Global Change Biology (2001) **7**, 613–629

OPINION

The role of land plants, phosphorus weathering and fire in the rise and regulation of atmospheric oxygen

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Abstract

The evolution of vascular plants and their spread across the land surface, beginning ~420 Ma, progressively increased the rate of weathering of phosphorus from rocks. This phosphorus supply promoted terrestrial and marine productivity and the burial of organic carbon, which has been the major source of O_2 over geological timescales. Hence, it is predicted that the rise of plants led to an increase in the O_2 content of the atmosphere from ~12 vol %, 570–400 Ma to its present level of ~21 vol % by ~340 Ma. Previous modelling studies suggest that O_2 then rose to ~35 vol % ~300 Ma. Such high concentrations are difficult to reconcile with the known persistence of forests, because rising O_2 increases the frequency and intensity of vegetation fires, tending to decrease biomass and cause ecological shifts toward faster regenerating ecosystems. Rising O_2 also directly inhibits C3 photosynthetic carbon assimilation and increases the production of toxic reactive oxygen species in cells. These effects suppress plant-induced phosphorus weathering and hence organic carbon burial, providing a sensitive negative feedback on O_2. A revised model predicts that this mechanism could have regulated atmospheric O_2 within the range 15–25 vol % for the last 350 million years.

Keywords: atmospheric oxygen, evolution, fire, land plants, phosphorus, weathering

Received 23 October 2000; revised version received 18 January 2001 and accepted 21 January 2001

Introduction

Atmospheric oxygen has increased sporadically over Earth history to its present partial pressure of pO_2 ~0.21 atm, which corresponds to ~21 vol % (percentage by volume). Prior to the origin of life, there was a negligible amount of oxygen in the atmosphere near the Earth's surface ($pO_2 < 10^{-13}$ atm) (Kasting 1993). Oxygenic photosynthesis evolved in cyanobacteria over 2700 Ma (million years ago) (Buick 1992; Brocks *et al.* 1999) and possibly as early as 3800 Ma (Schopf 1993; Mojzsis *et al.* 1996; DesMarais 2000). This provided a large source of oxygen, but very little accumulated in the atmosphere ($pO_2 < 0.0008$ atm) until 2200 Ma (Rye & Holland 1998), because of the existence of counterbalancing oxygen sinks. Between 2200 and 2000 Ma oxygen increased significantly, exceeding 0.002 atm (Rye & Holland 1998) and peaking above 0.03 atm (Holland & Beukes 1990). Oxygen remained above 0.002 atm in the mid-Proterozoic (2000–1000 Ma) (Rye & Holland 1998) and rose again in the late Proterozoic (~1000–570 Ma), probably in a series of pulses (Knoll *et al.* 1986; DesMarais *et al.* 1992; Logan *et al.* 1995; Canfield & Teske 1996). It has been hypothesized that this rise in oxygen triggered the Cambrian 'explosion' (the evolutionary diversification of large metazoans) (Knoll 1996; Thomas 1997), but the associated oxygen concentration is poorly constrained. Based on modern analogues, members of the Cambrian fauna flourishing ~540 Ma required only pO_2 ~0.02–0.04 atm (corresponding to ~2.5–5 vol % for a constant N_2 reservoir) (Holland 1984) while existing geochemical models predict O_2 15–20 vol % in the early Phanerozoic (570–400 Ma) (Berner & Canfield 1989; Berner *et al.* 2000). Vascular land plants evolved ~420 Ma and were widespread by ~370 Ma when the first charcoal appears in the fossil record (Rowe & Jones 2000; Cressler 2001), providing the earliest convincing evidence for O_2 > 15 vol %.

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The oxygen content of the atmosphere has been remarkably stable since plants established on the land surface. A continuous record of fossilized charcoal indicates that since ~350 Ma there has been sufficient oxygen to sustain natural fires. Combustion experiments indicate that fire cannot be sustained in dry paper at 17 vol % O_2 (Watson 1978), and burning wood is extinguished when O_2 is reduced to between 19 and 13 vol %, depending on the orientation of the fuel (Rasbash & Langford 1968).

Forests have been widespread throughout the past 350 My, indicating that fires have never been so frequent as to prevent their regeneration. However, a small increase in O_2 above 21 vol % causes a large decrease in the ignition energy required to start a fire, which generates a rapid increase in fire probability (Watson 1978; Watson *et al*. 1978). The continuous existence of forests sets an upper limit on O_2 that has been estimated as ~25 vol % (Watson 1978; Lenton & Watson 2000b), although others argue for a higher limit (Beerling *et al*. 1998).

It is inferred that oxygen has remained within about 15–25 vol % of the atmosphere since the early Carboniferous. This is remarkable because the total reservoir of oxygen in the atmosphere and ocean is cycled through net primary production and heterotrophic respiration every ~4500 y, and the burial of reduced matter in sedimentary rocks and subsequent oxidative weathering replaces the oxygen reservoir every ~3.2 My. Yet the size of the reservoir has varied by less than a factor of 2 over a period of 350 My.

The results of geochemical modelling studies add to the 'oxygen puzzle'. Data on the abundance and organic carbon and pyrite sulphur contents of different sediment types have been used to force a mass-balance model (Berner & Canfield 1989) that predicts that atmospheric oxygen rose to ~35 vol % in the Carboniferous (~300 Ma), dropped to ~15 vol % in the Triassic (~200 Ma) and rose again to ~27 vol % in the Cretaceous–early Tertiary (~50 Ma). Similar oxygen variations are predicted when carbon and sulphur isotope records are used to drive a model with isotope fractionation sensitive to oxygen level (Berner *et al*. 2000). A rise and fall of insect gigantism (including giant dragonflies with 70 cm wingspans) occurred around 300 Ma and has been linked to the postulated peak of O_2 (Graham *et al*. 1995). However, the maximum O_2 predictions of the models appear inconsistent with the known persistence of forests, suggesting that the models are missing some key mechanisms that stabilize the reservoir of atmospheric oxygen.

Biogeochemical oxygen cycle

Figure 1 summarizes the main components of the biogeochemical oxygen cycle. The main source (input flux) of O_2 over geological timescales is the small remainder (currently ~0.1%) of that liberated by global net primary productivity, which is not consumed in aerobic respiration by heterotrophs or methane oxidation. This flux corresponds to the small amount of organic carbon that is buried in new sediments, escaping aerobic respiration or conversion to methane and subsequent oxidation. The effect of organic carbon burial is equivalent to that of photosynthesis:

$$CO_2 + H_2O \rightarrow CH_2O + O_2. \qquad (1)$$

The counter-balancing sink (output flux) of O_2 over long timescales is the oxidative weathering of organic carbon exposed in rocks on the continents and (to a lesser extent) the oxidation of organic carbon degassed by volcanic and metamorphic activity. This is sometimes called the 'respiration' of the rocks, because the overall chemical reaction is equivalent to aerobic respiration:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O. \qquad (2)$$

Currently ~1 × 10^{13} mol y^{-1} of O_2 are exchanged as a result of organic carbon burial and weathering (Betts & Holland 1991). Burial and weathering fluxes of the other main redox elements, iron and sulphur, provide secondary sources and sinks of O_2. Iron pyrite (FeS_2) is produced by bacteria that use sulphate and iron oxides as oxidants, converting both iron and sulphur to reduced form and liberating O_2. For each mole of sulphur buried 15/8 mol of O_2 are liberated. The reaction is reversed when pyrite undergoes oxidative weathering. Currently ~1.65 × 10^{12} mol y^{-1} of O_2 are exchanged as a result of pyrite burial and weathering (Van Cappellen & Ingall 1996). The total atmosphere–ocean O_2 reservoir is ~3.8 × 10^{19} mol (Betts & Holland 1991). Dividing this by the total net input flux of O_2 with respect to burial of reduced matter in the crust of ~1.2 × 10^{13} mol y^{-1}, gives a 'geological' residence time for O_2 of ~3.2 My. This is the average amount of time an oxygen atom spends in the atmosphere–ocean–biosphere system before being consumed in oxidizing reduced matter from the crust.

