

Redfield revisited

2. What regulates the oxygen content of the atmosphere?

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Abstract. The continuous charcoal record, interpreted with the aid of the results of combustion experiments, indicates that the mixing ratio of atmospheric oxygen has varied remarkably little over the past 350 Myr. We develop a dynamic feedback model of the coupled P, N, C, and O₂ cycles and use perturbation analysis and a case study of the past 40 Myr to test various feedback mechanisms that have been proposed to stabilize atmospheric oxygen. These mechanisms involve alterations in nutrient driven productivity and the subsequent burial flux of organic carbon, which provides the main source of atmospheric oxygen. Suppression of the burial of phosphorus sorbed to iron minerals under anoxic conditions in ocean bottom waters tends to increase the ocean nutrient inventory and provide negative feedback against declining oxygen [Holland, 1994]. However, denitrification is enhanced by anoxia, tending to reduce the nutrient inventory and amplify declining oxygen [Lenton and Watson, this issue]. If organic phosphorus removal from the ocean is also suppressed under anoxic conditions, this improves oxygen regulation [Van Cappellen and Ingall, 1994], as does direct enhancement of organic carbon burial due to reduced oxygen concentration in bottom waters [Betts and Holland, 1991]. However, all of the ocean-based feedback mechanisms cease to operate under increases in oxygen that remove anoxia from the ocean. Fire frequency is extremely sensitive to increases in oxygen above 21% of the atmosphere, readily suppressing vegetation on the land surface. This should transfer phosphorus from the land to the ocean, causing less carbon to be buried per unit of phosphorus and providing a weak negative feedback on oxygen [Kump, 1988]. However, a new proposal that increases in oxygen suppress the biological amplification of rock weathering and hence the input of phosphorus to the Earth system provides the most effective oxygen regulation of all the mechanisms considered. A range of proxies suggests that the input of available phosphorus to the ocean may have been significantly reduced 40 Myr ago, suppressing new production and organic carbon burial in the model. With only ocean-based feedback, the atmospheric oxygen reservoir is predicted to have shrunk from ~26% of the atmosphere 40 Myr ago. However, when land plant mediated negative feedback on phosphorus weathering is added, oxygen is regulated within 19-21% of the atmosphere throughout the past 40 Myr, in a manner more consistent with paleorecords.

1. Introduction

The relatively constant size of the atmospheric oxygen reservoir over Phanerozoic time is one of the most remarkable aspects of the Earth system, and it presents a long-standing puzzle. The ~350 Myr continuous charcoal record [Cope and Chaloner, 1985] indicates that oxygen has been sufficient to produce fires throughout this time, while combustion experiments indicate that it is not possible to sustain fire, even in dry paper, at an oxygen mixing ratio of 17% [Watson, 1978]. Thus the mixing ratio of atmospheric oxygen appears

to have been >17% throughout the last ~350 Myr. Furthermore, the probability of ignition for fuel with a moisture content of 20%, typical of the leaf litter where fires often begin, is extremely sensitive to increases in oxygen mixing ratio above 21% (Figure 1). Model studies driven by the results of combustion experiments indicate that as O₂ mixing ratio increases there is a rapid rise in the frequency of fires that would soon prevent the regeneration of forests [Watson, 1978]. Even with a persistently wet climate, it seems unlikely that O₂ >30% would be compatible with dense vegetation [Watson, 1978].

For oxygen to have been maintained within the narrow bounds of ~17 to ~30% of the atmosphere, over a timescale ~100 times longer than the residence time of oxygen in the atmosphere, demands that regulatory feedback mechanisms exist [Holland, 1984; Lovelock, 1995]. The oxidizing atmosphere is the product of past photosynthesis and a constraint on the growth of many organisms, being required by aerobes but toxic to cell function [Fridovich, 1977] as well

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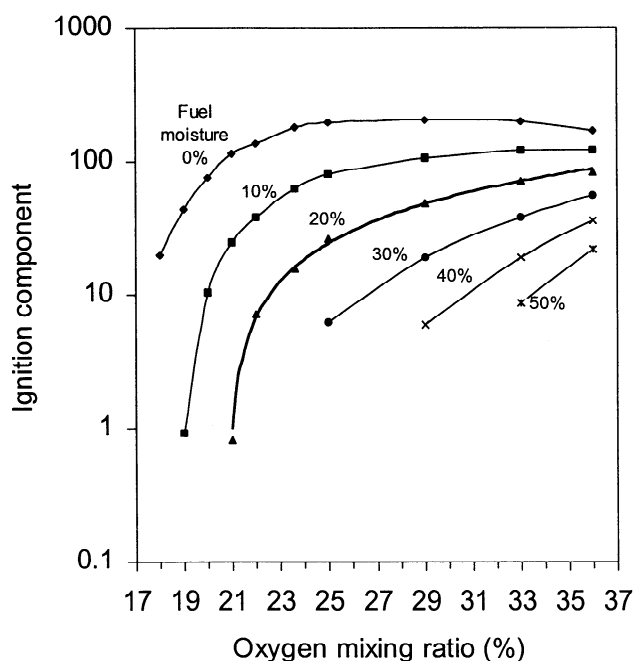


Figure 1. Dependence of ignition probability on oxygen mixing ratio and fuel moisture content. From the experiments of *Watson* [1978]. Ignition component, a measure of the relative probability of ignition, is plotted as a function of oxygen mixing ratio (in percent by volume) for varying moisture contents of paper fuel (0, 10, 20, 30, 40, and 50%). Experiments were conducted at 17, 18, 19, 20, 21, 22, 23.6, 25, 29, 33, and 36% oxygen for each fuel moisture content [Watson, 1978]. Only positive values of the ignition component are shown. At 17% oxygen, the probability of ignition is zero even for completely dry paper (fuel moisture = 0%). The curves tend to asymptote toward the situation where every spark will cause ignition. Most striking is the extreme sensitivity of ignition probability to changes in the mixing ratio of oxygen over a narrow range. Near 21% oxygen, this sensitivity is greatest for fuel of 20% moisture content, which is typical of leaf litter when rain has not recently fallen. The bold line is a best fit to this data set, which we use to model the effect of oxygen on fire frequency.

as affecting the frequency of fires [Watson *et al.*, 1978]. That oxygen is both a product of life and a constraint on growth implies some form of feedback between the activities of organisms and the size of the atmospheric oxygen reservoir [Lovelock, 1995]. Redfield [1958] was among the first to

address how oxygen could be stabilized at 21% of the atmosphere. He proposed a negative feedback mechanism, involving sulphate-reducing bacteria in marine sediments, whereby a decrease in oxygen will be counteracted by increased reduction of sulphate and burial of reduced sulphur, liberating free oxygen. However, the anaerobic reduction of sulphate requires a source of electrons, often organic carbon, which in being oxidized is not buried, thus undermining the potential negative feedback [Garrels and Perry, 1974].

Geochemical mass-balance studies predict peak oxygen levels of 35% in the Late Carboniferous and minimum levels of <15% in the Triassic [Berner and Canfield, 1989]. These predictions derive from a model that assumes that increases in sediment burial rate must be accompanied by increases in erosion rate and that younger rocks weather faster, thus generating "rapid recycling" of C and S [Berner and Canfield, 1989]. Both effects tend to damp changes in oxygen. Yet, at face value, the model predictions [Berner and Canfield, 1989] are incompatible with both upper and lower bounds on oxygen suggested above, from combustion experiments [Watson, 1978]. A recent model study of the Carboniferous assuming 35% oxygen predicts fires recurring every 1–5 years [Beerling *et al.*, 1998]. If this had been realized, it would have altered the course of plant evolution. Furthermore, we think the quantification of fire frequency adopted by Beerling *et al.* [1998], supposedly based on the same data as is used herein, is mistaken such that the predicted fire frequencies are significant underestimates. The solution may lie in including further negative feedback mechanisms in the model of Berner and Canfield [1989] which could reduce the maximum oxygen levels predicted in the Carboniferous to ~25% (R. A. Berner, personal communication, 1997). The question is, what are the feedback mechanisms?

