceans is given by the following simplified expression representative of all calcium silicates (Berner 2004):



Mg ions liberated from Mg silicates exchange with calcium in marine basalts (Berner 2004), leading to the deposition of CaCO<sub>3</sub> rather than MgCO<sub>3</sub>. The weathering of Ca and Mg carbonates releases both Ca<sup>2+</sup> and CO<sub>2</sub>, resulting in no net change in [CO<sub>2</sub>]<sub>a</sub> on timescales of millions of years, and places the emphasis on continental silicate rocks in controlling long-term CO<sub>2</sub> sequestration in the oceans.

In the third part of the paper, we report results from global simulations analysing how declining [CO<sub>2</sub>]<sub>a</sub> and climatic cooling in the late Miocene (11.6–5.3 Ma) alters biological weathering of silicate rocks by terrestrial ecosystems (Taylor *et al.* 2011, 2012). Our approach uses a process-based model describing the effects of plants and mycorrhizal fungi on mineral weathering via their influence on the ‘biological proton cycle’



**Fig. 1.** Earth’s atmospheric CO<sub>2</sub> and tectonic history over the past 50 Ma. Shaded bands indicate [CO<sub>2</sub>]<sub>a</sub> estimates from the alkenone proxy and circles from the boron isotope proxy (redrawn after Pagani *et al.* 2009).

in soils (Banwart, Berg & Beerling 2009; Taylor *et al.* 2011, 2012). We focus on the late Miocene because it represents a time of global warmth, relative to now, and encompasses intervals of mountain building, including the uplift of the Himalayas and the Alps between 14 and 8 Ma (Jiménez-Moreno, Fauquette & Suc 2008). Global-scale analyses are achieved with a well-defined modelling strategy (Taylor *et al.* 2011, 2012) using late Miocene (11.6–5.3 Ma) climates simulated for four [CO<sub>2</sub>]<sub>a</sub> values (400, 280, 180 and 100 p.p.m.) by the Hadley Centre coupled ocean–atmosphere general circulation model, HadCM3L (C. D. Bradshaw, D. J. Lunt, R. Flecker, U. Salzmann, A. M. Haywood, M. J. Pound unpubl. data). Overall, these simulations provide a rigorous basis for addressing the combined effects of [CO<sub>2</sub>]<sub>a</sub> and climate on terrestrial silicate weathering by plants (Goddéris & Donnadieu 2009).

### Ecosystem CO<sub>2</sub> starvation and the late Cenozoic carbon cycle

Polar ice-core records indicate that Earth's [CO<sub>2</sub>]<sub>a</sub> varied between *c.*180 and 300 p.p.m. during the last eight glacial cycles (Siegenthaler *et al.* 2005; Luthi *et al.* 2008), while the boron isotopic signatures of fossilized foraminifera shells indicate that it varied between similar limits (*c.* 220–280 p.p.m.) over the past 2.1 Ma (Hönisch *et al.* 2009). Other CO<sub>2</sub> proxy evidence (Pagani *et al.* 2009; Beerling & Royer 2011) suggests that [CO<sub>2</sub>]<sub>a</sub> did not drop below 200–250 p.p.m. for at least the last 24 Ma of the Cenozoic. This lack of variability in the lower boundary of [CO<sub>2</sub>]<sub>a</sub> (Fig. 1) is surprising because major tectonic episodes, and coincident environmental conditions, should have enhanced the global weathering of Ca- and Mg-bearing silicate minerals and contributed to a major long-term CO<sub>2</sub> sink by precipitation of oceanic carbonate sediments, via eqn 1 (Berner 2004).

The current paradigm incorporated into geochemical carbon cycle models represents a negative feedback between [CO<sub>2</sub>]<sub>a</sub>, climate and weathering of Ca and Mg silicates that constitutes a thermostat (Walker, Hays & Kasting 1981; Berner, Lasaga & Garrels 1983), whereby falling [CO<sub>2</sub>]<sub>a</sub> produces a colder, drier climate that retards weathering. It operates even in the absence of life and likely played a key role in stabilizing Earth's long-term climate and preventing a runaway greenhouse atmosphere as the luminosity of the ageing Sun increased (Walker, Hays & Kasting 1981; Berner, Lasaga & Garrels 1983). It is supported by observational evidence from ice cores and deep ocean sediments, indicating a fine balance between [CO<sub>2</sub>]<sub>a</sub> and marine carbonate cycle over the past 650 000 years (Zeebe & Caldeira 2008) that requires a strong continental weathering feedback to be maintained. However, this temperature-dependent feedback paradigm does not explain why [CO<sub>2</sub>]<sub>a</sub> has been constrained to never fall below a consistent minimum value for the past 24 Ma when global temperatures were warmer than pre-industrial conditions and major, low-latitude (*i.e.* wet and warm conditions) tectonic uplift and denudation events are known to have occurred (Fig. 1). Under these past conditions, silicate weathering rates should have been higher than today, promoting lower [CO<sub>2</sub>]<sub>a</sub>

and global temperatures well below average pre-industrial levels (Berner & Kothavala 2001; Pagani *et al.* 2005). Indeed, a very small, sustained imbalance in the carbon cycle results in very large changes in [CO<sub>2</sub>]<sub>a</sub> (Berner & Caldeira 1997). For example, the substantial [CO<sub>2</sub>]<sub>a</sub> fall at *c.* 34 Ma (Fig. 1) only required a sustained < 0.01 PgC year<sup>-1</sup> offset between carbon input and output (Kerrick & Caldeira 1998). But this is not observed for the past 24 Ma, suggesting that other strong feedbacks maintain the balance of the geochemical carbon cycle over this long interval of time.

To explain these observations, a mechanistic 'Earth system' hypothesis postulates that a lower limit of [CO<sub>2</sub>]<sub>a</sub> is buffered by a strong negative feedback, caused by a diminished capacity of land plants to weather Ca- and Mg-bearing silicates as [CO<sub>2</sub>]<sub>a</sub> falls to critically low 'starvation' levels (Pagani *et al.* 2009). Vascular plants, and their symbiotic mycorrhizal fungal partners, accelerate rates of chemical weathering by a factor of 1.5 to < 10 (Berner, Berner & Moulton 2003). Roots fracture rocks and increase the mineral surface area, soil pH is lowered by root-respired CO<sub>2</sub> and organic carbon oxidation, organic acids and proton exchange during nutrient uptake. The activity of metals, and saturation states, is also lowered by chelation by organic ligands secreted from rootlets and their associated micro-organisms; further details are discussed in the following sections. Global rates of silicate chemical weathering are therefore linked to biologically enhanced weathering through the health of terrestrial ecosystems.

Falling productivity with falling [CO<sub>2</sub>]<sub>a</sub> across geologic timescales, particularly at sites in upland regions with active orogenies where silicate weathering rates are high, occurs because the C<sub>3</sub> photosynthetic pathway of trees exhibits major reductions in efficiency of CO<sub>2</sub> fixation as the atmospheric ratio CO<sub>2</sub> : O<sub>2</sub> becomes critically low (Jordan & Ogren 1984; Long 1991). Under the atmospheric CO<sub>2</sub> : O<sub>2</sub> ratio typical of much of the past 24 Ma (Fig. 1), the efficiency of the primary carboxylating enzyme, Rubisco (ribulose-1,5-bisphosphate carboxylase/oxygenase), is compromised. This is because O<sub>2</sub> competes with CO<sub>2</sub> for the acceptor molecule ribulose biphosphate leading to photorespiratory CO<sub>2</sub> release (Ehleringer & Björkman 1977), reducing the rates of carbon fixation. Photorespiration is further enhanced at higher temperatures altering the solubility of O<sub>2</sub> and specificity of Rubisco in favour of its oxygenase activity (Jordan & Ogren 1984; Long 1991); thus, the minimum [CO<sub>2</sub>]<sub>a</sub> in the past could also be linked to average global temperature.