Within the atmosphere–ocean–biosphere system, each oxygen atom is consumed in heterotrophic respiration and liberated again by net primary production once every ~4500 y. This 'biological' residence time of O_2 is calculated by dividing the O_2 reservoir by the gross input flux of O_2 as a result of net primary production of ~8.4 × 10^{15} mol y^{-1}. However, the reservoir of reduced organic carbon in living and dead biomass of ~2.4 × 10^{17} mol (Schlesinger 1997) is over two orders of magnitude smaller than the O_2 reservoir. Therefore, changes in its size cannot greatly affect the amount of O_2 in the atmosphere (Duursma & Boisson 1994).

Stabilization of the amount of O_2 in the atmosphere relies on the long-term input or output flux of O_2 being

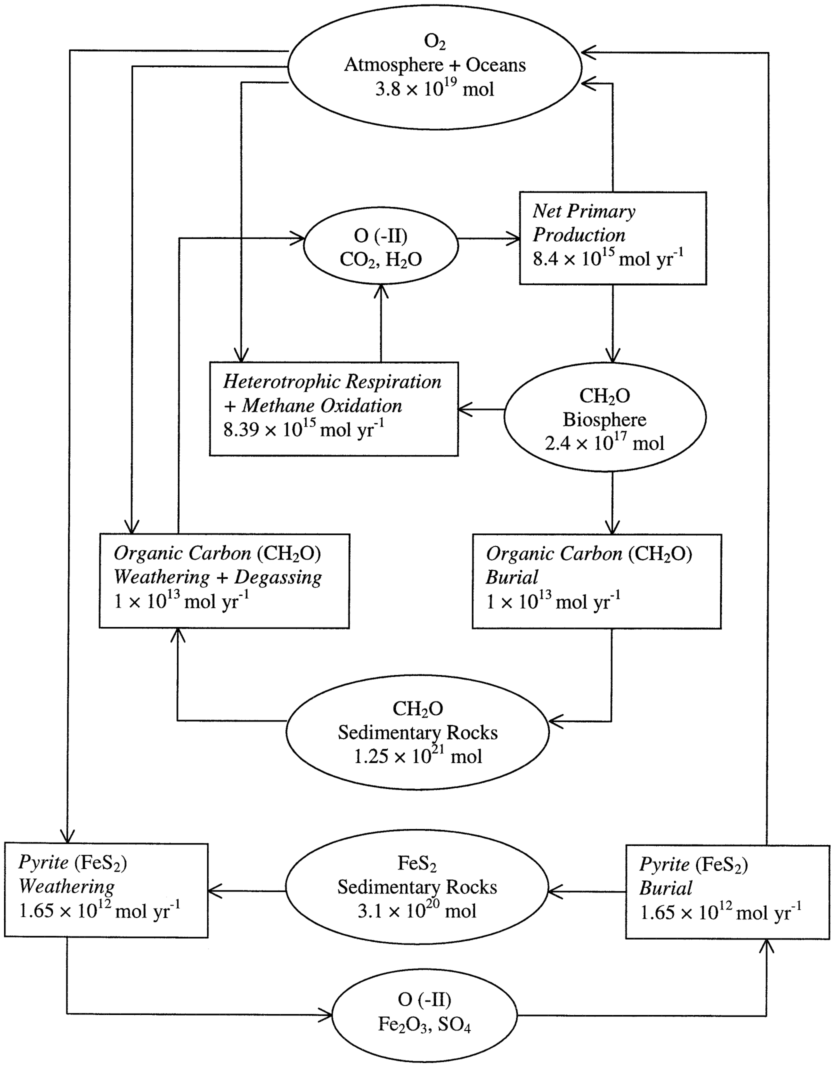

Fig. 1 The biogeochemical oxygen cycle. Ovals indicate reservoirs in moles of O_2 or reducing equivalents. Boxes indicate fluxes in moles of O_2 per year. Estimated values are from Schlesinger (1997), Betts & Holland (1991), Berner & Canfield (1989) and Van Cappellen & Ingall (1996).

sensitive to the O_2 concentration in a manner that counteracts change. This is described as 'negative feedback' — a change in the size of a reservoir causing a counteracting change in the input to or output from that reservoir. The long-term sink (output flux) of O_2 appears to be insensitive to the O_2 content of the atmosphere because nearly all the reduced matter exposed by weathering gets oxidized (the rocks bearing the majority of organic carbon and pyrite sulphur are shales that weather rapidly and completely) and reduced volcanic gases are also completely oxidized. Rising O_2 cannot increase the rate of exposure of sedimentary rocks to oxidative weathering, and O_2 would have to fall significantly before oxidation became incomplete. Hence, the rate of oxygen consumption is determined largely by the rate at which reduced matter is exposed to the atmosphere, and the regulation of atmospheric O_2 is thought to rely on negative feedback on the main source (input flux) of O_2: organic carbon burial (Walker 1974).

Organic carbon burial

Both marine and terrestrial productivity contribute to the eventual burial flux of organic carbon. At present most of this burial occurs in marine sediments on continental shelves and slopes (Hedges & Keil 1995). Global net primary production is roughly equally divided between the land and ocean. About 0.7% of terrestrial net primary productivity accumulates as soil organic matter (Schlesinger 1990), but this is approximately balanced by loss of organic carbon down rivers, leaving little organic carbon burial on land. The river organic carbon flux ($\sim 3.3 \times 10^{13}$ mol y^{-1}) is more than enough to account for all the organic carbon buried at sea (Schlesinger & Melack 1981), but much of it is labile and gets oxidized in estuaries and the marine environment. The refractory component ($\sim 1.25 \times 10^{13}$ mol y^{-1}) is more likely to reach marine sediments (Ittekkot 1988). About 0.3% of marine productivity ($\sim 1.3 \times 10^{13}$ mol y^{-1})

also reaches marine sediments (Berner 1982), and further oxidation occurs there. Of the organic carbon eventually buried, 10–50% is estimated to be land plant material (Haddad & Martens 1987; Kump 1993) implying that 90–50% is marine organic matter. In past epochs there was more organic carbon burial in sedimentation basins on land, e.g. in the coal swamps of the Carboniferous. Over the past 350 My, relatively coarse data for the abundance of different rock types (Ronov 1976) and approximate figures for their organic carbon content (Berner & Canfield 1989), suggest that ~77% of organic carbon has been buried in marine sediments and ~23% in terrestrial sediments. Prior to ~350 Ma, burial occurred almost exclusively in marine sediments.

The burial flux of organic carbon derived from terrestrial productivity depends on the flux of organic carbon produced on land and how resistant it is to consumption by heterotrophs. Only those compounds that are most difficult to biodegrade escape respiration. Lignins are most stable and make up the main component of buried terrestrial organic matter (Hedges *et al*. 1985). Terrestrial organic carbon production over long timescales is limited by nutrient supply, especially nitrogen and phosphorus. Phosphorus limitation is more widespread than generally acknowledged (Elser *et al*. 2000). In intermediate age soils (~20 ky) nitrogen and phosphorus can be co-limiting, but in old soils (~1 Myr) phosphorus tends to become the sole limiting nutrient (Chadwick *et al*. 1999). Phosphorus can even be limiting in young soils (~100 y) (Schlesinger *et al*. 1998). Nitrogen can be fixed from the atmosphere according to demand and hence may track phosphorus availability (Walker & Syers 1976), but phosphorus can only be supplied from rock weathering, or sources such as airborne dust and bird guano that ultimately depend on weathering (Chadwick *et al*. 1999). Therefore, the weathering flux of phosphorus provides the ultimate control of organic matter accumulation in terrestrial ecosystems and net loss from them (McGill & Cole 1981), which in turn affects the burial flux of terrestrially derived organic carbon.