Most existing feedback proposals involve changes in the rate of organic carbon burial in sediments (the source of oxygen), often modulated by changes in biological productivity and the cycling of phosphorus. These are summarized in Table 1. We use a dynamic model of the coupled biogeochemical cycles of P, N, C, and O₂ [Lenton, 1998b; Lenton and Watson, this issue] as a common framework to test their regulatory capacity. We begin by describing the basic, ocean-only model (M1) in section 2. The regulatory capacity of different ocean-based feedback mechanisms is then tested in section 3 by making independent variants of the model (M5, M6). In section 4, the model is extended to include land plants and the effect of oxygen

Table 1. Feedback Mechanisms on Oxygen

Key Process Involved	Sign of Feedback	Model Variant	Reference(s)
Denitrification	+	All	Lenton and Watson [this issue]
Iron-sorbed phosphorus burial suppressed by anoxia	-	All	Holland [1994], Van Cappellen and Ingall [1994]
Organic phosphorus burial suppressed by anoxia	-	M5	Ingall and Jahnke [1994], Van Cappellen and Ingall [1994]
Organic carbon burial enhanced by anoxia	-	M6	Betts and Holland [1991], Holland [1973]
Phosphorus transfer to the ocean	-	M7	Kump [1988, 1993]
Biological amplification of phosphorus weathering	-	M8	proposed in this work

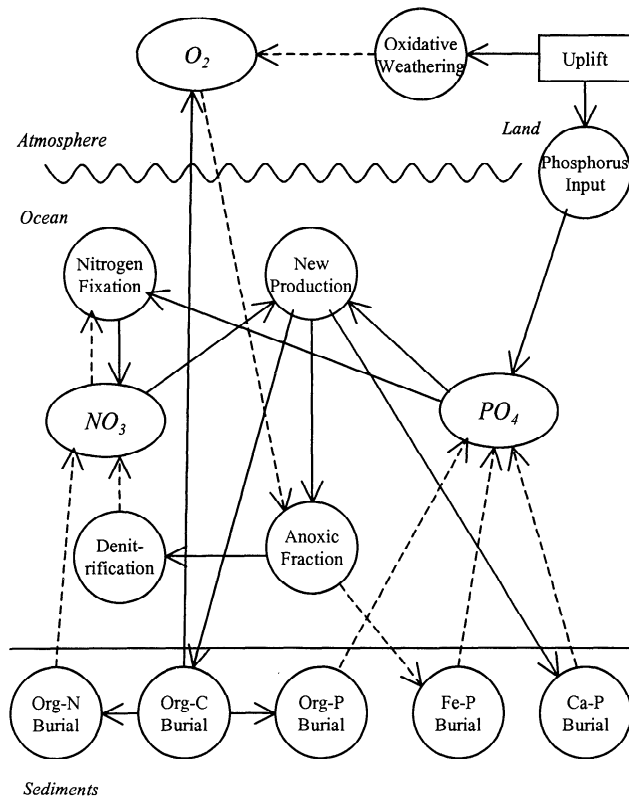


Figure 2. Basic ocean model (M1). Reservoirs are indicated by ovals, dependent variables are indicated by circles, and there is a single input parameter, Uplift. New Production is a switch solely dependent on the concentration of the limiting nutrient, which is usually nitrate. The arrows indicate a functional dependence of one component on another and show the direction of causality. The arrows follow the convention of Riggs [1970]. A solid arrow indicates a direct relationship. For example, an increase in anoxic fraction causes an increase in denitrification (equally, a decrease in anoxic fraction causes a decrease in denitrification). A dashed arrow indicates an inverse relationship. For example, an increase in anoxic fraction causes a decrease in Fe-P burial (iron-sorbed phosphorus burial). A feedback loop exists where a closed loop of arrows can be followed around the diagram. Loops containing an odd number of broken arrows (inverse relationships) are negative feedbacks, whereas those containing none, or an even number, are positive feedbacks. If the anoxic fraction falls to zero, the causal connections to Fe-P burial and denitrification switch off.

mixing ratio on fire frequency and photosynthesis. Variants of this whole system model (M7, M8) are used to test land-based feedback mechanisms in section 5. In section 6 we make a historical case study of the past 40 Myr by using two alternative proxies of chemical weathering rate to force the initial (M1) and final (M8) variants of the model and contrast their predictions of oxygen. Then, in section 7, we attempt a synthesis with the companion paper [Lenton and Watson, this issue], assessing the potential for coupled regulation of atmospheric oxygen, deep-ocean nitrate and phosphate in Redfield ratio, and ocean oxygen supply and demand (limiting nutrient) toward Redfield ratio. Section 8

summarizes our conclusions regarding the regulation of atmospheric oxygen.

2. Basic Ocean Model (M1)

All the model variants presented in this paper are extensions of the same basic ocean model (M1), illustrated in Figure 2. The equations of the basic model are summarized in Table 2 and explained in this section (for a more detailed justification see Lenton and Watson [this issue]). The initial sizes of the reservoirs, fluxes, and the model constants are given in Table 3. The model includes three reservoirs, deep ocean phosphate, deep ocean nitrate, and atmospheric oxygen equilibrated with the surface ocean. Oxygen is expressed as the concentration dissolved in high-latitude surface waters that ventilate the deep ocean, which is directly proportional to the atmospheric partial pressure of oxygen (Henry's Law) because we assume the temperature and salinity of these waters remain constant in the simulations. We use Redfield ratios of P:N:C:-O₂ = 1:16:117:170 [Anderson and Sarmiento, 1994] for the composition of organic matter and the stoichiometry of respiration. The model is forced by the nondimensional parameter uplift, U , which drives continental weathering (and is initially identical to W used by Lenton and Watson [this issue]).

Both nitrogen and phosphorus potentially limit new production, N , given by (1). Nitrate limits new production when below Redfield ratio to phosphate (i.e., when $NO_3/16 < PO_4$), and phosphate limits when below Redfield ratio to nitrate (i.e., when $PO_4 < NO_3/16$). The limiting nutrient is completely used up in the generation of new production, which is expressed in terms of the concentration of organic carbon produced. New production in turn determines the oxygen demand of respiration. The degree of anoxia in the ocean is described by the anoxic fraction, A , and is determined by the balance of oxygen supply and demand in (2). The anoxic fraction is defined as the fractional area of the ocean where annual average oxygen concentration falls to <10% saturation at some point in the water column.

Marine organic carbon (Org-C) burial, F_{Org-C} , provides a source of oxygen and determines the removal fluxes of organic phosphorus and nitrogen to sediments. Existing evidence suggests that new production and therefore the concentration of limiting nutrient in the surface ocean exert the dominant control on marine organic carbon burial [Betts and Holland, 1991; Pedersen and Calvert, 1990]. On the basis of data relating primary production to sedimentation rate [Müller and Suess, 1979] and sedimentation rate to organic carbon burial [Henrichs and Reeburgh, 1987], organic carbon burial is assumed to be a quadratic function of new production, given by (3) and independent of ocean anoxia. The nonlinearity implies that increases in new production occur primarily in the shelf environments where a greater fraction of production is preserved than in the deep ocean [Van Cappellen and Ingall, 1994]. A sensitivity study in which the power relating organic carbon burial to changes in new production was altered over the range 1-3 revealed that this does not have a great impact on the final steady state of oxygen [Lenton, 1998b]. The output of atmospheric oxygen is determined by the rate of oxidative weathering of reduced materials in continental rocks. This sink is assumed to be

Table 2. Equations of the Basic Ocean Model (M1)

Weathering (W)	New production (N)	Anoxic fraction (A)
The forcing parameter, $W=1$ for the initial steady-state	$N = \min\left(\frac{117}{16}\text{NO}_3, 117\text{PO}_4\right)$	$A = 1 - k_1 \frac{\text{O}_2}{\text{O}_{2(0)}} \frac{N_0}{N}$
Oxygen (O_2)	Nitrate (NO_3)	Phosphate (PO_4)
$F_{\text{Org-C}} = k_2 \left(\frac{N}{N_0}\right)^2$ (3)	$F_{\text{N-Fix}} = k_3 \left(\frac{\text{PO}_4 - \text{NO}_3/16}{\text{PO}_{4(0)} - \text{NO}_{3(0)}/16}\right)$ (5)	$F_{\text{P-in}} = k_5 W$ (8)
$F_{\text{Ox-W}} = k_2 W$ (4)	$F_{\text{De-N}} = k_4 \left(1 + \frac{A}{A_0}\right)$ (6)	$F_{\text{Org-P}} = \frac{F_{\text{Org-C}}}{250}$ (9)
	$F_{\text{Org-N}} = \frac{F_{\text{Org-C}}}{37.5}$ (7)	$F_{\text{Fe-P}} = \frac{k_6}{k_1} (1 - A)$ (10)
$m_{\text{O}_2} = \frac{\text{O}_2}{k_{10} + \text{O}_2}$ (15)		$F_{\text{Ca-P}} = k_7 \left(\frac{N}{N_0}\right)^2$ (11)
$\frac{d\text{O}_2}{dt} = k_9 (F_{\text{Org-C}} - F_{\text{Ox-W}})$ (12)	$\frac{d\text{NO}_3}{dt} = k_3 (F_{\text{N-Fix}} - F_{\text{De-N}} - F_{\text{Org-N}})$ (13)	$\frac{d\text{PO}_4}{dt} = k_8 \left(\begin{matrix} F_{\text{P-in}} - F_{\text{Fe-P}} \\ - F_{\text{Org-P}} - F_{\text{Ca-P}} \end{matrix}\right)$ (14)

saturated; that is, virtually all the reduced material that is exposed gets oxidized [Holland, 1973; Walker, 1974]. Hence the rate of continental uplift, U , limits the rate of oxidative weathering, $F_{\text{Ox-W}}$, in (4).