This mechanism represents a first-order response of terrestrial C<sub>3</sub> ecosystems to declining [CO<sub>2</sub>]<sub>a</sub>, with high photorespiration rates severely reducing the influence of plants on silicate weathering and continued [CO<sub>2</sub>]<sub>a</sub> drawdown. It is supported by carbon isotope analyses of fossils, vegetation modelling and experiments. Carbon isotopic composition of fossils of *Juniperus* dating to the last ice age, when [CO<sub>2</sub>]<sub>a</sub> was low (*c.* 180 p.p.m.), indicates that this woody shrub operated with a leaf intercellular CO<sub>2</sub> concentration is equivalent to 113 p.p.m. (Ward *et al.* 2005). Such low internal leaf CO<sub>2</sub> concentrations are consistent with those reported for glacial trees of *Pinus flexilis* (110 p.p.m.) from the Great Basin, USA (Van de Water,

Leavitt & Betancourt 1994), but are unprecedented in modern vegetation and indicative of CO<sub>2</sub> starvation because they approach the CO<sub>2</sub> compensation point for net C<sub>3</sub> photosynthesis (Ward *et al.* 2005).

Vegetation modelling predicts steep nonlinear declines in tropical and global terrestrial net primary production (NPP), root biomass and transpiration rates as [CO<sub>2</sub>]<sub>a</sub> falls below 200 p.p.m. under pre-industrial climate conditions (Pagani *et al.* 2009), in line with experimental evidence for a range of plant functional types from trees to grasses (Gill *et al.* 2002; Gerhart & Ward 2010; Kgope, Bond & Midgley 2010; Lewis, Ward & Tissue 2010). When these low [CO<sub>2</sub>]<sub>a</sub> thresholds for plant productivity are incorporated into a geochemical model, they limit the drawdown of [CO<sub>2</sub>]<sub>a</sub> by biological weathering (Pagani *et al.* 2009).

Evidence for low [CO<sub>2</sub>]<sub>a</sub> and concomitant vegetation responses presented thus far represents a milestone in our understanding of the interplay between climate, geosphere and terrestrial biosphere over millions of years. In the following section, we critically review the literature to reveal a broader range of ecological interactions and mechanisms through which CO<sub>2</sub> starvation could limit biological weathering processes and entrain a negative feedback on further [CO<sub>2</sub>]<sub>a</sub> decline during mountain uplift.

### Biological mechanisms of silicate weathering

The direct ability of plants, and their root symbiotic partnerships with fungi (mycorrhizas), to enhance weathering, is driven by three main mechanisms (Berner, Berner & Moulton 2003; Taylor *et al.* 2009) related to the capacity of roots and associated micro-organisms to (i) physically and chemically increase mineral surface areas, (ii) lower soil solution pH via respiration, exudation of organic acids and proton exchange during nutrient uptake, and (iii) exude organic chelators in the mycorrhizosphere enhancing mineral dissolution and nutrient supply for plant growth. All of these weathering activities contribute to acquisition of mineral nutrients by plants from rocks.

Phosphorus is the principal mineral nutrient that often constrains productivity in terrestrial ecosystems. Its primary source is the weathering of calcium phosphate minerals (Blum *et al.* 2002; Jobbagy & Jackson 2003) that often form accessory constituents in silicate rocks (Klein 2002). Recent conceptual developments, and experimental evidence, link the biological weathering of primary Ca-silicate/phosphate minerals to increasing P uptake by roots and mycorrhizal fungi (Landeweert *et al.* 2001; Leake *et al.* 2008; Smits *et al.* 2008), fuelled by photosynthate (Leake *et al.* 2004). Of the two major types of mycorrhiza, the ectomycorrhizal fungi (EM) associate with the roots of a subset of ecologically dominant trees and are considered to be especially effective at mineral weathering in comparison with arbuscular mycorrhizal fungi (AM) (Taylor *et al.* 2009). EM fungi increase the rate of mineral dissolution over AM fungi through two mechanisms. First, although both AM and EM fungi focus cation and proton exchange at the scale of mineral grains, only EM fungi ensheath root tips and

take control of uptake activity by preventing root–mineral contact. Second, EM fungi secrete copious amounts of organic acids (e.g. oxalic acid) at the scale of individual grains of Ca- and Mg-rich minerals and rocks, such as apatite and basalt (Landeweert *et al.* 2001; Leake *et al.* 2008), but there is little evidence of such secretions by AM fungi (Taylor *et al.* 2009).

### [CO<sub>2</sub>]<sub>a</sub> dependency of biological processes linked to silicate weathering

Both experimental evidence and modelling investigations consistently indicate that as [CO<sub>2</sub>]<sub>a</sub> approaches Earth's minimum zone (180–200 p.p.m.), NPP and nutrient demand of forest trees and grasslands declines, together with proportional and total carbon allocation to roots (Gill *et al.* 2002; Pagani *et al.* 2009; Gerhart & Ward 2010; Kgope, Bond & Midgley 2010; Lewis, Ward & Tissue 2010). For example, soil CO<sub>2</sub> efflux in grasslands decreased by 300% as [CO<sub>2</sub>]<sub>a</sub> was experimentally reduced from 550 to 250 p.p.m. (Gill *et al.* 2002). Because biological weathering of silicate minerals is related to the combined activities of roots and associated symbiotic mycorrhizal fungi, fuelled by plant photosynthate, less carbon allocation below-ground is expected to diminish the energy available for these biotic weathering activities. This represents a first-order effect of falling [CO<sub>2</sub>]<sub>a</sub> on ecosystem weathering.

In addition to reducing the photosynthate carbon energy available for weathering, [CO<sub>2</sub>]<sub>a</sub>-linked changes in nutrient demand by plants can alter soil pH to affect weathering rates. For example, decreases in NPP under low [CO<sub>2</sub>]<sub>a</sub> reduce nutrient cation uptake and related proton extrusion, litter production and soil organic matter (SOM) (Polley *et al.* 1993). All of these effects decrease soil acidity. Furthermore, a lower N-demand by plants under low [CO<sub>2</sub>]<sub>a</sub>, decreases the production of C-costly antimicrobial and anti-herbivore compounds (e.g. lignin, phenolics and condensed tannins) (Gill *et al.* 2002), which in turn enhances SOM decomposition. This would again shift soil pH to become less acidic to further reduce weathering, as shown in process-based soil modelling (Banwart, Berg & Beerling 2009). Increased litter quality (lower C : N ratios at low [CO<sub>2</sub>]<sub>a</sub>) also reduces SOM accumulation by permitting faster and more complete decomposition (Smolander *et al.* 2005). More complete decomposition causes soils to become less acidic by recycling alkalinity and reduces leachable calcium–organic matter complexes such as Ca-fulvate (Ouattmane *et al.* 1999). Collectively, these indirect effects of low [CO<sub>2</sub>]<sub>a</sub> combine to make the subsurface environment less acidic and diminish the capacity for biological weathering.

Taken together, all of the factors considered previously suggest falling [CO<sub>2</sub>]<sub>a</sub>, and the low [CO<sub>2</sub>]<sub>a</sub> of Pleistocene glacials (Siegenthaler *et al.* 2005; Luthi *et al.* 2008; Hönisch *et al.* 2009), might favour a shift in AM over EM root–fungal symbioses in the long term. This is because AM plants are better adapted to soils with higher rates of N and P mineralization from organic matter than EM, which are favoured in soils rich in SOM (Smith & Read 2008). Reduction in soil acidity following CO<sub>2</sub> starvation of ecosystems will also favour AM, which are better adapted to take up P

from soils of circumneutral pH. In contrast, EM fungal partnerships are favoured by acid soils with depleted calcium pools where phosphorus binds to aluminium and iron and requires secretion of organic ligands to free the P.

A further factor favouring AM over EM plants operates through the reduced NPP of vegetation under low [CO<sub>2</sub>]<sub>a</sub> lowering nutrient demand and reducing the extent to which plants and their mycorrhizas weather minerals to meet part of this demand. In contemporary ecosystems, EM trees are amongst the most important functional groups of plants involved in acidifying soils, dissolving calcium from minerals and causing soils to become calcium depleted (Hüttl & Schaaf 1995; Blum *et al.* 2002). Furthermore, the net photosynthate costs to plants of maintaining EM are approximately double those of AM, so under CO<sub>2</sub> starvation, AM plants are likely to be favoured, and AM mycelial systems may continue to provide a better carbon-for-nutrient investment than growing more roots (Leake *et al.* 2004). Shifts in carbon cost-for-nutrient benefit ratio of EM and AM in response to low [CO<sub>2</sub>]<sub>a</sub> supply have never been investigated, but are likely to be amongst the most highly responsive components of soil-CO<sub>2</sub> feedbacks affecting mineral weathering rates.