The burial flux of organic carbon derived from marine productivity is determined primarily by sedimentation rate (the flux of organic carbon reaching the sediments) (Berner & Canfield 1989; Betts & Holland 1991), which is driven by primary productivity in the surface ocean (Müller & Suess 1979). The 'new' or 'export' production leaving the surface ocean is in turn determined by the supply flux of limiting nutrients to the surface ocean. Nitrogen is often the limiting nutrient in the surface ocean, in part because lack of iron limits nitrogen fixation (Falkowski 1997; Wu *et al*. 2000). Despite this, feedback mechanisms involving nitrogen fixation and denitrification cause nitrogen availability to track phosphorus availability (Lenton & Watson 2000a). Hence, it is changes in the reservoir of available phosphorus (as phosphate) in the ocean that determine marine productivity over long timescales (Lenton & Watson 2000a). The concentration of phosphate is controlled by the balance of input to the ocean via rivers and output from the ocean as different forms of phosphorus buried in marine sediments (Van Cappellen & Ingall 1994; Lenton & Watson 2000a). Phosphorus is carried by rivers in solution, in organic matter and bound to iron oxides. At the river–ocean interface, bacterial decomposition of organic matter and desorption from oxides releases phosphorus to solution (Berner & Rao 1994). These supplies of phosphorus to the ocean are ultimately fuelled by rock weathering on land. Hence, phosphorus weathering affects the burial fluxes of both marine and terrestrially derived organic carbon.

Hypothesized regulatory mechanisms

The negative feedback mechanisms on organic carbon burial that have been hypothesized to regulate the oxygen content of the atmosphere are summarized in Table 1 and most of them have been evaluated quantitatively elsewhere (Betts & Holland 1991; Kump 1993; Van Cappellen & Ingall 1996; Colman *et al*. 1997; Lenton & Watson 2000b).

Declining atmospheric oxygen tends to increase ocean anoxia. This may increase the efficiency of organic carbon burial in marine sediments (Holland 1973; Walker 1974), but available data suggest that any effect is weak (Betts & Holland 1991). The amount of time that organic carbon is exposed to oxygen in the sediments affects how much is preserved (Hartnett *et al*. 1998), but this may be controlled more by sedimentation flux than the oxygen content of bottom waters. More promising marine mechanisms involve redox control of the phosphorus cycle. Under anoxic bottom waters, less phosphorus is removed by sorption to iron minerals (Colman & Holland 2000) and the recycling of phosphorus from organic matter reaching the sediments is greater (Ingall & Jahnke 1994). Both effects tend to increase the amount of phosphate in the ocean, generating increased productivity and organic carbon burial (Van Cappellen & Ingall 1996). Rising oxygen ventilates the ocean and reverses these responses, tending to decrease organic carbon burial. However, all the marine mechanisms rely on there being some anoxia in ocean bottom waters. They are effective against declining oxygen but rising oxygen can remove anoxia and hence switch off the feedbacks (Lenton & Watson 2000b).

The main immediate victims of rising oxygen would be plants on land, especially slowly regenerating forests, and it has been suggested that they play a role in oxygen regulation (Lovelock 1988). Increasing fire frequency

Table 1 Hypothesized negative feedbacks on atmospheric oxygen

Hypothesis	Comments
H1: Organic carbon burial efficiency in marine sediments increased under anoxic conditions (Holland 1973; Walker 1974)	Effect is weak (Betts & Holland 1991) and disappears if rising oxygen removes anoxia (Lenton & Watson 2000b)
H2: Burial of phosphorus sorbed to iron minerals in marine sediments suppressed by anoxia (Colman & Holland 2000)	Effect disappears if rising oxygen removes anoxia (Lenton & Watson 2000b)
H3: Burial of organic phosphorus in marine sediments suppressed by anoxia (Ingall & Jahnke 1994; Van Cappellen & Ingall 1994)	Effect uncertain (Colman *et al*. 1997) and disappears if rising oxygen removes anoxia (Lenton & Watson 2000b)
H4: Fire triggers phosphorus transfer to the ocean where less organic carbon is buried per unit of phosphorus (Kump 1988, 1993)	Lack of evidence for greater C/P burial ratio of land plant organic matter (Kump & Mackenzie 1996).
H5: Fire triggers ecological shifts that suppress lignin production (Lovelock 1988)	Weak unless lignin is a major component of organic carbon burial, effect on ecology developed in H8
H6: Oxygen enhances lignin degradation by fungi (Robinson 1990)	Weak unless lignin is a major component of organic carbon burial
H7: Oxygen suppresses land plant growth (Tolbert *et al*. 1995) and the burial of plant organic matter	Fate of phosphorus must also be considered, effect on growth incorporated in H8
H8: Oxygen suppresses the amplification of phosphorus weathering by plants, via fire effects on ecosystem structure and direct effects on net primary productivity (Lenton & Watson 2000b)	Explored further in this study

transfers phosphorus from the land to the ocean, causing a shift from terrestrial to marine productivity. This should reduce overall carbon burial (Kump 1988), because the C/P ratio of terrestrial biomass is greater than that of marine biomass (Redfield 1958; Elser *et al*. 2000). However, there is a lack of evidence in continental shelf sediments for an increase in C/P burial ratios as the shore is approached, where terrestrial material should be more prevalent (Ingall & Van Cappellen 1990; Kump & Mackenzie 1996). Furthermore, the feedback is weak when the majority of organic matter being buried is marine-derived, and could become positive if water-column anoxia caused the marine C/P burial ratio to exceed the terrestrial C/P burial ratio (Ingall & Jahnke 1994; Lenton & Watson 2000b).

An alternative suggestion is that fire-induced changes in ecosystem composition suppress lignin production and, hence, reduce this component of organic carbon burial (Lovelock 1988). Increasing oxygen also enhances lignin degradation by fungi (Robinson 1990). However, lignin only makes up a small fraction of the total organic carbon burial flux, thus limiting the potential for changes in lignin burial to influence the oxygen balance. The detrimental effect of increasing oxygen on plant growth (Tolbert *et al*. 1995) has the potential to provide negative feedback by suppressing the burial of land plant matter. However, the fate of phosphorus must also be considered (Lenton & Watson 2000b). If, as vegetation is suppressed, more phosphorus is transferred to the ocean, then marine productivity and organic carbon burial will be enhanced (Kump 1988). Problems with these existing hypotheses led to a new proposal for oxygen regulation involving feedback on the source of phosphorus from the biological amplification of rock weathering (Lenton & Watson 2000b). This incorporates the effects of fires on ecosystem structure and of oxygen on plant growth and is developed herein.

Amplification of phosphorus weathering by plants

Vascular plant communities amplify the rate of weathering of many elements by about an order of magnitude relative to lichen and moss cover. Table 2 summarizes existing comparative studies, most of which underestimate plant-induced weathering by not accounting for the accumulation of ions in soil or vegetation (Benedetti *et al*. 1994). In the one study that took both factors into account, plants amplified weathering by a factor of 10 for Ca^{2+} and 18 for Mg^{2+} (Bormann *et al*. 1998). Accumulation of these ions in soils increased weathering rate estimates by factors of 3.3 for Ca^{2+} and 12.8 for Mg^{2+}, whilst accumulation in both vegetation and soils increased estimates by factors of 8 for Ca^{2+} and 23 for Mg^{2+} (Bormann *et al*. 1998). This suggests the need for significant upward revisions of the other estimates in Table 2.