The equations describing the nitrogen cycle remain the same in all the model variants. The deficit of nitrate below Redfield ratio to phosphate linearly determines the selective advantage of nitrogen fixation and the resultant flux into the reservoir of available nitrogen, $F_{\text{N-Fix}}$ in (5). Denitrification, $F_{\text{De-N}}$ is given by (6) and comprises functionally distinct water-column and sedimentary components, which are initially of equal magnitude. Water-column denitrification varies linearly with the anoxic fraction; that is, denitrification occurs wherever oxygen falls sufficiently low to make nitrate the preferred electron acceptor. Sedimentary denitrification is constant, on the grounds that there will be sufficient anoxia to favor denitrification at some depth in the sediment even when there is no anoxia in bottom waters. Organic nitrogen burial, $F_{\text{Org-N}}$, is a function of the organic carbon burial flux and the C/N burial ratio, given by (7).

Most of the model variants involve changes in the equations describing the phosphorus cycle. In the basic model, phosphorus input, $F_{\text{P-in}}$, given by (8), is determined by the rate of continental chemical weathering, which liberates phosphorus from rocks and is in turn determined by the rate of uplift, U . Phosphorus burial is divided into three major forms, organic phosphorus (Org-P), phosphorus sorbed to iron hydroxides (Fe-P), and phosphorus bound in calcium minerals (Ca-P). Organic phosphorus burial $F_{\text{Org-P}}$, given by (9), is initially assumed to be linearly dependent on organic carbon burial [Mach et al., 1987] and independent of anoxia

[Colman et al., 1997]. Iron-sorbed phosphorus burial, $F_{\text{Fe-P}}$ given by (10) is assumed to vary inversely with bottom-water anoxia [Holland, 1994], which is in turn taken to vary in proportion to the anoxic fraction [Van Cappellen and Ingall, 1994]. The true relation is almost certainly more complex than this, but it captures the key control [Colman and Holland, 1999]. Calcium-bound phosphorus burial $F_{\text{Ca-P}}$, given by (11), is mostly authigenic and is assumed to be proportional to the supply of phosphorus to the sediments in organic matter, which is quadratically dependent on new production.

The differential equations for the rate of change of size of the oxygen, nitrate and phosphate reservoirs are given by (12), (13), and (14) respectively. Equation (15) converts the oxygen reservoir into the oxygen atmospheric mixing ratio, m_{O_2} , assuming that the remainder of the atmosphere, which is mostly nitrogen, remains constant [Holland, 1978].

Oxygen output and phosphorus input are tightly coupled via the forcing parameter, uplift, in (4) and (8). This means that changes in weathering rates cause counteracting changes in both the oxygen sink and source, the latter via phosphorus driving productivity and organic carbon burial [Bernier, 1991; Colman et al., 1997; Garrels and Perry, 1974]. Increases in uplift cause organic carbon burial to increase more than oxidative weathering, tending to increase oxygen. Conversely, decreases in uplift cause organic carbon burial to decline more than oxidative weathering, tending to decrease oxygen. We test the model with standard perturbations, first increasing uplift by 50% then decreasing uplift by 50%. This allows comparison with the results of previous studies [Colman et al., 1997; Van Cappellen and Ingall, 1996].

Table 3. Basic Model (M1) Reservoirs, Fluxes and Constants

Reservoir	Description	Initial Size, mol	Concentration, $\mu\text{mol kg}^{-1}$	Model Constant	Reference(s) and Notes
PO ₄	phosphate in the deep ocean	3.1×10^{15}	2.2	PO ₄₍₀₎	from analysis of the World Ocean Atlas dataset (T. Tyrrell, personal communication, 1998)
NO ₃	biologically available nitrogen in the deep ocean	4.35×10^{16}	30.9	NO ₃₍₀₎	from analysis of the World Ocean Atlas dataset (T. Tyrrell, personal communication, 1998)
O ₂	oxygen in the atmosphere and the concentration dissolved in water ventilating the deep ocean	3.7×10^{19}	331.5	O ₂₍₀₎	reservoir from <i>Betts and Holland</i> [1991], concentration assuming ventilating waters are at 2°C and 35‰ salinity from <i>Levitus</i> [1982] using formula of <i>Weiss</i> [1970]
Flux	Description	Magnitude, mol yr ⁻¹	Model Constant	Reference and Notes	
$F_{\text{Org-C}}$	organic carbon (Org-C) burial	3.75×10^{12}	k_2	<i>Froelich et al.</i> [1982]	
$F_{\text{Ox-W}}$	oxidative weathering	3.75×10^{12}	k_2	for steady state	
$F_{\text{N-fix}}$	nitrogen fixation	8.7×10^{12}	k_3	for steady state	
$F_{\text{De-N}}$	denitrification	8.6×10^{12}	$2k_4$	<i>Codispoti and Christensen</i> [1985]	
$F_{\text{Org-N}}$	organic nitrogen (Org-N) burial	0.1×10^{12}	$(C/N)_{\text{burial}} = 37.5$	<i>Ingall et al.</i> [1993]	
$F_{\text{P-in}}$	riverine bioavailable phosphorus input	3.6×10^{10}	k_5	<i>Froelich et al.</i> [1982]	
$F_{\text{Fe-P}}$	iron-sorbed phosphorus (Fe-P) burial	0.6×10^{10}	k_6	<i>Van Cappellen and Ingall</i> [1994]	
$F_{\text{Org-P}}$	organic phosphorus (Org-P) burial	1.5×10^{10}	$(C/P)_{\text{burial}} = 250$	<i>Froelich et al.</i> [1982], <i>Van Cappellen and Ingall</i> [1994]	
$F_{\text{Ca-P}}$	calcium-bound phosphorus (Ca-P) burial	1.5×10^{10}	k_7	<i>Van Cappellen and Ingall</i> [1994]	
Constant	Description	Value	Reference and Notes		
P:N:C:-O ₂	Redfield ratios	1:16:117:170	<i>Anderson and Sarmiento</i> [1994]		
N_0	initial value of new production	$226.0 \times 10^{-6} \text{ mol kg}^{-1}$	organic carbon concentration estimated from Figure 1		
A_0	initial anoxic fraction	0.14	(1 - A_0)		
k_1	initial oxic fraction	0.86	for nitrate and phosphate		
k_8	conversion factor from deep sea reservoir size to average concentration	$7.1 \times 10^{-22} \text{ kg}^{-1}$			
k_9	conversion factor from oxygen atmospheric reservoir size to concentration dissolved in surface waters ventilating the deep ocean	$8.96 \times 10^{-24} \text{ kg}^{-1}$	temperature and salinity of ventilating waters is assumed constant		
k_{10}	represents constant atmospheric nitrogen reservoir	1247.1	$(79/21) \times O_{2(0)}$		

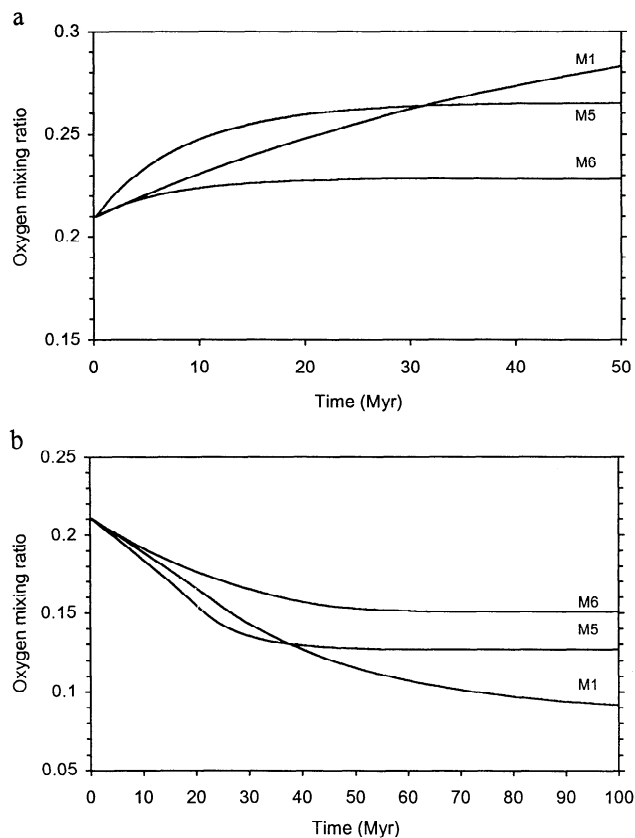


Figure 3. Atmospheric oxygen response to (a) 50% increase in uplift and (b) 50% decrease in uplift, for different ocean-based feedback systems: The basic model (M1), organic phosphorus burial suppressed by anoxia (M5), and organic carbon burial enhanced by anoxia (M6).