In addition to these local and regional-scale effects on plants, mycorrhizal fungi and soils, changes in [CO<sub>2</sub>]<sub>a</sub> also exert control on vegetation at the continental scale. For example, the well-documented origination and expansion of AM C<sub>3</sub> grasslands from Oligocene to early Miocene (25–15 Ma) at the expense of forests (Jacobs, Kingston & Jacobs 1999) attest to conditions unfavourable to forest productivity under low [CO<sub>2</sub>]<sub>a</sub> (Fig. 1). More recently, over the past 8 Ma, there has been a near-synchronous dramatic expansion around the world of grasses with the C<sub>4</sub> photosynthetic pathway (Cerling *et al.* 1997). C<sub>4</sub> grasses have a specialized CO<sub>2</sub> concentrating mechanism (CCM) providing an advantage in low [CO<sub>2</sub>]<sub>a</sub> by reducing photorespiratory CO<sub>2</sub> losses compared with the more common C<sub>3</sub> photosynthetic pathway (Pearcy & Ehleringer 1984) found in other grasses. Both C<sub>3</sub> and C<sub>4</sub> grasses exclusively associate with AM fungi (Smith & Read 2008).

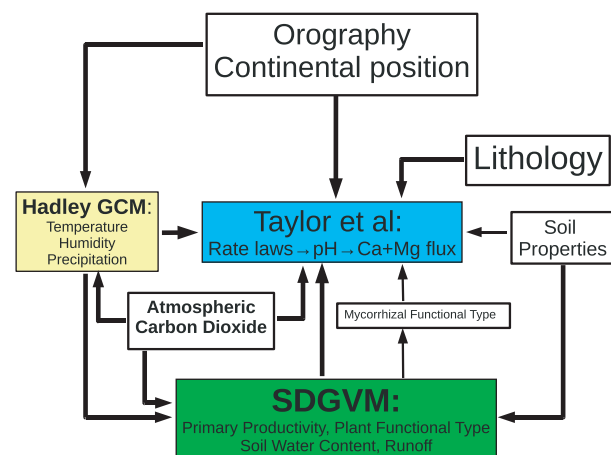
According to current evidence, low [CO<sub>2</sub>]<sub>a</sub>, climate change and fire together appear to have promoted the loss of forests and the spread of C<sub>4</sub> grasslands over the past 8 Ma (Bond, Midgley & Woodward 2003; Beerling & Osborne 2006; Bond 2008) which, in turn, may have switched the Earth system to an alternative, lower weathering regime. Grasslands arrest, and can even reverse, the acidification and calcium depletion that normally occurs in forest soils (Hüttl & Schaaf 1995). Reforestation of C<sub>3</sub> pampas grasslands, for example, caused soil pH to fall from 5.6 to 4.6 within 50 years and the exchangeable Ca in the top 30 cm of the soil profiles to drop by 40% (Jobbagy & Jackson 2003). The carbon cost of grasslands maintaining AM fungi is *c.* 10% of net fixation, compared with 25% for trees maintaining EM fungi (Leake *et al.* 2004). Under [CO<sub>2</sub>]<sub>a</sub> starvation, C<sub>4</sub> grasses in particular are likely to be favoured because of their CCM physiology, with both C<sub>3</sub> and C<sub>4</sub> grasses being favoured over EM trees because their mycorrhizal partners provide a less expensive carbon-for-nutrient investment (Leake *et al.* 2004). Calcium loss through

plant-driven weathering, therefore, can be strongly controlled by plant and mycorrhizal functional groups in contemporary ecosystems.

## Synthesis

Evidence considered earlier consistently points to falling [CO<sub>2</sub>]<sub>a</sub> causing diminishing rates of terrestrial biological weathering and leaching of Ca and Mg from primary silicate and phosphate minerals, by four related mechanisms: decreasing NPP leading to (i) decreasing below-ground C allocation, reducing the surface area of contact between minerals and roots and mycorrhizal fungi and (ii) reduced demand for soil nutrients decreasing the active exudation of protons and organic acids by fine roots and mycorrhizas in weathering in weathering of calcium-rich minerals; (iii) lower carbon cost-for-nutrient benefits of AM fungi favouring these over EM fungal associations, resulting in less weathering, and (iv) conversion of forest to C<sub>3</sub> and C<sub>4</sub> grassland arresting Ca leaching losses which typically occur under many kinds of forest (Hüttl & Schaaf 1995; Jobbagy & Jackson 2003).

A common feature emerging from the CO<sub>2</sub> experiments conducted to date is that NPP (Polley *et al.* 1993; Gill *et al.* 2002; Kgope, Bond & Midgley 2010; Lewis, Ward & Tissue 2010) and below-ground carbon allocation are both sensitive to [CO<sub>2</sub>]<sub>a</sub> that approach the Earth system minimum (180–200 p.p.m.). Plant and mycorrhizal responses to falling [CO<sub>2</sub>]<sub>a</sub> are therefore hypothesized to translate into a decline in weathering rates of Ca–silicate and phosphate minerals via the suite of mechanisms outlined earlier. Reduced Ca phosphate mineral weathering under low [CO<sub>2</sub>]<sub>a</sub> therefore could entrain a negative feedback, in which decreased release of phosphorus limits the productivity and biomass of forest ecosystems and their capacity to further weather minerals (Jobbagy & Jackson 2003; Wardle, Walker & Bardgett 1994).



**Fig. 2.** Schematic of the modelling strategy adopted to investigate late Miocene CO<sub>2</sub> and climate change influences biological weathering (after Taylor *et al.* 2012). Arrows denote inputs and outputs of the Hadley Centre ocean-atmosphere general circulation model (Cox *et al.* 2000) the Sheffield Dynamic Global Vegetation Model (Beerling & Woodward 2001) and weathering models (Taylor *et al.* 2011, 2012).

**Table 1.** Dominant mycorrhizal types assigned to the six plant functional types simulated by the Sheffield Dynamic Global Vegetation Model

Leaf habit	Typical forest type	AM (%)	EM (%)
Evergreen broadleaved	Tropical rainforest	100	0
Evergreen needle-leaved	Boreal forest		100
Deciduous broadleaved	Temperate forest		100
Deciduous needle-leaved	<i>Larix</i> forest		100
C <sub>3</sub> grasslands	–	100	
C <sub>4</sub> grasslands	–	100	

AM, arbuscular mycorrhiza; EM, ectomycorrhiza.

**Table 2.** Average equilibrium land surface late Miocene climatology (excluding Antarctica) simulated at four atmospheric CO<sub>2</sub> concentrations by the Hadley Centre coupled ocean-atmosphere general circulation model

Atmospheric CO <sub>2</sub> concentration (p.p.m.)	Mean annual temperature (°C)	Mean annual precipitation (mm year <sup>-1</sup> )
100	-4.9	532.4
180	5.3	663.4
280	9.6	689.6
400	13.4	692.9