Plants amplify weathering through a range of mechanisms (Schwartzman & Volk 1991). Soils are 'biotic constructs', which retain water and maintain aqueous

Table 2 Amplification of weathering by vascular plants

Reference(s)	Vegetation	Contrasted with	Location	Factors accounted for	Element	Amplification
(Bormann *et al.* 1998)	Red pine	Moss / lichen	Hubbard Brook, New Hampshire	Accumulation in vegetation and soil	Ca^{2+} Mg^{2+}	10 18
(Moulton & Berner 1998)	Birches / evergreen trees	Moss / lichen (no soil)	West Iceland	Accumulation in vegetation	Ca^{2+}, Na^{+}, HCO_3-, Si Mg^{2+} K^{+}	2-3* 3-5* 110-150*
(Drever & Zobrist 1992; Moulton & Berner 1998)	Deciduous forest	Rock (un-vegetated)	Southern Swiss Alps	Temperature differences with elevation	HCO_3^-, Si	8**
(Arthur & Fahey 1993)	Forest (spruce and fir, 6% of watershed)	Whole watershed (mostly un-vegetated)	Colorado Rocky Mountains		$Ca^{2+} + Na^{+} + Mg^{2+} + K^{+}$	3.5**
(Cawley *et al.* 1969)	Higher plants	Lichen	Central Iceland		HCO_3^-	2-3**

*Does not account for accumulation in soils hence underestimate (Bormann *et al.* 1998).
**Does not account for accumulation in vegetation or soils hence greater underestimate (Bormann *et al.* 1998).

contact with a high surface area of mineral grains, thus maximizing weathering (Breemen 1993). Vegetation enhances the hydrological cycle, increasing precipitation (Betts 1999), which increases weathering rate (White & Blum 1995). Root respiration and heterotrophic respiration of plant litter generate increased soil pCO_2 and thus acidify soil water (Andrews & Schlesinger 2001). Some plants secrete organic acids from their roots. Symbiotic mycorrhizal fungi also secrete organic acids and chelating agents that dissolve minerals and enhance rock porosity (Cochran & Berner 1996; Jongmans *et al*. 1997). Tree roots enhance physical weathering by splitting rocks. Plants remove the soluble products of weathering, enhancing the reactions that produce them (by Le Chatelier's principle).

Natural selection may have driven the evolution of rock weathering traits because plants that amplified weathering, directly or in symbiosis with mycorrhizal fungi, benefited by acquiring phosphorus and other rock-bound nutrients (Lenton 1998). The amplification factor for weathering of phosphorus has not been measured directly but is likely to be greater than that for Ca, Mg or the bulk weathering of rock, given that plants have a high requirement for phosphorus, rocks are ultimately the only source and P-rich apatite is relatively easily weathered compared to Ca and Mg bearing silicates. The 'cycling ratio' for phosphorus in terrestrial ecosystems of ~50 (the ratio of the flux through photosynthesis to the input flux) is among the highest for any element (Volk 1998), indicating that it is in high demand relative to its availability from rocks. In contrast, the calcium cycling ratio is ~1, indicating that the source from weathering meets biotic requirements.

Different types of rock weather at different rates, and most studies have focused on silicate minerals, because weathering of these provides a key control of carbon dioxide and global temperature over geological timescales (Brady 1991; Berner 1994). However, the weathering of phosphorus-rich minerals is what is important for oxygen control. Phosphorus is incorporated in sedimentary rocks in three main forms: as calcium phosphate minerals (including carbonate fluorapatite), as organic matter, and bound to iron minerals (Van Cappellen & Ingall 1996). After diagenesis, much of the phosphorus is converted to carbonate fluorapatite (Ruttenberg & Berner 1993). Phosphorus is also present in igneous rocks, especially in igneous fluorapatite (Guidry & Mackenzie 2000).

Weathering of sedimentary and igneous calcium phosphates (apatites) is the largest phosphorus source (Guidry & Mackenzie 2000) and its rate is strongly influenced by plant activities, temperature and acidity. Rock phosphates are alkaline and thus dissolve more readily in acid and waterlogged soils. Some plants dissolve rock phosphates by excreting citric and malic (organic) acids (e.g. rape, white lupin) (Dinkelaker *et al.* 1989; Hoffland *et al.* 1992), others by taking up an excess of cations over anions and thus generating an H^+ efflux (e.g. field bean, ryegrass, Rhodes grass) (Bekele *et al.* 1983). High Ca uptake (e.g. buckwheat) may also encourage dissolution of calcium phosphate minerals (Bekele *et al*. 1983).

As ecosystems develop, phosphorus is converted from mineral form to occluded (oxide-bound phosphate), nonoccluded (sorbed phosphate) and organic forms (Walker & Syers 1976). After ~20 000 y, weathering reduces mineral phosphorus to negligible concentrations (Walker & Syers 1976; Crews *et al*. 1995). Plants respond to phosphorus deficiency by root elongation growth, root hair formation, increased extra-cellular phosphatase activity, allocation of carbohydrate to roots, and release of exudates (amino acids, other organic acids and sugars) (Dinkelaker *et al*. 1989). Through these mechanisms, plants increase their phosphorus uptake and decouple it from the oxidative consumption of organic carbon (McGill & Cole 1981). Release of oxalate (e.g. slash pine) increases the availability of organic and inorganic phosphorus in soils by triggering ligand-exchange reactions at phosphorus-bearing oxide surfaces (Fox & Comerford 1992a). Phosphatase enzymes convert organic phosphorus to inorganic form, thus making it available to plants (Fox & Comerford 1992b). By allocating carbohydrate to roots and releasing exudates, plants encourage infection by mycorrhizal fungi that enhance their phosphorus uptake efficiency (Marx *et al*. 1977). Phosphate-solubilizing bacteria in the rhizosphere can also enhance plant growth (Laheurte & Berthelin 1988).

Phosphorus loss is thought to peak as ecosystems become established and to decline as the soil is stabilized (Walker & Syers 1976), although total phosphorus shows no consistent trend with age in Hawaiian soils (Crews *et al*. 1995). Ultimately, undisturbed ecosystems tend towards a steady state with low phosphorus input and losses, and high internal phosphorus cycling (Filippelli & Souch 1999). In such a state, plants have extracted all the available mineral phosphorus and are no longer enhancing primary weathering. However, the whole process of ecosystem development and weathering can be reset, for example by glacial scouring (Filippelli & Souch 1999).

By extracting phosphorus from continental rocks and converting it to biologically available forms, plants stimulate terrestrial and marine productivity and organic carbon burial, thus stimulating the major source of oxygen to the atmosphere. Without plants it is suggested that phosphorus weathering would be incomplete, and that the flux of biologically available phosphorus to the land and ocean would be suppressed.

The rise of plants and atmospheric oxygen

If the amplification of phosphorus weathering by plants is significant, it implies that the rise of plants may have first forced O_2 up to the present concentration. Prior to plants, the weathering flux of phosphorus would have been smaller, the burial flux of organic carbon correspondingly reduced, and the oxygen concentration of the atmosphere significantly lower (a revised estimate is made below). As plants evolved, this accelerated the rate of rock weathering, supplying an increased flux of phosphorus to the land and ocean, thus driving increased organic carbon production and burial and a rise of O_2.

Early plants and their effects on weathering

The earliest land plants (embryophytes) probably appeared by the end of the Cambrian period (~510 Ma), but were nonvascular and restricted to moist habitats (Raven 1995; Niklas 1997; Strother 2000). Upright vascular plants appeared ~420 Ma in the Silurian period, but they were small, lacked roots and mostly reproduced with spores that tied them to moist conditions (Raven 1995). Key plant effects on weathering evolved during the Devonian period (400–360 Ma) (Algeo & Scheckler 1998). Shallow rooting began ~390 Ma and with it came the potential to significantly affect weathering processes. The first trees (the archeaopterids) appeared ~380 Ma, and then seed plants evolved ~365 Ma. The successful colonization of the land by vascular plants may have relied on the evolution of a mutually beneficial symbiosis with mycorrhizal fungi (Pirozynski & Malloch 1975; Simon *et al*. 1993). Fungal hyphae appear able to selectively weather nutrient-rich intrusions in rocks (Cochran & Berner 1996) and supply nutrients directly to the plant (Jongmans *et al*. 1997). Arborescence (tree stature) increased maximum rooting depths, soil mixing (rhizoturbation) and net primary productivity. The seed habit freed plants from reproductive dependence on moist lowlands and allowed colonization of drier uplands, thus increasing the geographical extent of vascular plants. A combination of these effects increased weathering rates, as seen in early forest soils (Retallack 1997).