3. Testing Ocean-Based Feedback

The basic model contains two feedback mechanisms on oxygen (Table 1). The dependence of iron-sorbed phosphorus burial on anoxia introduces a negative feedback. This was originally described in terms of switches in sink between iron-sorbed and organic phosphorus burial [Holland, 1994]. Under anoxic conditions, phosphorus tends to be buried with organic carbon, but under oxic conditions there is a shift in favor of its burial by adsorption and reaction with iron hydroxides. Therefore increases in atmospheric oxygen may cause less carbon to be buried per unit of phosphorus and less oxygen to be released to the atmosphere. The direct relationship between anoxia and water-column denitrification generates a counteracting positive feedback on oxygen. For example, a decrease in oxygen causes increases in anoxia and denitrification that tend to reduce the level of nitrate, the limiting nutrient, and hence organic carbon burial.

3.1. Iron-Sorbed Phosphorus Burial Suppressed by Anoxia, Denitrification Enhanced by Anoxia (M1)

The positive and negative feedbacks on oxygen in the basic model combine to give a weak net negative feedback. In response to a 50% increase in uplift forcing up oxygen, the feedback system is unable to prevent anoxia disappearing from the ocean water column, at which point the feedback switches off, leaving oxygen rising (Figure 3a). In a mass-balance model, the rise in oxygen could not continue indefinitely because the extra organic carbon being buried would eventually be exposed, generating an increase in oxidative weathering. However, the 100 Myr timescale of crustal overturn is such that the oxygen reservoir would experience a large change in size. Analytical solutions reveal

Table 4. Response of Oxygen to Perturbations of Uplift

Model Variant	Description	Change in Uplift, %	Change in O ₂ Reservoir, % of Present Reservoir Size ¹	Final O ₂ Reservoir, 10 ¹⁹ mol	Final O ₂ Atmospheric Fraction, vol%
<i>Control System</i>					
M1	Basic model	+50	no steady state	-	-
		-50	-64.3	1.32	8.7
<i>Ocean Only</i>					
M5	Org-P burial suppressed by anoxia	+50	+35.5	5.01	26.5
		-50	-45.3	2.02	12.7
M6	Org-C burial enhanced by anoxia	+50	+11.1	4.12	22.8
		-50	-33.2	2.47	15.1
<i>Whole System</i>					
M7	Vegetation feedback on P transfer to the ocean	+50	+14.7	4.24	23.4
		-50	-55.5	1.65	10.6
M8	Vegetation feedback on P weathering	+50	+0.9	3.73	21.2
		-50	-27.0	2.70	16.3

¹Present size of oxygen reservoir = 3.7×10^{19} mol.

that under increases in uplift of greater than ~16%, the oxygen reservoir does not reach a steady state [Lenton and Watson, this issue]. In a different model [Colman *et al.*, 1997], also with negative feedback on oxygen via changes in iron-sorbed phosphorus burial, oxygen is stabilized under the same perturbation. The main difference is that we model a nitrogen cycle and positive feedback on oxygen via changes in denitrification.

Under a 50% decrease in uplift, oxygen stabilizes at only 8.7% of the atmosphere (Figure 3b, Table 4). The initial reduction in phosphorus input to the ocean triggers a decline in the size of the phosphate and nitrate reservoirs and the flux of organic carbon burial, causing anoxia to disappear from the water column and oxygen to decline. When some anoxia returns to the ocean, this switches on the feedback, tending to force up phosphate and nitrate (the limiting nutrient) and the fluxes of new production and organic carbon burial, until oxygen stabilizes [Lenton and Watson, this issue].

3.2. Organic Phosphorus Burial Suppressed by Anoxia (M5)

A further phosphorus-mediated, negative feedback on oxygen has been proposed, whereby a decrease in oxygen generates a decrease in organic-phosphorus burial and therefore an increase in phosphate, new production and organic carbon burial [Ingall and Jahnke, 1994; Ingall *et al.*, 1993; Van Cappellen and Ingall, 1996]. We add this extra negative feedback in variant M5 of the model by altering the equation for organic phosphorus burial to:

$$F_{\text{Org-P}} = F_{\text{Org-C}} \left(\frac{(1-A)}{(C/P)_{\text{oxic}}} + \frac{A}{(C/P)_{\text{anoxic}}} \right). \quad (16)$$

This replaces (9). $(C/P)_{\text{oxic}} = 217$ and $(C/P)_{\text{anoxic}} = 4340$ are used in order to maintain an initial organic phosphorus burial flux of 1.5×10^{10} mol yr⁻¹. These values differ slightly from those of Van Cappellen and Ingall [1994] because we adopt a smaller initial value for the anoxic fraction, but the representation of the carbon and phosphorus cycles is otherwise similar.

The additional negative feedback enables oxygen to reach steady under increases in uplift of up to 87% [Lenton and Watson, this issue]. Under a 50% increase in uplift, atmospheric oxygen comes to steady state at 26.5% of the atmosphere (Figure 3a, Table 4), while under a 50% decrease in uplift, oxygen stabilizes at 12.7% of the atmosphere (Figure 3b, Table 4). The system comes to steady state faster, but the initial rate of change of oxygen is greater (Figure 3) because of positive feedback on phosphate. Our results are similar to those obtained by Colman *et al.* [1997] when forcing the model of Van Cappellen and Ingall [1996] with coupled changes in phosphorus input to the ocean and oxidative weathering, owing to changes in uplift. The response of oxygen is reversed if phosphorus input is uncoupled to changes in oxidative weathering, as in Van Cappellen and Ingall [1996].

3.3. Organic Carbon Burial Efficiency Enhanced by Anoxia (M6)

A classic proposal for oxygen regulation, often attributed to Redfield [1958], is that the burial of organic carbon is enhanced under anoxic conditions because anaerobic decay of organic matter is slower than aerobic decay [Barghoorn, 1952]. If so, a decrease in oxygen would be counteracted by an increase in ocean anoxia and the burial flux of organic carbon [Holland, 1973]. The time period that sedimentary organic matter is exposed to oxic conditions will determine the extent of any effect of oxygen on organic carbon preservation [Hedges and Keil, 1995]. An inverse, nonlinear relationship has recently been found between this ‘‘oxygen exposure time’’ in marine sediments and organic carbon burial efficiency [Hartnett *et al.*, 1998], reviving the suggestion that certain types of organic matter can only be degraded by aerobic bacteria. Oxygen exposure time is a function of both the organic carbon rain (sedimentation) rate and the oxygen concentration of bottom waters. A rise in the rain rate decreases oxygen exposure time as does a decrease in bottom water oxygen concentration, both factors tending to increase organic carbon burial [Hartnett *et al.*, 1998]. Oxygen exposure time has only been estimated for a limited number of sites [Hartnett *et al.*, 1998]. In contrast, the effect of bottom water oxygen concentration on organic carbon burial efficiency has been analysed for data from 69 locations and was found to be either a negligible or a small but significant contributor to the regulation of oxygen [Betts and Holland, 1991].