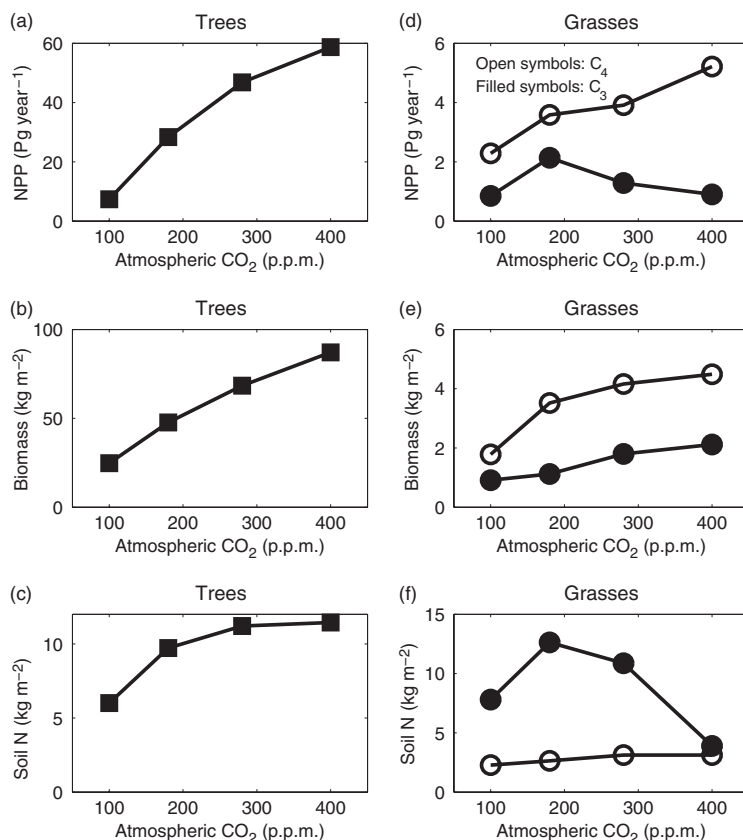
The following section evaluates the effect of falling [CO<sub>2</sub>]<sub>a</sub> and climate cooling during the late Miocene (11.6–5.3 Ma) on terrestrial biological weathering. We focus on the late Miocene

because it represents a time of global warmth, relative to now, with extensive palaeobotanical evidence for boreal forests reaching 80°N, areas of savannas in central USA, the Middle East and on the Tibetan Plateau Areas, and modern arid desert regions being covered by grasslands, shrublands, savannas and woodlands (Micheels *et al.* 2007; Pound *et al.* 2011). Major orogenic events included the uplift of the Himalayas with effects on global atmospheric circulation and the Asian Monsoon, and uplift of the Alps between 14 Ma and the present (Jiménez-Moreno, Fauquette & Suc 2008).

### Modelling terrestrial ecosystem silicate weathering responses to CO<sub>2</sub> and late Miocene climate cooling

#### MODELLING STRATEGY

We modelled the response of silicate weathering by terrestrial ecosystems to [CO<sub>2</sub>]<sub>a</sub> and climatic cooling by driving a process-based model of mineral weathering by plants and mycorrhizal fungi (Taylor *et al.* 2011, 2012) with a series of HadCM3L climates obtained under four different [CO<sub>2</sub>]<sub>a</sub> values (Fig. 2). Our weathering model simulates the effect of nutrient uptake by fine roots and mycorrhizal fungi on soil chemistry and the biological proton cycle. The biological proton cycle is controlled by the stoichiometry of reactions during the uptake of mineral nutrients by plants and symbiotic root fungi during growth and the subsequent return of these nutrients to the soil during decomposition of organic matter (Banwart, Berg &

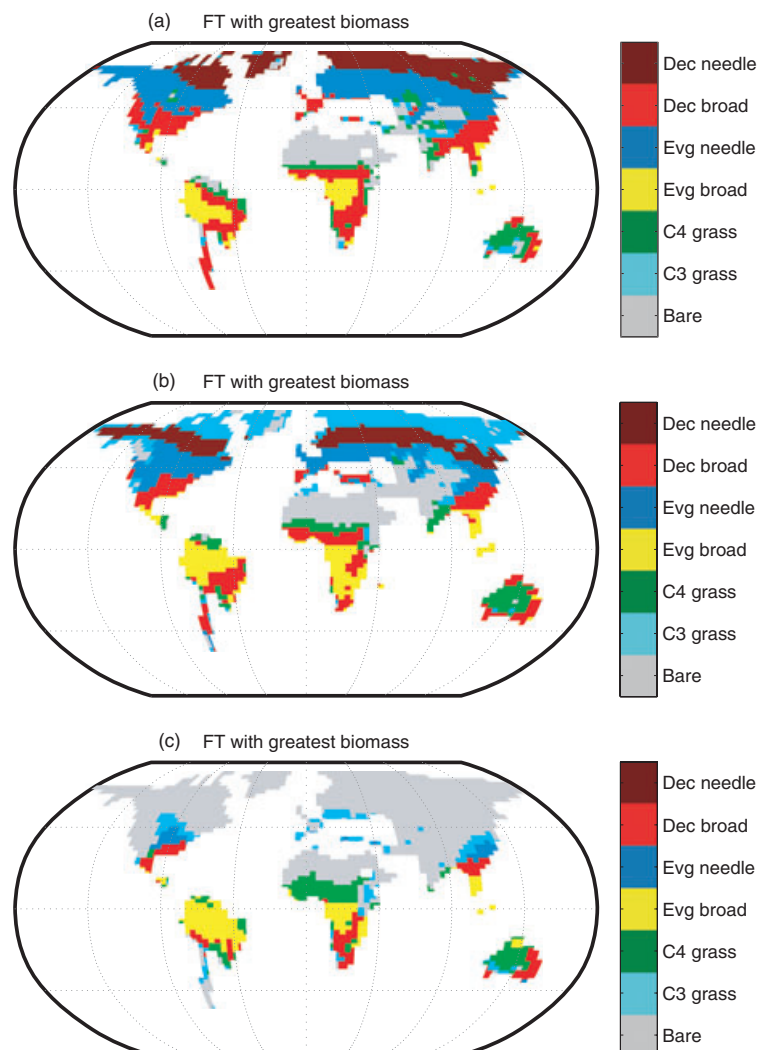
**Fig. 3.** Simulated global responses of (a) net primary production, (b) biomass and (c) soil nitrogen (N) for trees to falling late Miocene [CO<sub>2</sub>]<sub>a</sub> (400, 280, 180 and 100 p.p.m.), and climate change. (d–f) as for (a–c) but for grasslands, with either the C<sub>3</sub> or C<sub>4</sub> photosynthetic pathway.

Beerling 2009). Overall, these reactions determine the net flux of protons into and out of the subsurface environment and, therefore, the acid–base balance and its influence on the pH of the mineral weathering environment. Numerical routines are employed for calculating weathering rates on silicate rocks (basalt and granite) that incorporate simple yet rigorous equilibrium chemistry (Stumm & Morgan 1995) and rate laws (Palandri & Kharaka 2004; Brantley 2008).

The biological proton cycle weathering model is coupled to the Sheffield Dynamic Global Vegetation Model (SDGVM, Beerling & Woodward 2001), which is used to simulate the terrestrial carbon and nitrogen cycles. We force this coupled model offline with the Hadley Centre GCM (HadCM3L, Gordon *et al.* 2000; Pope *et al.* 2000; Cox *et al.* 2000) simulated Miocene climates (Fig. 2). SDGVM predicts the productivity and distribution of six major functional types of vegetation (Beerling & Woodward 2001) that are assigned a dominant AM or EM status (Table 1) after Read (1991). Simulated global patterns of vegetation activity, plant functional types, land surface hydrology and climate, in conjunction with an underlying lithological map of major rocks types (Amiotte-Suchet, Probst & Ludwig 2003), are used to model the biological proton cycle and soil solution chemistry. These provide the basis

for calculating spatially resolved Ca + Mg fluxes released by mineral dissolution, which are later corrected for the abiotic effects of run-off and erosion (Taylor *et al.* 2012). Our approach has been previously validated at the catchment scale with measurements from a global compendium that includes watersheds containing a range of vegetation types including boreal, temperate and tropical forests (Taylor *et al.* 2012).

In the simulations reported here, we used global Miocene climates (monthly fields of temperature, precipitation) simulated by HadCM3L at four [CO<sub>2</sub>]<sub>a</sub> values (100, 180, 280 and 400 p.p.m.) (Table 2). Details of the HadCM3L set-up (Cox *et al.* 2000), the boundary conditions of the simulations and comparison of the 280 p.p.m. [CO<sub>2</sub>]<sub>a</sub> climate with palaeoclimate evidence are given elsewhere (C. D. Bradshaw, D. J. Lunt, R. Flecker, U. Salzmann, A. M. Haywood, M. J. Pound unpubl. data). The assumed late Miocene palaeogeography and ice sheet extent is that of Markwick (2007), indicative of the interval 11.6–5.3 Ma. Model runs at each [CO<sub>2</sub>]<sub>a</sub> were integrated over 2100 years to ensure equilibrium of the ocean and atmosphere and mean climates generated using the last 50 years of the simulations. The rationale for these simulations is that we assume Miocene CO<sub>2</sub> and climate are broadly coupled, as suggested by palaeoevidence (Kürschner, Kvacek



**Fig. 4.** Simulated global distribution of plant functional types in the late Miocene for (a) 400 p.p.m. [CO<sub>2</sub>]<sub>a</sub> and climate; (b) 180 p.p.m. [CO<sub>2</sub>]<sub>a</sub> and climate; and (c) 100 p.p.m. [CO<sub>2</sub>]<sub>a</sub> and climate.