Global consequences

A plant-induced increase in weathering in the Devonian has previously been linked to increased nutrient supply to the ocean, high marine productivity, increased ocean anoxia and high sedimentary organic carbon fluxes (Algeo & Scheckler 1998), but not to rising O_2. Rising O_2 has been independently inferred from rock data (Ronov 1976) and carbon isotopes (Hayes *et al*. 1999) that indicate an increase in global organic carbon burial rate. Models driven by such data predict a rise in O_2 reaching 21 vol % ~350 Ma (Berner & Canfield 1989; Berner *et al*. 2000). Rising O_2 in the Devonian is also consistent with the first appearance of fossil charcoal ~370 Ma

(Rowe & Jones 2000; Cressler 2001). The proposal that the evolution of rooted plants in the Devonian led to an increase in O_2 complements existing suggestions that this led to a simultaneous order-of-magnitude decrease in atmospheric CO_2 concentration and significant global cooling (Berner 1994).

Previous discussions linking the activities of plants to atmospheric O_2 have focused on the Carboniferous and on processes other than weathering (Berner & Canfield 1989; Robinson 1990; Berner 1999). The appearance of land plants provided a new source of organic carbon for burial. For the first time, significant amounts of organic carbon were buried on land and transported to the ocean via rivers. Lignin provided an important component. There is some indication that early trees were more lignin rich than those of today, and that there may have been a significant delay in the evolution and spread of fungi that can biodegrade lignin (Robinson 1990). These effects must have begun in the Devonian but had their greatest impact in the Carboniferous when the presence of extensive, poorly drained flatlands and large coastal plains allowed the development of vast swamps on the continents (Berner 1999).

Figure 2 shows a tentative scenario for changes in phosphorus cycling, organic carbon burial and atmospheric oxygen resulting from the rise of land plants. Lower O_2 levels prior to the appearance of land plants would have generated a more anoxic ocean (Fig. 2a). As a consequence, phosphorus may have been more efficiently recycled from marine sediments (Table 1: H2, H3) counteracting the lower phosphorus input to the ocean, and organic carbon may have been more efficiently buried (H1). The postulated increase in phosphorus weathering during the Devonian would have generated transient increases in the reservoir of phosphate in the ocean, marine productivity and anoxia that supported a high marine organic carbon burial flux (Fig. 2b). Marine phosphate responds much faster than atmospheric O_2 because it has a much shorter geological residence time of ~10–20 ky at present (Colman & Holland 2000; Lenton & Watson 2000a) (although the residence time in the past is uncertain). As O_2 rose and CO_2 and temperature fell, phosphorus weathering would have decreased again. Ocean anoxia would also have declined, potentially reducing the efficiency of phosphorus recycling (H2, H3) and organic carbon burial (H1) in the ocean. The system may have reached a state similar to today (Fig. 2c) in the early Carboniferous ~350 Ma.

The hypothesis that the rise of land plants first caused oxygen to reach 21 vol % of the atmosphere is attractive partly because the mechanisms for oxygen regulation, that were present before plants appeared, are not very effective at preventing oxygen from rising significantly above the present level (Lenton & Watson 2000b). Thus,

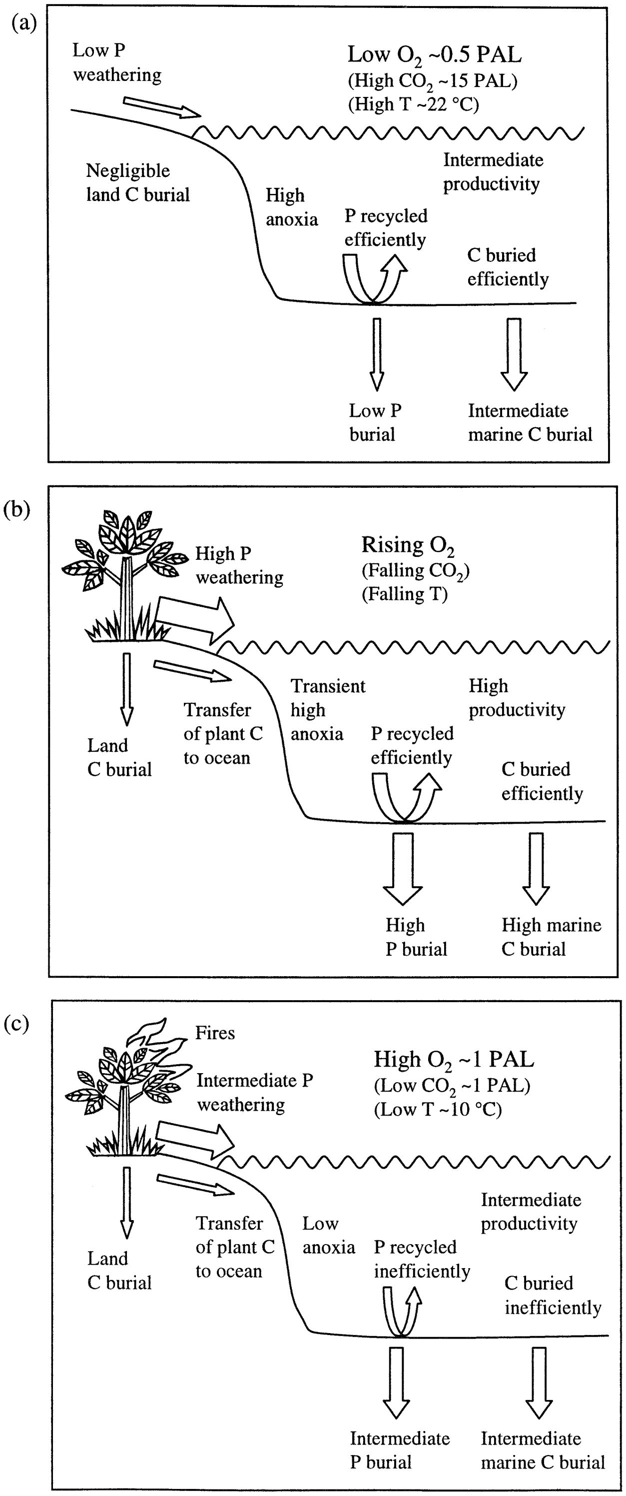

Fig. 2 Postulated changes in phosphorus cycling, organic carbon burial and atmospheric oxygen resulting from the rise of land plants: (a) preplant state, (b) transient behaviour, and (c) new state with plants. (PAL, present atmospheric level in atm.) Changes in atmospheric CO_2 and temperature are those predicted by Berner (1994).

if some process had caused oxygen to exceed 21 vol % before the advent of vascular plants there may have been nothing to stop it rising further and creating a fire regime hostile to the evolution of land plants.

Negative feedback on oxygen

If land plants were responsible for increasing the oxygen content of the atmosphere, they also inadvertently generated detrimental effects on future generations of vegetation. Increases in atmospheric oxygen lower the ignition energy of fire, inhibit photosynthetic carbon fixation, and increase the production of toxic oxygen species in cells, thus suppressing vegetation. These effects have the potential to stabilize the oxygen content of the atmosphere by suppressing phosphorus weathering and organic carbon burial (Fig. 3) (Lenton & Watson 2000b).

Effects of increasing oxygen on land plants

The effect of the oxygen mixing ratio (vol %) on ignition energy has been quantified experimentally and related to fire probability (Watson 1978). For paper fuel of moisture content ~20%, representative of the leaf litter where forest fires often start, the probability of ignition increases very steeply with increases in oxygen above 21 vol % (Lenton & Watson 2000b). The resulting increase in the frequency and intensity of fires will tend to reduce biomass and trigger ecological shifts from forest toward faster regenerating ecosystems (e.g. grassland).