To quantify the maximum potential negative feedback effect of anoxia on organic carbon burial, in model variant M6, we use the burial efficiency function of Betts and Holland [1991]. The concentration of oxygen in bottom waters is assumed linearly related to that in surface waters and is thereby linearly related to the size of the atmospheric oxygen reservoir (following Henry’s Law). A weak relationship between atmospheric oxygen and burial efficiency is consistent with the data [Betts and Holland, 1991]. Organic carbon burial is modeled as the product of the flux of carbon to sediments, which remains quadratically dependent on new production, and the burial efficiency:

$$F_{\text{Org-C}} = k_2 \left(\frac{N}{N_0} \right)^2 A e^{-BO_2}. \quad (17)$$

This replaces (3). $A = 2.127$, O_2 is the concentration dissolved in surface waters (in mol kg⁻¹), and $B = 2277$ mol⁻¹ kg. This approach captures the same two key controls on organic carbon burial as oxygen exposure time. To isolate the effect of anoxia on organic carbon burial efficiency, the organic phosphorus burial flux is kept independent of anoxia, by giving it the same functional dependence as Ca-P burial, (11) replacing (9). Organic nitrogen burial remains proportional to organic carbon burial because the C/N burial ratio is independent of anoxia [Ingall and Van Cappellen, 1990].

The additional negative feedback on organic carbon burial efficiency stabilizes the response to a 50% increase in uplift

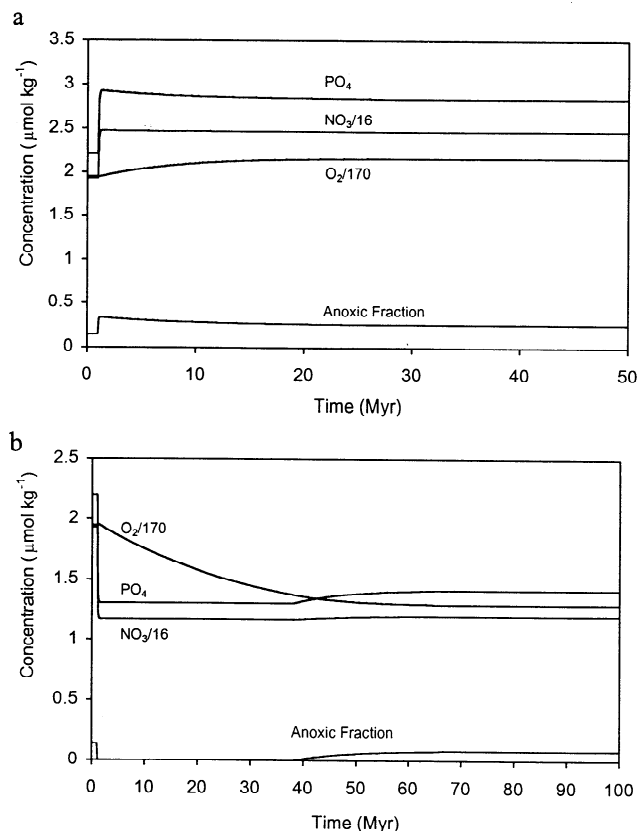


Figure 4. Maximum effect of anoxia on organic carbon burial efficiency (M6), response to (a) 50% increase in uplift and (b) 50% decrease in uplift. The diagrams show the proximity of phosphorus, nitrogen, and oxygen in the ocean to the Redfield ratio requirements of marine organisms. “ PO_4 ” is the average deep ocean phosphate concentration. “ $NO_3/16$ ” is the average deep ocean nitrate concentration, divided by the Redfield ratio requirement of photosynthesisers (16 moles of nitrogen per mole of phosphorus). “ $O_2/170$ ” is the oxygen concentration dissolved in surface waters that ventilate the deep ocean, divided by the Redfield ratio requirement of respirers (170 moles of oxygen per mole of phosphorus). “ $O_2/170$ ” is also proportional to the size of the atmosphere-ocean oxygen reservoir. The anoxic fraction of the ocean is plotted on the same scale but is dimensionless and can only vary between zero and one.

(Figure 4a, Figure 3a). As oxygen rises, this forces a decline in the burial efficiency of organic carbon. It also increases the removal of iron-sorbed phosphorus, reducing the concentrations of phosphate and nitrate, and hence the sedimentation flux of organic carbon. Thus both mechanisms contribute to reduce the burial flux of organic carbon and oxygen stabilizes at 22.8% of the atmosphere (Table 4). Regulation is also improved in response to a 50% decrease in uplift (Figure 4b, Figure 3b) with oxygen stabilizing at 15.1% of the atmosphere (Table 4). The feedback on organic carbon burial efficiency is complemented by activation of the negative feedback via changes in iron-sorbed phosphorus burial, when anoxia returns to the ocean.

Our model produces more effective oxygen regulation than that of *Betts and Holland* [1991] because it also incorporates negative feedback via iron-sorbed phosphorus burial.

However, the quantified dependence of organic carbon burial on anoxia is the maximum possible effect consistent with the data, which is also consistent with there being no effect at all [*Betts and Holland*, 1991].

3.4. Summary

All the ocean-based proposals for oxygen regulation considered in sections 3.1 to 3.3 depend on there being some anoxia in the ocean but increases in atmospheric oxygen may readily generate complete oxia in the ocean, thus switching off the feedback mechanisms [*Kump and Mackenzie*, 1996; *Lenton and Watson*, this issue]. The principal victims of increases in atmospheric oxygen are organisms on land, and this has led previous investigators to propose that land life is in some way involved in regulating oxygen [*Kump*, 1988; *Lovelock*, 1995; *Watson et al.*, 1978].

4. Extending the Model

We extend the model (Figure 5) to include the effects of oxygen on land plants and to evaluate proposals of feedback on atmospheric oxygen involving land biota. The extended model deals more completely with the source and fate of

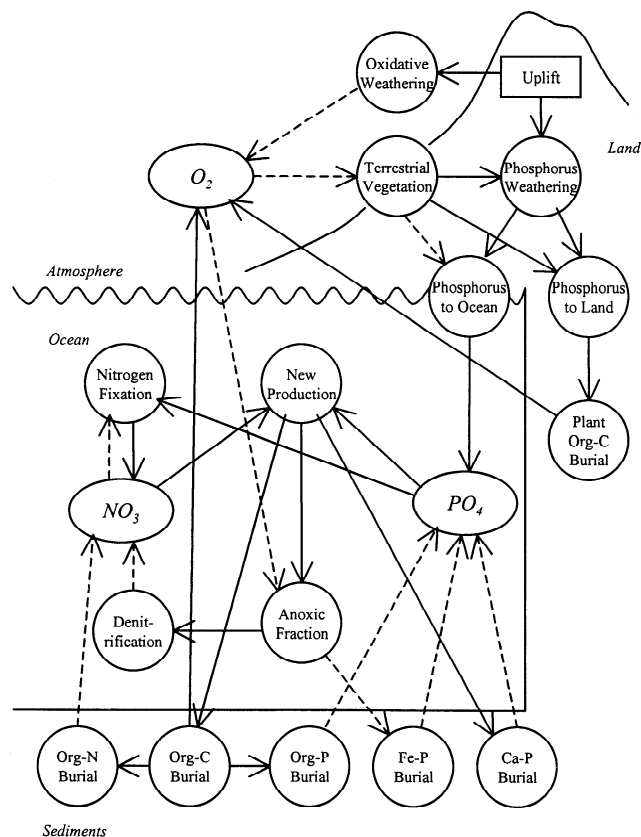


Figure 5. Extended model. This includes the effects of oxygen mixing ratio on terrestrial vegetation via fire frequency and suppression of photosynthesis (the Warburg effect). Terrestrial vegetation can in turn affect the distribution of weathered phosphorus between the land and the ocean (included in M7) or directly alter phosphorus weathering (included in M8). Labeling conventions are the same as in Figure 2.