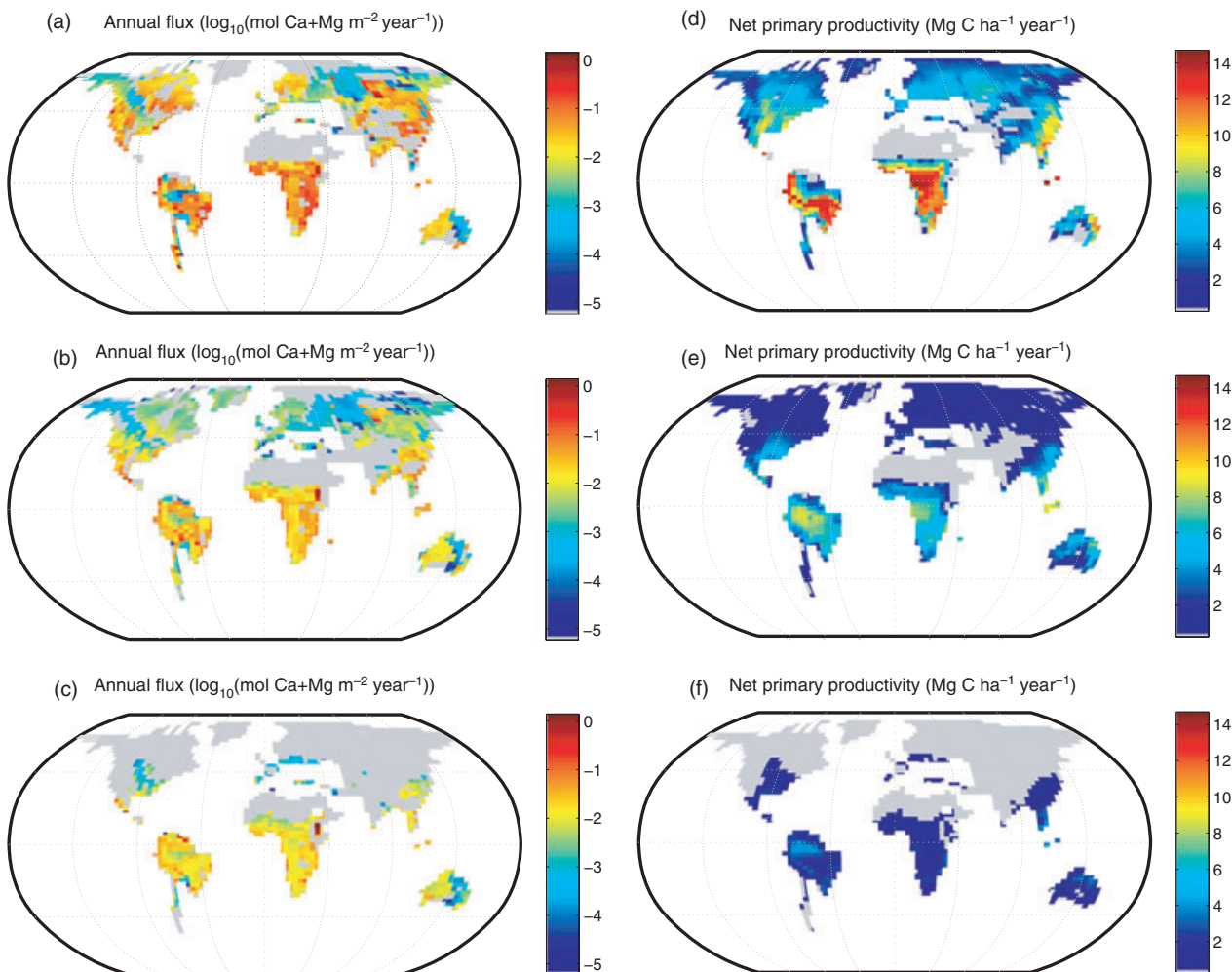
& Dilcher 2008; Lear, Mawbey & Rosenthal 2010). The alternative scenario whereby Miocene climate warmth is maintained by other factors (Shevenell, Kennett & Lea 2004; Pagani *et al.* 2005) as  $[\text{CO}_2]_a$  declines with the uplift of major orogenies is not considered here.

#### $[\text{CO}_2]_a$ AND MIOCENE CLIMATE EFFECTS ON TERRESTRIAL PRODUCTIVITY AND WEATHERING

Forests dominate global terrestrial primary production on Earth and are primary drivers of biological weathering on land (Berner 2004). In our late Miocene simulations, forest NPP, biomass and soil nitrogen (N) concentrations decline nonlinearly as  $[\text{CO}_2]_a$  decreases from 400 to 100 p.p.m. and the climate cools (Fig. 3a–c). Forest NPP and biomass are diminished both directly by decreasing  $[\text{CO}_2]_a$  reducing photosynthesis and indirectly by the reductions in geographical extent of boreal, temperate and tropical forests (Fig. 4a,b) owing to a cooling climate and increased aridification (Table 2). Aridification results from a less vigorous hydrological cycle in a cooler lower  $[\text{CO}_2]_a$  climate reducing evaporation from the oceans (Table 2). As the climate cools and becomes more arid with

the drop in  $[\text{CO}_2]_a$  from 400 to 180 p.p.m.,  $\text{C}_3$  grasslands expand into the high northern latitudes where they replace regions formerly occupied by boreal forests (Fig. 4a,b). This has the effect of allowing the global productivity of  $\text{C}_3$  grasslands to slightly increase (Fig. 3d). As a result of the spread of  $\text{C}_3$  grasslands into the cool high latitudes, soil N concentrations beneath this biome increase, an effect enhanced by the cool high-latitude climate slowing the rates of organic matter mineralization (Fig. 3f). The productivity of Miocene  $\text{C}_4$  grasslands declines as  $[\text{CO}_2]_a$  drops to 180 p.p.m. in spite of their CCM adaptation because of a cooling in the warm tropical/subtropical environments lowering photosynthetic efficiency (Fig. 3d,e). Under a 100 p.p.m.  $[\text{CO}_2]_a$  and climate, the terrestrial productivity of the biosphere declines (Fig. 3) drastically with the loss of forests and grasslands throughout extensive areas of the northern hemisphere because of aridity and low year-round temperatures (Fig. 4c).

These simulated responses of vegetation and soils extend earlier modelling results with pre-industrial climates (Pagani *et al.* 2009) by revealing biomass and soil nutrient responses to decreasing  $[\text{CO}_2]_a$  and Miocene climatic cooling, rather than  $[\text{CO}_2]_a$  alone, as examined previously. Although SDGVM does



**Fig. 5.** Global maps of terrestrial weathering under (a) 400 p.p.m.  $[\text{CO}_2]_a$  and climate and (b) 180 p.p.m.  $[\text{CO}_2]_a$  and climate and (c) 100 p.p.m.  $[\text{CO}_2]_a$  and climate. Panels (d–f) display corresponding maps of simulated terrestrial net primary production.