The effect of O_2/CO_2 ratio on photosynthetic carbon fixation by Rubisco has been measured for a few species, and results from the literature are summarized in Table 3. In C3 plants, total growth (dry matter accumulation), vegetative growth rate and leaf photosynthetic CO_2 uptake rate are suppressed by elevated O_2. This is in agreement with the predictions of a biochemical model (Farquhar *et al.* 1980; Beerling *et al.* 1998). At given CO_2 and temperature levels, an O_2 compensation point exists above which net O_2 uptake occurs and plants slowly senesce, although net CO_2 fixation continues (Tolbert *et al.* 1995). The O_2 compensation points for tobacco and spinach are only 27 and 28 vol % O_2 at 350 ppmv CO_2. The implication is that 35 vol % O_2 and present CO_2 levels would prevent the growth of at least some C3 plants. The birch seedlings grown under 35 vol % O_2 and 350 ppmv CO_2 (Beerling *et al.* 1998) were not studied for a sufficient period to determine whether they would survive and reach reproductive maturity (D. J. Beerling, pers. comm.). However, both birch and tobacco are relatively recently evolved, and photosynthetic rates in more ancient groups (cycad, ginkgo and ferns) are less sensitive to increasing O_2 (Beerling *et al.* 1998).

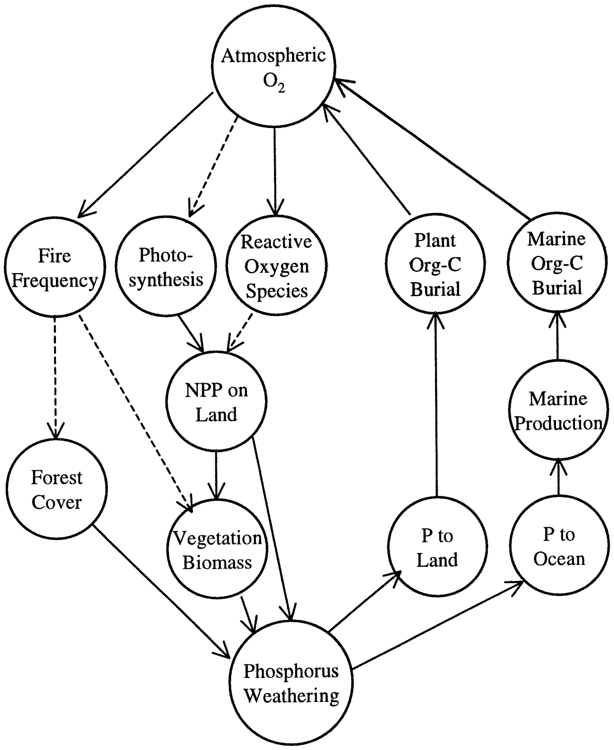

Fig. 3 Hypothesized oxygen regulator involving land plants and their amplification effect on phosphorus weathering (H8). Bold arrows indicate a direct relationship (e.g. increasing O_2 increases fire frequency). Dashed arrows indicate an inverse relationship (e.g. increasing fire frequency decreases forest cover). Negative feedback loops, which have an odd number of inverse relationships, can be traced around the diagram.

Global net primary productivity (NPP) is predicted to decline by ~20% for a postulated increase in O_2 from 21 to 35 vol % with 300 ppmv CO_2 (Beerling & Berner 2000) although other studies suggest plants would not survive (Tolbert *et al.* 1995). The rate of production of toxic reactive oxygen species in cells also increases with O_2 concentration (Raven *et al.* 1994). The resulting damage should demand increased maintenance respiration, tending to further reduce NPP (Raven *et al.* 1994). However, modest increases in CO_2 counteract the detrimental effects of elevated O_2 (Tolbert *et al.* 1995; Beerling & Berner 2000).

Suppression of phosphorus weathering

Changes in ecosystem composition caused by rising fire frequency should suppress phosphorus weathering, because herbaceous ecosystems have shallower rooting systems than forests and sometimes have lower productivity (Kelly *et al.* 1998). When rainforest is converted to pasture, productivity declines, soil organic carbon is

Table 3 Experimentally determined effects of elevated O_2 on plant growth

Species	Type	CO_2 (vol%)	Temp (°C)	O_2 (vol%)	Measured variable	Time	Effect (relative to 21 vol % O_2)	Reference
Glycine max (soybean)	C_3	0.03	-	40	Dry matter accumulation	70 days	-45%	(Quebedeaux & Hardy 1975)
		0.06	-	40		70 days	-68%	
Panicum bisculatum	C_3	0.032	30	40	Vegetative growth rate	14 days	-38%	(Quebedeaux & Chollet 1977)
						26 days	-25%	
Panicum milioides	C_3-C_4	0.032	30	40		14 days	-14%	
						26 days	-20%	
Panicum miliaceum	C_4	0.032	30	40		26 days	None	
Spinacea oleracea (spinach)	C_3	0.035	20	28*	O_2 exchange	-	-100%*	(Tolbert *et al.* 1995)
Nicotiana tobacum (tobacco)	C_3	0.035	20	27*	O_2 exchange	-	-100%*	(Tolbert *et al.* 1995)
		0.022	20	23*		-	-100%*	
		0.07	20	35*		-	-100%*	
		0.035	20	35	CO_2 uptake	-	-23%	(Tolbert *et al.* 1995)
		0.035	25	35		-	-38%	(Beerling *et al.* 1998)
Betula pubescens (birch)	C_3	0.035	25	35	CO_2 uptake	-	-29%	(Beerling *et al.* 1998)

*O_2 compensation point, no net O_2 exchange

lost, and base cations are retained, suggesting an overall decline in weathering rate (Kelly *et al.* 1998). CO_2 sequestration by weathering is significantly less in moist temperate grassland than deciduous forest (Chadwick *et al.* 1994). However, greater weathering fluxes of Si, Ca, Mg, K and Na have been measured in grassland than in beech forest (Lelong *et al.* 1990). If weathering fluxes of phosphorus were greater under grassland than forest, this would contradict the suggested mechanism. However, there is a need to consider other herbaceous ecosystems, because grasslands originated relatively recently in the Tertiary. At very high fire frequencies the survival of any vegetation would be threatened, and weathering must then be significantly suppressed.

Declining NPP caused by rising O_2 should also suppress phosphorus weathering because NPP provides the source of carbohydrates for the plant and mycorrhizal fungal processes that enhance weathering, and it is the source of organic carbon for heterotrophic respiration in the soil that enhances weathering. Suppression of NPP causes biomass and soil organic carbon stores to decline and weathering rate has been positively linked to NPP, biomass and soil organic carbon (Kelly *et al.* 1998).

Closing the loop

Suppression of phosphorus weathering reduces the supply of phosphorus to the land and ocean, which in turn suppresses marine and terrestrial productivity and organic carbon burial, providing a negative feedback against rising oxygen (Fig. 3). The decline of oxygen is counteracted by increased plant growth, rock weathering and phosphorus supply to the land and ocean, that fuels organic carbon burial. Model studies suggest that this feedback mechanism is the most effective oxygen regulator yet proposed (Lenton & Watson 2000b). The set point of the regulator appears to be determined by an extreme sensitivity of ignition energy and fire frequency to rises in oxygen above 21 vol % of the atmosphere. This is to some degree determined by the moisture content of the fuel, such that under a wetter climate the set point may shift to a somewhat higher oxygen level. Also, evolution of fire tolerant and/or fire exploiting plant strategies could alter the feedback and increase the threshold somewhat.