Table 5. Terrestrial Extension of the Model

Fire Frequency (F)	Vegetation Biomass (V)	Photosynthesis (P)
$F = 586.2m_{O_2} - 122.1$ (18)	$V = \frac{20P}{F + 19}$ (19)	$P = 1.5 - 0.5 \frac{m_{O_2}}{0.21}$ (20)
Phosphorus Weathering (F_{PW}), Burial in Land Plant Matter (F_{PL}) and Input to the Ocean (F_{P-in})	Alternative Functions for Phosphorus Weathering and the Fraction Buried in Land Plant Matter	Terrestrially Derived Organic Carbon Burial (F_{TOrg-C}) and Revised Oxygen Balance
$F_{PW} = k_{11}U$ (21)	$F_{PW} = k_{11}U(0.1 + 0.9V)$ (28)	$F_{TOrg-C} = (C/P)_{land} F_{PL}$ (24)
$F_{PL} = LF_{PW}$ (22)		$\frac{dO_2}{dt} = k_9 \left(\begin{array}{l} F_{Org-C} + F_{TOrg-C} \\ - F_{Ox-W} \end{array} \right)$ (25)
$F_{P-in} = (1 - L)F_{PW}$ (23)		
$L = k_{12}$ (26)	$L = k_{12}V$ (27)	
New and Revised Constants	Description	Reference and Notes
$(C/P)_{land} = 1000$	burial ratio for terrestrially-derived organic matter	<i>Kump</i> [1988]
$k_{11} = 3.675 \times 10^{10}$ mol yr ⁻¹	initial phosphorus input flux from weathering	from terrestrial organic carbon burial of 0.75×10^{12} mol yr ⁻¹ and $(C/P)_{land} = 1000$, plus phosphorus input to ocean
$k_{12} = 0.02041$	initial fraction of phosphorus input buried in land plant matter	
$k_2 = 4.5 \times 10^{12}$ mol yr ⁻¹	initial oxidative weathering flux	for steady state

phosphorus. The new and revised equations are presented in Table 5 and explained in subsections 4.1 to 4.3, 5.1 and 5.2.

4.1. Fire Frequency Effect on Biomass

We take "ignition component" (Figure 1) as a measure of fire frequency. This is a numerical indicator of the probability of a fire resulting from a natural ignition source such as a lightning strike and is used to assess the probability of wildfires in the United States [*Deeming et al.*, 1972]. A value of 100 corresponds to the highest probability of ignition encountered in the field, (i.e., under 21% oxygen, in dry fuel at high ambient temperatures). *Watson* [1978] used laboratory measurements of ignition energy to derive ignition components for fuels of controlled moisture content, under atmospheres having oxygen concentrations differing from the present day. It was assumed that for a given fuel, a one-to-one relationship exists between ignition component and minimum ignition energy. Measurements of ignition energy at 21% oxygen but at different moisture contents were used to establish the form of this relationship, while measurements of ignition energy in atmospheres other than 21% were then used to predict ignition components as a function of atmospheric oxygen. The experiments were performed using paper as a substitute for natural forest or grassland fuel. Here, we take fuel of 20% moisture as being representative of the leaf litter where fires often begin [*Watson*, 1978]. A linear approximation (18) for the dependence of fire frequency, F , on oxygen mixing ratio, shown as the bold line in Figure 1, provides an excellent approximation to this data. For fuel of

this moisture content, the ignition component is (coincidentally) equal to 1 at 21% oxygen, but it can increase by nearly 2 orders of magnitude to 85 at 36% oxygen.

We consider fire frequency as one type of disturbance tending to determine the type of vegetation and limit vegetation biomass. Above a certain frequency of disturbance, no forest is able to regenerate and a region reverts to faster regenerating systems such as grassland. Grasslands (and before their advent, herbacious systems) have a much lower biomass per unit of area (or limiting nutrient) than forests and produce less of the difficult to biodegrade lignins. At higher frequencies of disturbance, even the persistence of grasses may be threatened. The pattern is one of decreasing biomass with increasing oxygen and fire frequency.

We assume that land plant biomass, V , given in normalized form by (19), is in steady state over the long timescales considered in the model (the time step is 100 years). Net primary production (NPP) increases biomass and is assumed to be a constant fraction of photosynthesis (P). Natural death, litter supply to the soil, grazing, fires, and other disturbances such as parasitism and disease all tend to decrease biomass. Only the frequency of fires is assumed to be variable. We assume that fires currently limit global vegetation biomass by ~5%. This is reasonable, as grasslands presently cover nearly one-fifth of the Earth's land surface [*Parton et al.*, 1993]. Fires have the potential to be the most important factor suppressing terrestrial vegetation. If oxygen increases to 36%, (19) predicts that fires reduce vegetation to <20% of its present biomass.

4.2. Warburg Effect on Photosynthesis

The "Warburg effect" [Fridovich, 1977] describes the direct limitation of C₃ plant growth by oxygen. In C₃ photosynthesis, oxygen and carbon dioxide compete for the enzyme Rubisco which acts either as oxygenase or carboxylase [Edwards and Walker, 1983]. Thus an increase in oxygen mixing ratio reduces net photosynthesis, while a decrease in oxygen increases net photosynthesis, the effect being sensitive to the ratio of carbon dioxide to oxygen in the air. An oxygen compensation point exists (for a given carbon dioxide concentration) at which photosynthesis is matched by photooxidation and above which net plant growth should not be possible [Tolbert *et al.*, 1995]. For tobacco plants (*Nicotiana glauca*) growing in 350 ppm CO₂, this was found to be at 27% oxygen mixing ratio [Tolbert *et al.*, 1995]. Under a reduction in oxygen to 5%, vegetative growth in some crops (e.g., soybean) increases by five fold [Edwards and Walker, 1983].

We use the results of plant growth experiments with Birch (*B. pubescens*) [Beerling *et al.*, 1998] to quantify the direct effect of oxygen mixing ratio on land plant photosynthesis, P , in (20). This provides a weaker dependence than suggested by studies of crops [Edwards and Walker, 1983; Tolbert *et al.*, 1995]. A linear relation agrees well with the predictions of a biochemical model [Farquhar *et al.*, 1980]. NPP is assumed to be a constant fraction of photosynthesis, although it has been estimated that NPP may be somewhat less sensitive to changes in oxygen [Beerling *et al.*, 1998]. We assume that the atmospheric carbon dioxide reservoir remains constant in our simulations, although this is clearly a limitation in our historical case study. Ignoring C₄ plants does not greatly affect our considerations (of the past at least) because C₄ plants have only become significant at a global scale in the last 7 Myr [Cerling *et al.*, 1993] and currently comprise only a small fraction of global biomass [Duursma and Boisson, 1994].

It has been suggested that the inhibition of photosynthesis by oxygen provides direct negative feedback against increases in atmospheric oxygen [Tolbert *et al.*, 1995], on the assumption that C₃ plants are the major source of atmospheric oxygen. However, over geologic timescales it is the small remainder of primary production that does not get respired and is buried in new sediments, which is the source of oxygen. To properly quantify the effects of suppressing vegetation, the fate of phosphorus must be considered. If oxygen suppresses terrestrial plant growth then more phosphorus may be transferred to the ocean, thus potentially allowing more production there [Kump, 1988].

4.3. The Fate of Phosphorus

The input flux of reactive phosphorus from chemical weathering of rocks, F_{PW} , is initially assumed to be proportional to the rate of uplift, U , in (21). This phosphorus may reach the sediments in land plant organic matter or in marine organic matter. A small fraction, L , of the weathered phosphorus is buried in land plant matter, with burial flux, F_{PL} , given by (22). The remainder forms the supply of reactive phosphorus to the ocean, F_{P-in} , given by (23), which replaces (8).

Terrestrially derived organic carbon burial, F_{TOrg-C} , given by (24) is dependent on the supply of phosphorus to the land and the C/P burial ratio. $(C/P)_{land} = 1000$ is used as representative of lignins, which are only produced by land plants and are the most resistant of all organic carbon compounds to degradation, making them the most likely to be buried and incorporated in sediments [Kump, 1988]. The revised oxygen balance is given by (25), which replaces (12).

The fraction of total organic carbon burial that is terrestrially derived has become the subject of some debate. An upper estimate is ~50% over Phanerozoic time [Kump, 1993]. Contemporary rivers with a high sediment load do transport large amounts of organic carbon [Ittekkot *et al.*, 1985]. However, on the basis of lignin content and $\delta^{13}C$, the majority of organic carbon buried appears to be of marine origin, even in coastal sediments with a high input of terrigenous organic carbon [Haddad and Martens, 1987; Hedges and Keil, 1995]. We assume that the burial flux of terrestrially derived organic carbon is presently only one-fifth of that from marine production, i.e., 0.75×10^{12} mol yr⁻¹. This represents a phosphorus sink of 7.5×10^8 mol yr⁻¹ (from C/P = 1000). Adding this to the initial flux of available phosphorus to the ocean of 3.6×10^{10} mol yr⁻¹ [Froelich *et al.*, 1982] implies a total phosphorus input from weathering of $k_{11} = 3.675 \times 10^{10}$ mol yr⁻¹. The initial flux of oxidative weathering is increased to $k_2 = 4.5 \times 10^{12}$ mol yr⁻¹ for steady state. The initial fraction of the phosphorus weathering flux buried in land plant matter (L) is $k_{12} = 0.02041$. If L is assumed to be constant, as in (26), the extended model reduces to the basic ocean model.