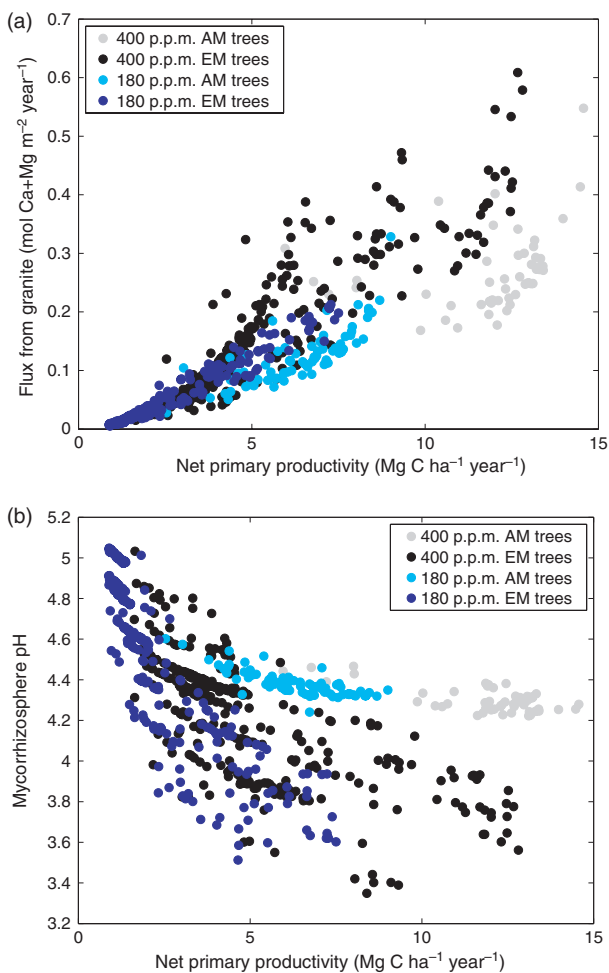


not directly simulate soil P supply and uptake, for which mycorrhizas play a critical role (Smith & Read 2008), there is a strong relationship between soil carbon and nitrogen contents, mycorrhizal activity and occurrence, and soil P (Read 1991; Woodward & Smith 1994; Beerling & Woodward 2001). Given that this situation often holds in forested regions, reductions in the N content of forest soils (Fig. 3c) point to a reduced demand for P under CO<sub>2</sub> starvation conditions (180–200 p.p.m.) and the requirement for mycorrhizas to supply them by weathering Ca-rich phosphate minerals.

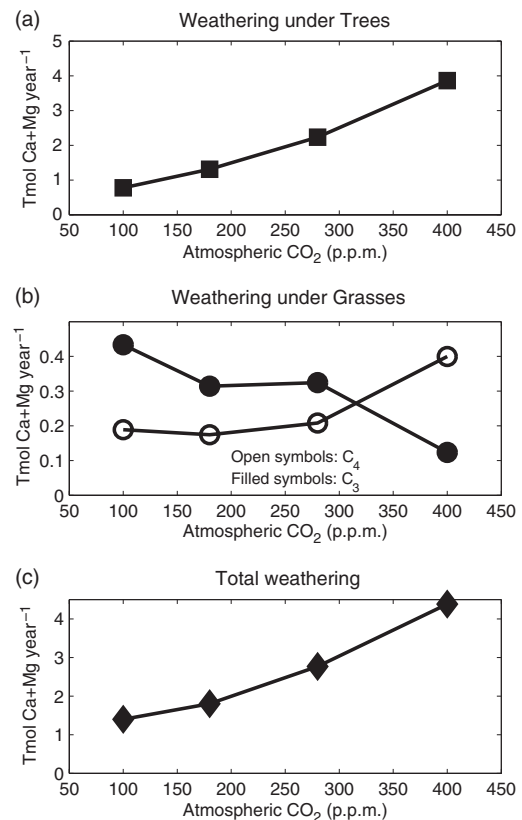
Global maps identify geographical patterns of weathering by plants and the areas producing the highest Ca + Mg fluxes from the dissolution of rocks (silicate weathering ‘hotspots’) (Fig. 5). Under the 400 p.p.m. [CO<sub>2</sub>]<sub>a</sub> and climate, weathering hotspots are located in the humid tropics, and on primary silicate terrains (i.e. granite and basalt) of eastern North America and eastern Asia (Fig. 5a). Comparison of the Ca + Mg flux weathering map at 400 p.p.m. [CO<sub>2</sub>]<sub>a</sub> and climate with that for the 180 p.p.m. [CO<sub>2</sub>]<sub>a</sub> and climate (Fig. 5b) reveals that terres-

trial weathering is diminished by an order of magnitude in the same regions with the imposition of a cool, low [CO<sub>2</sub>]<sub>a</sub> world (Fig. 5a,b). Regional-scale reductions in weathering correspond to those areas where low [CO<sub>2</sub>]<sub>a</sub> and climate limit terrestrial NPP (Fig. 5c,d), because the two sets of processes are linked via biological proton cycling in soils (Banwart, Berg & Beerling 2009). Climatic cooling, in combination with low NPP, drives reduced weathering in mid-latitude regions (Fig. 5). However, in the tropics, where relatively warm climates are maintained under low [CO<sub>2</sub>]<sub>a</sub>, land plants suffer the penalty of a high photorespiratory burden leading to reduced NPP and weathering (Fig. 5). Under the 100 p.p.m. [CO<sub>2</sub>]<sub>a</sub> and climate, weathering is concentrated in the low latitudes throughout Africa, South America and Australia where low NPP and vegetation cover is maintained (Figs 4c and 5c,f).

For individual forested grid cells, falling [CO<sub>2</sub>]<sub>a</sub> and climatic cooling reduces terrestrial NPP and slows the biological proton cycle by reducing nutrient uptake through roots and mycorrhizal fungi, thereby increasing pH and decreasing mineral dissolution. This is illustrated for the 400 and 180 p.p.m. [CO<sub>2</sub>]<sub>a</sub> simulations in Fig. 6a,b. In consequence, there is a tight coupling between increasing NPP of forests and increasing Ca + Mg weathering fluxes from silicate rocks, with a low [CO<sub>2</sub>]<sub>a</sub> and cooler climate switching the terrestrial biosphere to a lower productivity, lower weathering regime. Weathering rates track changes in soil pH in the vicinity of roots and



**Fig. 6.** Relationship between tree net primary production and (a) annual weathering of Ca + Mg from silicate rocks and (b) pH of the soil solution in the immediate vicinity of the roots and symbiotic fungi (termed the mycorrhizosphere). All fluxes are uncorrected for the effect of erosion and run-off on weathering to illustrate functional linkages between plant and fungal biology and geochemical processes.



**Fig. 7.** Simulated response of global terrestrial weathering by (a) forests, (b) C<sub>3</sub> and C<sub>4</sub> grasslands, and (c) for the terrestrial biosphere to falling late Miocene [CO<sub>2</sub>]<sub>a</sub> (400, 280, 180 and 100 p.p.m.) climate cooling.

mycorrhizal fungi (i.e. the mycorrhizosphere) driven by changes in NPP, with increasing NPP acidifying the soil solution (Fig. 6b). Silicate weathering fluxes of Ca + Mg by AM forests are typically lower for a given NPP than those by EM forests, regardless of the  $[\text{CO}_2]_a$  and climate. This effect arises because EM fungi secrete organic acids and focus all uptake activities required to support growth at individual mineral grains (Leake *et al.* 2008), whereas AM fungi share the burden of nutrient uptake with roots.

Overall, declining  $[\text{CO}_2]_a$  between 400 and 100 p.p.m. and climatic cooling translate into a six fold decline in the capacity of trees to weather silicate rocks at the global scale (Fig. 7a). Terrestrial weathering by both C<sub>3</sub> and C<sub>4</sub> grasslands tends to be about an order of magnitude less than that by forests and make a smaller contribution to total silicate weathering at the global scale (Fig. 7b). These results support the supposition that grasslands exert much less vigorous effects on continental silicate weathering than trees (Goddéris & Donnadieu 2009; Pagani *et al.* 2009). Weathering by C<sub>3</sub> grasslands increases with falling  $[\text{CO}_2]_a$  (Fig. 7b) because of their geographical expansion into high latitudes (Fig. 4a,b). Grasslands arrest, and can even reverse, the acidification and calcium depletion that normally occurs in forest soils (Hüttel & Schaaf 1995) but this mechanism is not represented in our modelling. Consequently, we may be overestimating the importance of grasslands in terrestrial weathering with declining  $[\text{CO}_2]_a$ .

Overall, a decline in  $[\text{CO}_2]_a$  between 400 and 100 p.p.m. and associated late Miocene climate cooling diminishes the capacity of the terrestrial biosphere to weather continental silicate minerals by a factor of 4 (Fig. 7c). This implies a strongly diminished biologically mediated long-term sink for CO<sub>2</sub> that would slow the rate of its decline during major orogenic events in the final 24 Ma of the Cenozoic (Fig. 7c).