Revised Phanerozoic oxygen predictions

In order to illustrate the potential importance of the highlighted mechanism, it has been incorporated in an existing model (Berner & Canfield 1989) and revised predictions made of atmospheric oxygen over Phanerozoic time (the last 570 My). The methodology is described in the Appendix and results are shown in Fig. 4. An α factor is introduced, which represents the amplification of phosphorus weathering with plants relative to its value without them, including indirect effects of changes in CO_2 and global surface temperature. The control run ($\alpha = 1$) attempted to reproduce the results of Berner & Canfield (1989). This is contrasted with a run in

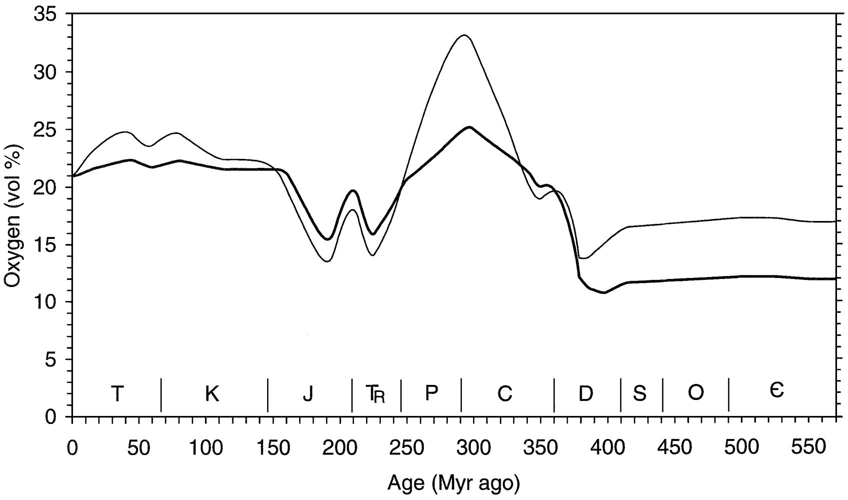

Fig. 4 Predicted atmospheric oxygen over Phanerozoic time (the last 570 My), based on Berner & Canfield's (1989) mass-balance model and forcing data. The feint line (control run) is an attempt to reproduce their results. The effect of plants on phosphorus weathering and resulting negative feedback on oxygen (Fig. 3) were then added to the model as described in the appendix. Plants are assumed to have begun to affect phosphorus weathering 400 Ma and to have doubled its rate by 360 Ma ($\alpha = 2$). From then on half of the phosphorus weathering flux is affected by vegetation. The bold line shows the revised oxygen predictions. The different geological periods are indicated: Cambrian (Є), Ordovician (O), Silurian (S), Devonian (D), Carboniferous (C), Permian (P), Triassic (TR), Jurassic (J), Cretaceous (K), Tertiary (T).

which the appearance of widespread, deep-rooted vascular land plants (and counteracting changes in CO_2 and temperature) are assumed to have doubled the rate of phosphorus weathering ($\alpha = 2$). Correspondingly, half of the phosphorus weathering flux is affected by vegetation.

The value of α is poorly constrained but is probably greater than 1 and significantly less than 10. Plants alone may initially have amplified phosphorus weathering by a factor of ~10 (Table 2 and discussion above), but CO_2 and temperature declined until the weathering rate of silicate minerals once again balanced volcanic and metamorphic inputs of CO_2 (Berner & Caldeira 1998). The weathering flux of phosphorus from silicates would have declined accordingly. Declining temperature would also have suppressed the weathering rates of other phosphorus bearing minerals. The estimated activation energy for dissolution of phosphorus-rich apatite (~63 kJ mol^{-1}) (Guidry & Mackenzie 2000) is in the range of values for different silicates (Brady 1991), indicating a similar responsiveness to temperature change. Declining CO_2 reduces soil water acidity, thus slowing the dissolution of many minerals, including calcium phosphates. However, phosphorus weathering is decoupled from silicate weathering by plants selectively extracting phosphorus from rocks. This allows $\alpha > 1$ with plants increasing the efficiency of phosphorus weathering relative to silicate weathering.

Cambrian, Ordovician and Silurian (570–400 Ma)

The assumption that the phosphorus weathering flux was lower before rooted vascular plants leads to lower estimates for O_2 in Earth's atmosphere in the interval 570–400 Ma. In the illustrative scenario ($\alpha = 2$), O_2 ~12 vol % (corresponding to 1.95×10^{19} mol) is predicted, rather than O_2 ~17 vol % (2.93×10^{19} mol) in the control case ($\alpha = 1$). The lower O_2 estimate is consistent with the O_2 requirements of the Cambrian fauna (Holland 1984) and carbon isotope records (Hayes *et al*. 1999).

Devonian (400–360 Ma)

O_2 is predicted to have risen sharply during the Devonian as plants evolved their key effects on phosphorus weathering. In the illustrative scenario ($\alpha = 2$), O_2 rises from ~11 vol % at the start of the Devonian (400 Ma), to ~ 20 vol % at its close (360 Ma). This corresponds to a doubling of the O_2 reservoir size from ~1.75×10^{19} mol to ~3.5×10^{19} mol. O_2 is predicted to have exceeded the threshold for combustion of ~15 vol % at ~375 Ma, which is consistent with the earliest known appearance of fossil charcoal (Rowe & Jones 2000; Cressler 2001).

Carboniferous and Permian (360–250 Ma)

The highlighted negative feedback mechanism has the potential to greatly suppress the predicted oxygen peak ~300 Ma in the late Carboniferous. Much organic carbon was being buried on land in coal basin sediments at this time (Ronov 1976), tending to increase atmospheric O_2. However, the negative feedback reduces the maximum predicted organic carbon burial flux from 9.7×10^{12} mol y^{-1} in the control run ($\alpha = 1$) to 6.9×10^{12} mol y^{-1} ($\alpha = 2$). O_2 peaks at ~25 vol % ($\alpha = 2$), the upper limit suggested for the persistence of forests, rather than ~35 vol % as previously predicted (Berner & Canfield 1989; Berner *et al*. 2000). If it is assumed that the plant biota increased the phosphorus weathering flux by more than a factor of two, then the O_2 peak is even lower (e.g. for a factor of $\alpha = 5$, O_2 peaks at 23.4 vol % with peak organic carbon burial of 6.3×10^{12} mol y^{-1}). If their effect was weaker, peak O_2 is closer to the original predictions. The critical control is not the overall change in phosphorus weathering because of plants but the sensitivity of phosphorus weathering to changes in O_2 via its effects on plants. If one assumes that there was no overall change in phosphorus weathering flux resulting from plants, but that the entire flux became sensitive to O_2 (using eqns A3–A5 in the Appendix), then there is maximum damping of O_2 variation with a predicted peak at 22.8 vol % around 300 Ma.

Triassic and Jurassic (250–150 Ma)

In the Triassic and early Jurassic, minima in organic carbon burial have been inferred and minima of oxygen predicted (Berner & Canfield 1989), which may be too low to sustain fires and account for charcoal production at this time. The highlighted feedback is less effective against declining oxygen than increasing oxygen but does increase the O_2 minima somewhat from ~14 vol % ($\alpha = 1$) to ~16 vol % ($\alpha = 2$) at 225 Ma and from ~13.5 vol % to ~15.5 vol % at 190 Ma.

Cretaceous, Tertiary and Quaternary (150–0 Ma)

In the Cretaceous and early Tertiary, rock abundance data suggest that organic carbon burial increased, predominantly in the ocean. Reduced phosphorus supply to the ocean from suppressed vegetation and weathering could have counteracted the tendency for oxygen to rise. The highlighted feedback lowers O_2 peaks ~80 Ma and ~40 Ma from ~25 vol % ($\alpha = 1$) to ~22 vol % ($\alpha = 2$). The effect of the highlighted feedback on oxygen predictions for the past 40 million years is comparable to that found in a more complex model subjected to different forcing records (Lenton & Watson 2000b). The present study extends the previous work further into the past and emphasizes the potential importance of land plants in regulating the oxygen content of the atmosphere.