5. Testing Land-Based Feedback

Figure 6 shows the overall dependence of land plant biomass (V) on oxygen mixing ratio in the extended model. Increases in oxygen mixing ratio above 21% rapidly suppress vegetation as a result of changes in fire frequency. At ~24% oxygen, fires match other limiting factors, and vegetation is suppressed to half its original biomass, while at ~30% oxygen, vegetative biomass is reduced to one fifth of its present value.

5.1. Phosphorus Transfer to the Ocean (M7)

Increases in oxygen mixing ratio, fire frequency, and the suppression of the terrestrial biota plausibly cause the transfer of phosphorus from the land to the ocean [Kump, 1988]. If the carbon buried per unit of phosphorus is greater for terrestrial than marine organic matter and the input of phosphorus from weathering remains constant, an increase in oxygen will cause a decrease of total carbon burial and negative feedback on oxygen [Kump, 1988]. This mechanism combines positive feedback via changes in marine organic carbon burial with negative feedback via changes in terrestrially derived organic carbon burial. To quantify the feedback effect, we assume that the fraction of the reactive phosphorus input that ends up buried as land plant matter is linearly dependent on the biomass of terrestrial vegetation, in (27), which replaces (26). The rate of burial of land plant organic carbon $\frac{d}{dt}$ therefore becomes linearly dependent on vegetative biomass (v).

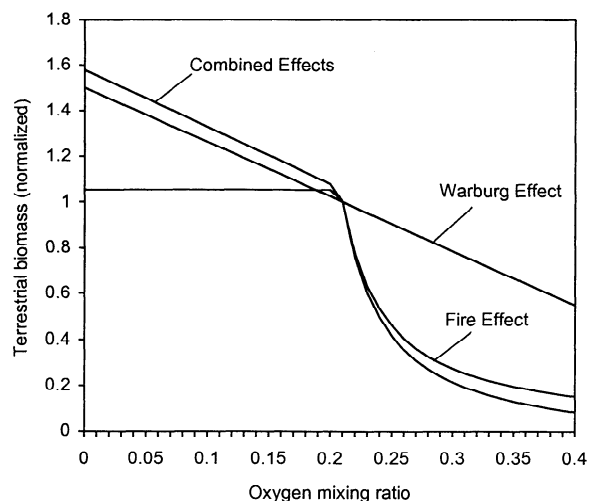


Figure 6. Estimated dependence of land plant biomass on atmospheric oxygen mixing ratio showing the contributions of fire frequency and the Warburg effect.

The feedback proposed by *Kump* [1988] is reasonably effective against increases in uplift that tend to force up oxygen. Figure 7a shows the response to a 50% increase in uplift. The rise in oxygen triggers a decline in terrestrial vegetation and a gradual increase in phosphorus input to the ocean. Total carbon burial declines because the reduction in terrestrially derived organic carbon burial dominates over the slight increase in marine organic carbon burial. Oxygen stabilizes at 23.4% of the atmosphere (Table 4, Figure 8a), causing a ~50% decline in terrestrial vegetation. Such a large decline is needed to generate the necessary reduction in terrestrially derived and total organic carbon burial.

Terrestrial vegetation is less sensitive to decreases in oxygen. Figure 7b shows the response to a 50% decrease in uplift. As oxygen declines, terrestrial vegetation is enhanced, mostly through alleviation of the Warburg effect and this generates an increase in both terrestrially derived organic carbon burial and overall carbon burial. However, it is not until oxygen has fallen to the point that some anoxia is reintroduced to the ocean (and the negative feedback on oxygen from changes in Fe-P burial is activated) that organic carbon burial rises to match oxidative weathering. Oxygen stabilizes at 10.6% of the atmosphere (Table 4, Figure 8b).

We have considered an upper limit on the terrestrially derived organic carbon burial flux by assuming that it is of the same magnitude (3.75×10^{12} mol yr⁻¹) as the marine organic carbon burial flux. Oxygen then stabilizes at 21.4% of the atmosphere in response to a 50% increase in uplift and 14.2% of the atmosphere in response to a 50% decrease in uplift.

Feedback on phosphorus transfer to the ocean improves oxygen regulation, as long as the C/P ratio of land plant matter is higher than that of marine organic matter. However, there is a lack of evidence for increases in the C/P ratio of marine sediments on moving toward the shore, where one might expect a greater fraction of terrestrial material to be deposited [Ingall and Van Cappellen, 1990]. Indeed, under anoxic conditions, marine organic matter can be buried with a

C/P ratio as high as 4000 [Ingall and Jahnke, 1994; Ingall et al., 1993]. If the average C/P burial ratio of marine organic matter exceeds that of terrestrial organic matter, the sign of the overall feedback postulated by *Kump* [1988] would become positive.

5.2. Biological Amplification of Phosphorus Weathering (M8)

The limitations of all the oxygen regulation mechanisms considered thus far suggest that we consider new proposals. It has long been recognized that land plants and their associated soil microbial community enhance weathering rates [Bernier and Maasch, 1996]. Biological amplification of weathering is thought to contribute to the regulation of carbon dioxide and climate over geologic timescales [Bernier, 1998; Lovelock and Whitfield, 1982; Schwartzman and Volk, 1989, 1991]. We hypothesize that biological amplification of chemical weathering also contributes to the regulation of atmospheric oxygen, by modulating the input of reactive phosphorus to the surface Earth system.

Table 6 summarizes data from natural and experimental ecosystems indicating that higher plants amplify weathering by about an order of magnitude [Bernier, 1998; Cochran and Bernier, 1996] relative to lichen or moss cover. Most studies

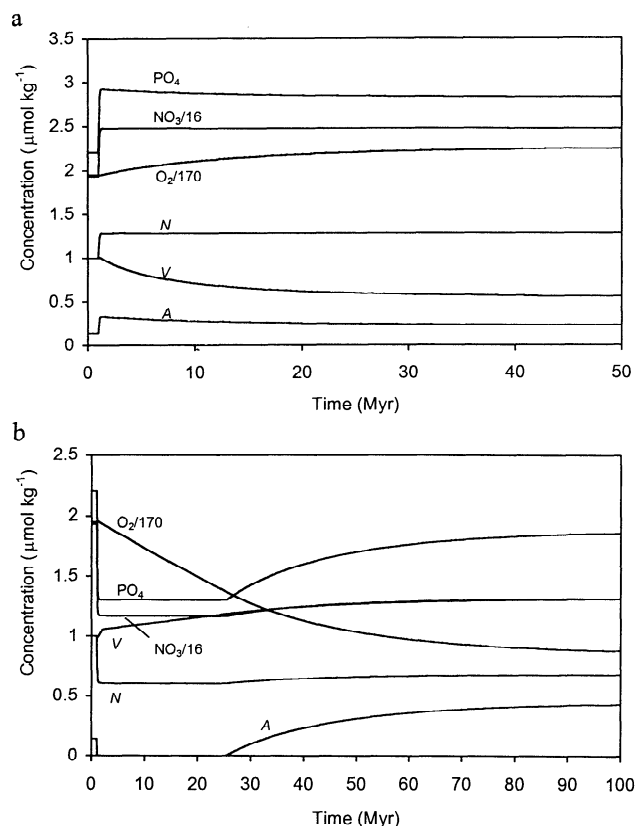


Figure 7. Vegetation feedback on phosphorus transfer to the ocean (M7), response to (a) 50% increase in uplift and (b) 50% decrease in uplift. Three dimensionless variables are shown: *N* is a normalized measure of new production in the ocean, *V* is a normalized measure of the biomass of terrestrial vegetation and *A* is the anoxic fraction of the ocean.