## Conclusions

Our critical synthesis of the literature identified four mechanisms by which CO<sub>2</sub> starvation could limit ecosystem weathering of silicates on land. We evaluated two of these mechanisms linking weathering rates to plant primary productivity under a range of  $[\text{CO}_2]_a$  and late Miocene climate change scenarios: (i) decreasing below-ground C allocation reducing the surface area of contact between minerals and fine roots and mycorrhizal fungi and (ii) lower demand for soil nutrients reducing proton exchange and organic acid exudation in weathering of calcium-rich minerals. Global-scale simulations indicate that both mechanisms combine to diminish terrestrial weathering by vegetation and mycorrhizal fungi as  $[\text{CO}_2]_a$  falls from 400 to 100 p.p.m. and the climate cools non-linearly by a factor of 4. These results provide process-based model support for the existence of negative biological feedback mechanism weakening the long-term sink for atmospheric CO<sub>2</sub> as it declines with the uplift of mountainous terrains. However, more complete analyses require the representation of the two further proposed ecological mechanisms identified to attenuate biological weathering: reduced Ca leaching from forest soils and shifts in EM to AM associations in trees.

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## References

- Amiotte-Suchet, A., Probst, J.-L. & Ludwig, W. (2003) Worldwide distribution of continental rock lithology: implications for the atmospheric/soil CO<sub>2</sub> uptake by continental weathering and alkalinity river transport to the oceans. *Global Biogeochemical Cycles*, **17**, 1038–1051.
- Banwart, S.A., Berg, A. & Beerling, D.J. (2009) Process-based modeling of silicate mineral weathering responses to increasing atmospheric and climate change. *Global Biogeochemical Cycles*, **23**, GB4013 doi:10.1029/2008GB003243.
- Beerling, D.J. (2007) *The Emerald Planet. How Plants Changed Earth's History*. Oxford University Press, Oxford.
- Beerling, D.J. & Osborne, C.P. (2006) The origin of the savanna biome. *Global Change Biology*, **12**, 2023–2031.
- Beerling, D.J. & Royer, D.L. (2011) Convergent Cenozoic CO<sub>2</sub> history. *Nature Geoscience*, **4**, 418–420.
- Beerling, D.J. & Woodward, F.I. (2001) *Vegetation and the Terrestrial Carbon Cycle. Modelling the First 400 Million Years*. Cambridge University Press, Cambridge.
- Berner, R.A. (2004) *The Phanerozoic Carbon Cycle*. Oxford University Press, Oxford.
- Berner, E.K., Berner, R.A. & Moulton, K.L. (2003) Plants and mineral weathering: present and past. *Treatise on Geochemistry*, **5**, 169–188.
- Berner, R.A. & Caldeira, K. (1997) The need for mass balance and feedback in the geochemical carbon cycle. *Geology*, **25**, 955–966.
- Berner, R.A. & Kothavala, Z. (2001) GEOCARB III: a revised model of atmospheric CO<sub>2</sub> over Phanerozoic time. *American Journal of Science*, **301**, 182–204.
- Berner, R.A., Lasaga, A.C. & Garrels, R.M. (1983) The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *American Journal of Science*, **283**, 641–683.
- Blum, J.D., Klaue, A., Nezat, C.A., Driscoll, C.T., Johnson, C.E., Siccama, T.G. *et al.* (2002) Mycorrhizal weathering of apatite as an important calcium source in base-poor forest ecosystems. *Nature*, **417**, 729–731.
- Bond, W.J. (2008) What limits trees in C<sub>4</sub> grasslands and savannas? *Annual Reviews in Ecology, Evolution and Systematics*, **39**, 641–659.
- Bond, W.J., Midgley, G.F. & Woodward, F.I. (2003) The importance of low atmospheric CO<sub>2</sub> and fire in promoting the spread of grasslands and savannas. *Global Change Biology*, **9**, 973–982.
- Brantley, S. (2008) Kinetics of mineral dissolution. *Kinetics of Water-Rock Interaction* (eds S.L. Brantley, J. D. Kubicki & A.F. White), pp. 151–210. Springer, New York.
- Cerling, T., Harris, J.M., MacFadden, B.J., Leakey, M.G., Quadel, J., Eisenmann, V. & Ehleringer, J.R. (1997) Global vegetation change through the Miocene/Pliocene boundary. *Nature*, **389**, 153–158.
- Cox, P.M., Betts, R.A., Jones, C.D., Spall, S.A. & Totterdell, I.J. (2000) Acceleration of global warming due to carbon-cycle feedbacks in a coupled model. *Nature*, **408**, 184–187.
- Ehleringer, J. & Björkman, O. (1977) Quantum yields for CO<sub>2</sub> uptake in C<sub>3</sub> and C<sub>4</sub> plants: dependence on temperature, CO<sub>2</sub> and O<sub>2</sub> concentration. *Plant Physiology*, **59**, 86–90.
- Gerhart, L.M. & Ward, J.K. (2010) Plant responses to low [CO<sub>2</sub>] of the past. *New Phytologist*, **188**, 674–695.
- Gill, R.A., Polley, H.W., Johnson, H.B., Anderson, L.J., Maherali, H. & Jackson, R.B. (2002) Nonlinear grassland responses to past and future atmospheric CO<sub>2</sub>. *Nature*, **417**, 279–282.
- Goddéris, Y. & Donnadieu, Y. (2009) Biogeochemistry: climatic plant power. *Nature*, **460**, 40–41.
- Godwin, H. (1957) Arthur George Tansley 1871–1955. *Biographical Memoirs of Fellows of the Royal Society*, **3**, 227–246.
- Gordon, C., Cooper, C., Senior, C.A., Banks, H., Gregory, J.M., Johns, T.C. *et al.* (2000) The simulation of SST, sea ice extents and ocean heat transports in a version of the Hadley Centre coupled model without flux adjustments. *Climate Dynamics*, **16**, 147–168.