Importance of other processes

A number of feedback mechanisms have probably operated together to stabilize atmospheric oxygen over Phanerozoic time. The model developed above already includes an inverse dependence of pyrite sulphur burial on the size of the atmospheric oxygen reservoir (Berner & Canfield 1989). This is based on the principle that oxygen suppresses sulphate-reducing bacteria (Redfield 1958). Hence, rising O_2 suppresses pyrite burial thus decreasing the source of O_2 whilst falling O_2 stimulates pyrite burial and increases the source of O_2. Further negative feedbacks operating on organic carbon burial probably contributed to limiting O_2 variation (examples in Table 1). Positive feedback on the oxygen source can also occur (Lenton & Watson 2000b). (Positive feedback happens when a change in a reservoir triggers an amplifying change in the input to or output from that reservoir.) For example, as O_2 rises to the point where fires can start, some organic carbon is converted to charcoal, and charcoal is highly resistant to degradation, making it more likely to be buried (Lovelock 1988; Robinson 1991).

The evolution of land plants was not the only factor affecting weathering over Phanerozoic time. Mountain chains were formed several times, in each instance increasing physical erosion rates and tending to increase weathering. The effects of the recent Himalayan uplift on atmospheric oxygen have been considered in previous work (Lenton & Watson, 2000b).

Conclusion: future work

Limits on atmospheric oxygen variation since land plants became widespread need to be better constrained. In order to determine the lower limit on O_2 consistent with charcoal formation, combustion experiments should be performed with natural fuels rather than paper (Watson 1978). The upper limit on O_2 is more difficult to constrain. The effect of increased fire frequency on the structure of terrestrial ecosystems could be examined in more sophisticated vegetation models that can determine what O_2 concentration is consistent with the presence of forests. This also relies on an accurate translation from ignition energy to fire frequency. A lower limit on oxygen partial pressure in the Carboniferous could be determined by estimating the metabolic O_2 requirement of giant dragonflies present at the time. Direct effects of O_2/CO_2 on plant productivity also deserve further experimental quantification, especially as the results of existing studies appear to contradict one another (Tolbert *et al*. 1995; Beerling *et al*. 1998).

The responses of vegetation to O_2 and fires provide the initial links in the highlighted feedback mechanism (Fig. 3). The remaining processes could also be better quantified. The degree to which phosphorus weathering is amplified by different vegetation types could be measured, for example in the Hubbard Brook experimental sand boxes, adapting the methods used previously for other elements (Bormann *et al*. 1998). The effect of productivity on weathering rate is currently being determined using FACE (free-air CO_2 enrichment) experiments (Andrews & Schlesinger 2001). The importance of phosphorus supply from rock weathering in determining the burial flux of plant organic matter also needs more detailed consideration.

The hypothesized feedback mechanism should be tested as a whole for consistency with carbon and sulphur isotope records within a mass-balanced model. Existing carbon isotope records do not offer very strong constraints (Raymo 1997), but information about the isotopic composition of different reservoirs and isotope fractionation effects is improving. Ideally, variations in atmospheric carbon dioxide (Berner 1994) and global temperature should be simulated together with atmospheric oxygen and the biota, because of the effects of CO_2 and temperature on weathering rates, CO_2/O_2 and temperature on C3 plant productivity, and temperature on O_2 solubility. Tectonic forcing should also be taken into account. A model that can achieve this is being developed (by N. Bergman, T. M. Lenton and A. J. Watson) and initial results support the importance of plants in increasing and then stabilizing atmospheric oxygen.

Acknowledgements

I thank Andy Watson for first encouraging me to think about the effect of plants on atmospheric oxygen, Steve Long for inviting me to write this paper, and John Raven, Bill Schlesinger and three reviewers for their helpful comments.

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Appendix: model description

The hypothesized feedback was added to Berner & Canfield's (1989) 'fast-recycling' model. Their assumption of a 100-My residence time for young crustal reservoirs relative to conversion to old reservoirs was retained. The only alteration of the model was the addition of a forcing of total organic carbon burial by phosphorus weathering with the following rationale.

Phosphorus weathering provides the input fluxes of phosphorus to the land and the ocean. The model time steps of 1 My are much longer than the residence time of phosphorus in the ocean of ~10–20 ky. Therefore, when integrated over 1 My, phosphorus output from the ocean must match phosphorus input. Marine organic carbon burial in turn responds to total marine phosphorus burial (the C_{org}/P_{total} burial ratio is assumed to be fairly constant). The residence time of phosphorus in terrestrial ecosystems is also much less than the model time steps and phosphorus is assumed to limit terrestrial productivity over the long timescales considered. Terrestrial organic carbon burial therefore responds to phosphorus input from weathering (assuming a fairly constant C_{org}/P_{org} burial ratio).

The altered equation for total organic carbon burial flux (F_{BC}) with normalized forcing by phosphorus weathering (W_P) is:

$$F_{BC} = (1/12)\,(C_{MA}f_{MA} + C_{CB}f_{CB})\,F_T W_P. \qquad (A1)$$

C_{MA} and C_{CB} are fractional organic carbon contents by weight of marine clastic and coal basin sediments (retaining the assumptions that $C_{MA} = 0.004$ until 380 Ma and 0.006 since then, and $C_{CB} = 0.025$). f_{MA} and f_{CB} are fractions of total sedimentation as marine clastics and coal basin sediments. These forcings are derived from table 1 of Berner & Canfield (1989), assuming that the values given are representative of the mid-point of each period and interpolating linearly between these points. F_T is total sedimentation flux, assumed constant at 1.3×10^{16} g y^{-1}. The factor 1/12 converts from grams to moles of carbon.

Phosphorus weathering (W_P) is a normalized function of vegetation biomass (V):

$$W_P = \frac{1}{\alpha} + \left(1 - \frac{1}{\alpha}\right)V. \qquad (A2)$$

The α factor represents the amplification of phosphorus weathering flux with plants relative to its value without them, incorporating the indirect effects of changes in CO_2 and global temperature as well as the direct effect of plants. α also determines the fraction of the phosphorus weathering flux that is under the influence of vegetation.

Vegetation biomass (V) is a normalized function of net primary productivity (p) and fire frequency (f) (Lenton & Watson 2000b):

$$V = \beta\frac{20p}{19 + f}. \qquad (A3)$$

The β factor is used to represent the appearance of plants with an effect on phosphorus weathering. $\beta = 0$ until the start of the Devonian (400 Ma), β is then linearly increased to 1 over the 40 My of the Devonian, and $\beta = 1$ from 360 Ma to the present.

Net primary productivity and fire frequency are both normalized functions of oxygen mixing ratio (O_2) (Lenton & Watson 2000b):

$$p = \max\left(\left(1.5 - 0.5\left(\frac{O_2}{0.21}\right)\right),\ 0\right) \qquad (A4)$$

$$f = \max\,((586.2\ O_2 - 122.1),\ 0). \qquad (A5)$$

The model was constructed in a spreadsheet. Simulations were started with a 30 My spin-up in which all parameters were held at their initial values corresponding to 570 Ma, thus allowing the model reservoirs to approach steady state. A control run was performed for $\alpha = 1$, for which the equations reduce to the original model of Berner & Canfield (1989). Then the uncertain parameter α was varied. $\alpha = 2$ illustrates the effect of the highlighted feedback (Fig. 4). Further increases in α have a progressively weaker effect on oxygen predictions, because of the form of (A2). $\alpha = 8$ or more was found to generate an unrealistic disappearance of the young organic carbon reservoir in the early Phanerozoic.

The introduction of feedback alters the predicted history of organic carbon burial. This implies that in reality some other factors determining organic carbon burial in (A1) vary from their adopted value. As C_{MA} and C_{CB} are variable and uncertain, f_{MA} and f_{CB} are based on sparse data, and F_T is not constant in reality (Wold & Hay 1990), this is not unreasonable. Indeed, Berner & Canfield (1989) already include a negative feedback on pyrite sulphur burial, which alters its predicted history from that which would be inferred from their assumptions about the pyrite sulphur content of marine sediments and the rate of sedimentation.