- Harman, O.S. (2004) *The Man Who Invented the Chromosome. The Life of Cyril Darlington*. Harvard University Press, Cambridge, MA.
- Hönisch, B., Hemming, N.G., Archer, D., Siddall, M. & McManus, J.F. (2009) Atmospheric carbon dioxide concentration across the mid-Pleistocene transition. *Science*, **324**, 1551–1554.
- Hüttel, R.F. & Schaaf, W. (1995) Nutrient supply in forest soils in relation to management and site history. *Plant and Soil*, **168/9**, 31–41.
- Jacobs, B.F., Kingston, J.D. & Jacobs, L.L. (1999) The origin of grass-dominated ecosystems. *Annals of the Missouri Botanical Garden*, **86**, 90–643.
- Jiménez-Moreno, G., Fauquette, S. & Suc, J.-P. (2008) Vegetation, climate and palaeoaltitude reconstructions of the Eastern Alps during the Miocene based on pollen records from Austria, Central Europe. *Journal of Biogeography*, **35**, 1638–1649.
- Jobby, E.G. & Jackson, R.B. (2003) Patterns and mechanisms of soil acidification in the conversion of grasslands to forests. *Biogeochemistry*, **64**, 205–229.
- Jordan, D.B. & Ogren, W.L. (1984) The CO<sub>2</sub>/O<sub>2</sub> specificity of ribulose-1,5-bisphosphate carboxylase/oxygenase. Dependence on ribulosebisphosphate concentration, pH and temperature. *Planta*, **161**, 308–313.
- Kerrick, D.M. & Caldeira, K. (1998) Metamorphic CO<sub>2</sub> degassing from orogenic belts. *Chemical Geology*, **145**, 213–232.
- Kgope, B.S., Bond, W.J. & Midgley, G.F. (2010) Growth responses of African savanna trees implicate atmospheric [CO<sub>2</sub>] as a driver of past and current changes in savanna tree cover. *Austral Ecology*, **35**, 451–463.
- Klein, C. (2002) *The 22nd Edition of the Manual of Mineral Science*. John Wiley & Sons, London.
- Knoll, A.H. (2003) The geological consequences of evolution. *Geobiology*, **1**, 3–14.
- Kürschner, W.M., Kvacek, Z. & Dilcher, D.L. (2008) The impact of Miocene atmospheric carbon dioxide fluctuations in climate and the evolution of terrestrial ecosystems. *Proceedings of the National Academy of Sciences*, **105**, 449–453.
- Landeweert, R., Hoffland, E., Finlay, R.D., Kuyper, T.W. & van Breemen, N. (2001) Linking plants to rocks: ectomycorrhizal fungi mobilize nutrients from minerals. *Trends in Ecology and Evolution*, **16**, 248–254.
- Leake, J.R., Johnson, D., Donnelly, D., Muckle, G., Boddy, L. & Read, D. (2004) Networks of power and influence: the role of mycorrhizal mycelium in controlling plant communities and agroecosystem functioning. *Canadian Journal of Botany*, **82**, 1016–1045.
- Leake, J.R., Duran, A.L., Hardy, K.E., Johnson, I., Beerling, D.J., Banwart, S.A. & Smits, M.M. (2008) Biological weathering in soil: the role of symbiotic root-associated fungi biosensing minerals and directing photosynthate-energy into grain-scale mineral weathering. *Mineralogical Magazine*, **72**, 85–89.
- Lear, C.H., Mawbey, E.M. & Rosenthal, Y. (2010) Cenozoic benthic foraminiferal Mg/Ca and Li/Ca records: toward unlocking temperatures and saturation states. *Paleoceanography*, **25**, PA4215.
- Lewis, J.D., Ward, J.K. & Tissue, D.T. (2010) Phosphorous supply drives non-linear response of cottonwood (*Populus deltoids*) to increases in CO<sub>2</sub> concentration from glacial to future concentrations. *New Phytologist*, **187**, 438–448.
- Long, S.P. (1991) Modification of the response of photosynthetic productivity to rising temperature by atmospheric CO<sub>2</sub> concentrations: has its importance been underestimated? *Plant Cell and Environment*, **14**, 729–739.
- Luthi, D., Le Floch, M., Bereiter, B., Blunier, B., Barnola, J.M., Siegenthaler, U., Raynaud, D., Jouzel, J., Fischer, H., Kawamura, K. & Stocker, T.F. (2008) High-resolution carbon dioxide concentration record 650,000–800,000 years before present. *Nature*, **453**, 379–382.
- Markwick, P.J. (2007) The paleogeographic and paleoclimatic significance of climate proxies for data-model comparisons. *Deep-Time Perspectives on Climate Change: Marrying the Signal From Computer Models and Biological Proxies* (eds M. Williams, A.M. Haywood, F.J. Gregory & D.N. Schmidt), pp. 251–312. The Micropaleontological Society Special Publications, The Geological Society, London.
- Micheels, A., Bruch, A.A., Uhl, D., Utescher, T. & Mossbrugger, V. (2007) A late Miocene climate model simulation with ECHAM4/ML and its quantitative validation with proxy data. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **253**, 251–270.
- Ouatmane, A., Hafidi, M., El Gharous, M. & Revel, J.C. (1999) Complexation of calcium ions by humic and fulvic acids. *Analisis*, **27**, 428–432.
- Pagani, M., Zachos, J.C., Freeman, K.H., Tipler, B. & Bohaty, S. (2005) Marked decline in atmospheric carbon dioxide concentrations during the Paleogene. *Science*, **309**, 600–603.
- Pagani, M., Caldeira, K., Berner, R.A. & Beerling, D.J. (2009) The role of terrestrial plants in limiting atmospheric CO<sub>2</sub> decline over the past 24 million years. *Nature*, **460**, 85–88.
- Palandri, J. & Kharaka, Y. (2004) *A Compilation of Rate Parameters of Water-Mineral Interaction Kinetics for Application to Geochemical Modeling*. US Geological Survey Open File Report 2004-1068. Geological Survey, Menlo Park, CA.
- Pearcy, R.W. & Ehleringer, J. (1984) Comparative ecophysiology of C<sub>3</sub> and C<sub>4</sub> plants. *Plant, Cell and Environment*, **7**, 1–13.
- Polley, H., Johnson, H.B., Marino, B.D. & Mayeux, H.S. (1993) Increase in C<sub>3</sub> plant water-use efficiency and biomass over glacial-to-present CO<sub>2</sub> concentrations. *Nature*, **361**, 61–64.
- Pope, V.D., Gallani, M.L., Rowntree, P.R. & Stratton, R.A. (2000) The impact of new physical parametrizations in the Hadley Centre climate model: HadAM3. *Climate Dynamics*, **16**, 123–146.
- Pound, M.J., Haywood, A.M., Slazmann, U., Riding, J.B., Lunt, D.J. & Hunter, S.J. (2011) A Tortonian (Late Miocene, 11.61–7.25 Ma) global vegetation reconstruction. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **300**, 29–45.
- Read, D.J. (1991) Mycorrhizas in ecosystems. *Experientia*, **47**, 376–391.
- Shevenell, A.E., Kennett, J.P. & Lea, D.W. (2004) Middle Miocene southern ocean cooling and Antarctic cryosphere expansion. *Science*, **305**, 1766–1770.
- Siegenthaler, U., Stocker, T.F., Monnin, E., Lüthi, D., Schwander, J., Stauffer, B. et al. (2005) Stable carbon cycle-climate relationship during the late Pleistocene. *Science*, **310**, 1313–1317.
- Smith, S.E. & Read, D.J. (2008) *Mycorrhizal Symbiosis*. Academic Press, London.
- Smits, M., Bonneville, S., Haward, S. & Leake, J.R. (2008) Ectomycorrhizal weathering, a matter of scale? *Mineralogical Magazine*, **72**, 135–138.
- Smolander, A., Loponen, J., Suominen, K. & Kitunen, V. (2005) Organic matter characteristics and C and N transformations in the humus layer under two tree species, *Betula pendula* and *Picea abies*. *Soil Biology and Biochemistry*, **37**, 1309–1318.
- Stumm, W. & Morgan, J. (1995) *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. John Wiley & Sons, Chichester, UK.
- Tansley, A.G. (1935) The use and abuse of vegetational concepts and terms. *Ecology*, **16**, 284–307.
- Taylor, L.L., Leake, J.R., Quirk, J., Hardy, K., Banwart, S.A. & Beerling, D.J. (2009) Biological weathering and the long-term carbon cycle: integrating mycorrhizal evolution and function into the current paradigm. *Geobiology*, **7**, 171–191.
- Taylor, L.L., Banwart, S.A., Leake, J.R. & Beerling, D.J. (2011) Modelling the evolutionary rise of ectomycorrhiza on sub-surface weathering environments and the geochemical carbon cycle. *American Journal of Science*, **311**, 369–403.
- Taylor, L.L., Banwart, S.A., Valdes, P.J., Leake, J.R. & Beerling, D.J. (2012) Evaluating the effects of terrestrial ecosystems, climate and CO<sub>2</sub> on weathering over geological time: a global-scale process-based approach. *Philosophical Transactions of the Royal Society*, **367**, in press.
- Van de Water, P.K., Leavitt, S.W. & Betancourt, J.L. (1994) Trends in stomatal density and <sup>13</sup>C/<sup>12</sup>C ratios of *Pinus flexilis* needles during the last glacial-interglacial cycle. *Science*, **264**, 239–243.
- Walker, J.C.G., Hays, P.B. & Kasting, J.F. (1981) A negative feedback mechanism for the long-term stabilization of earth's surface temperature. *Journal of Geophysical Research*, **86**, 9776–9782.
- Ward, J.K., Harris, J.M., Cerling, T.E., Wiedenhoeft, A., Lott, M.J., Dearing, M.D. et al. (2005) Carbon starvation in glacial trees recovered from the Le Brea tar pits, southern California. *Proceedings of the National Academy of Sciences*, **102**, 690–694.
- Wardle, D.A., Walker, L.R. & Bardgett, R.D. (1994) Ecosystem properties and forest decline in contrasting long-term chronosequences. *Science*, **305**, 509–513.
- Woodward, F.I. & Smith, T.M. (1994) Global photosynthesis and stomatal conductance: modelling the controls by soils and climate. *Advances in Botanical Research*, **20**, 1–41.
- Zeebe, R.E. & Caldeira, K. (2008) Close mass balance of long-term carbon fluxes from ice-core CO<sub>2</sub> and ocean chemistry records. *Nature Geoscience*, **1**, 312–315.

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