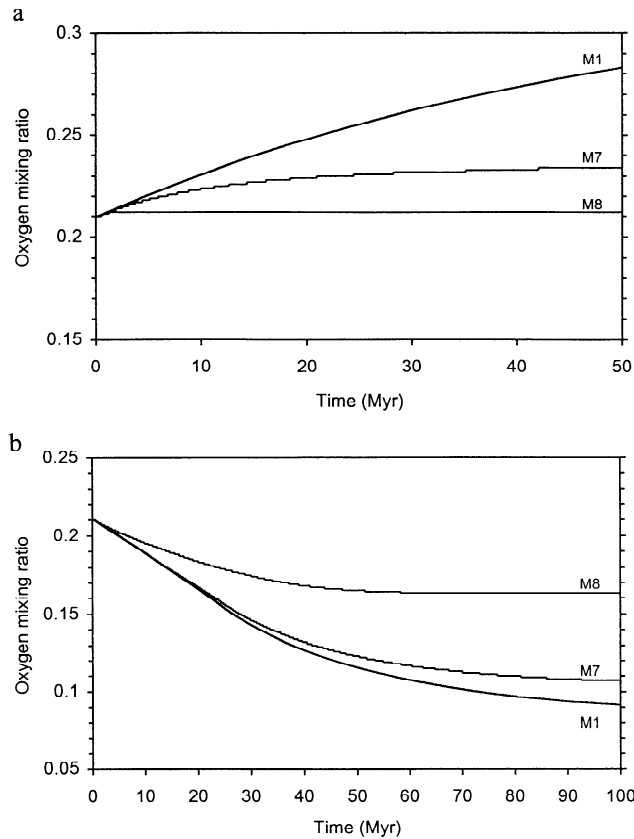


Figure 8. Atmospheric oxygen response to (a) 50% increase in uplift and (b) 50% decrease in uplift, for different vegetation-mediated feedbacks on phosphorus transfer to the ocean (M7) and phosphorus weathering (M8), contrasted with the basic model (M1).

contrast ion input from precipitation and output in stream water but do not account for accumulation in vegetation and/or soils and hence may greatly underestimate the degree of amplification [Bormann *et al.*, 1998]. The following biological processes amplify weathering rates [Berner, 1997; Schwartzman and Volk, 1991]: Root and microbial respiration generate increased soil $p\text{CO}_2$. Litter decomposes to carbonic and organic acids. Tree roots enhance physical weathering by splitting rocks, and their symbiotic microbes secrete organic acids and chelating agents that dissolve minerals, enhancing rock porosity [Berner and Cochran, 1998]. Polysaccharides produced by bacteria and fungi fracture mineral grains. Nitrifying and sulfur bacteria produce inorganic acids. Plants and microbes remove the soluble products of weathering, enhancing the reactions producing them (by Le Chatelier's principle). Plants stabilize soil, which retains water and maintains it in contact with a high surface area of mineral grains. Vegetation enhances the hydrological cycle, increasing precipitation on the land surface [Betts, 1999].

The amplification factor for weathering of phosphorus has not been measured directly but must be at least of similar magnitude to that for the bulk weathering of rock. Given that plants have a high requirement for phosphorus and rocks are ultimately the only source, it may be significantly greater than that for bulk rock, as is the case for the nutrient element, potassium. Indeed, acquisition of phosphorus and other rock-bound nutrients may be the evolutionary reason why plants and their associated soil microbes amplify rock weathering [Lenton, 1998a].

Figure 9 illustrates the hypothesized negative feedback on oxygen. Oxygen mixing ratio affects the abundance and type of vegetation and net primary production, such that changes in oxygen should trigger opposing changes in phosphorus weathering and the burial of organic carbon. For example, an

Table 6. Biological Amplification of Weathering by Higher Plants

Reference(s)	Vegetation	Contrasted With	Location	Factors Accounted For	Element	Amplification Factor
<i>Bormann et al.</i> [1998]	red pine	moss / lichen	experimental sandboxes at Hubbard Brook, New Hampshire	accumulation in vegetation and soil	Ca^{2+} Mg^{2+}	10 18
<i>Moulton and Berner</i> [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*
<i>Drever and Zobrist</i> [1992], <i>Moulton and Berner</i> [1998]	Deciduous forest	Rock (un-vegetated)	Southern Swiss Alps, different elevations	corrected for temperature differences	HCO_3^- , Si	8*
<i>Arthur and Fahey</i> [1993]	Forest (spruce and fir, 6% of watershed)	whole watershed (mostly un-vegetated)	Colorado Rocky Mountains		$\text{Ca}^{2+} + \text{Na}^+ +$ $\text{Mg}^{2+} + \text{K}^+$	3.5*
<i>Cawley et al.</i> [1969]	higher plants	lichen	Central Iceland		HCO_3^-	2-?*

*Underestimates because they do not account for accumulation in vegetation and/or soils [Bormann *et al.*, 1998].

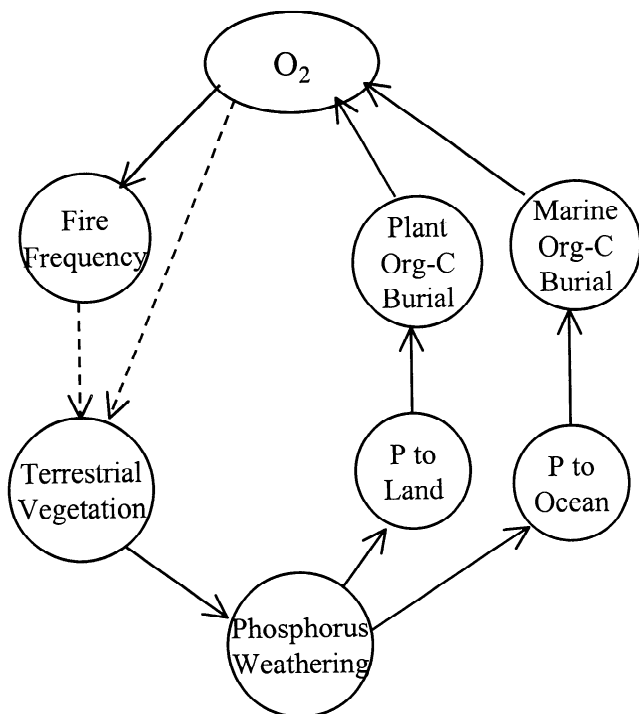


Figure 9. Hypothesized negative feedback on oxygen from biological amplification of phosphorus weathering. Land plants and the soil microbial community which depend on their net primary production increase the rate of chemical weathering and hence, we hypothesize, the flux of phosphorus liberated from rocks. This can determine the flux of land plant organic matter that is eventually buried. It also determines the flux of phosphorus to the ocean, which ultimately determines the amount of new production and the resultant flux of marine organic carbon burial. Organic carbon burial is the main source of oxygen. Oxygen mixing ratio in turn directly affects photosynthesis rates and indirectly affects terrestrial biomass by determining the frequency of fires, thus closing the feedback loop. Increases in oxygen are counteracted by reductions in phosphorus weathering flux and organic carbon burial. Decreases in oxygen are buffered by increased phosphorus weathering and organic carbon burial.

increase in oxygen tends to suppress terrestrial vegetation and phosphorus weathering. The reduced supply of phosphorus to the ocean will trigger a decline in nitrate, new production, and carbon burial, while reduced supply of phosphorus to land ecosystems will also suppress organic carbon production and burial. Both effects tend to counteract the rise in oxygen.

Equation (28), which replaces (21), assumes that the phosphorus weathering flux is linearly dependent on plant biomass in addition to a constant abiotic contribution and that plants presently amplify the weathering rate of rocks by a factor of 10. To independently examine the effect of this feedback, the fraction of weathered phosphorus that is buried in land plant matter (L) is kept constant at $k_{12} = 0.02041$, using (26).

Feedback on the rate of phosphorus weathering generates the most effective oxygen regulation of any of the systems considered thus far. In response to a 50% increase in uplift

(Figure 10a), oxygen stabilizes at 21.2% of the atmosphere within 3.5 Myr (Table 4, Figure 8a). Initially, the concentration of phosphate and nitrate in the ocean rise, such that total organic carbon burial exceeds oxidative weathering. As oxygen rises, this forces a decline in terrestrial vegetation and therefore the input of phosphorus to the land and ocean. This, in turn, generates a decline in both terrestrial and marine carbon burial until oxygen reaches steady state. The responsiveness of the feedback comes from the sensitivity of vegetation to increases in oxygen atmospheric fraction and fire frequency. Terrestrial biomass only has to decline by ~5% to achieve the new steady state.

In response to a decrease in uplift of 50% (Figure 10b), oxygen stabilizes at 16.3% of the atmosphere (Table 4, Figure 8b). As oxygen falls, this triggers a rise in terrestrial vegetation by eliminating all fires and through progressively alleviating the Warburg effect. This, in turn, increases phosphorus weathering, terrestrial, and marine organic carbon burial. A small amount of anoxia returns to the ocean, activating further negative feedback by suppressing Fe-P burial, and oxygen is stabilized. The final oxygen mixing ratio is the closest of all the model variants to the lower-bound inferred for the last 350 million years. This is notable because the rate of uplift is high on the present Earth relative to almost all of the Phanerozoic [Edmond, 1992].

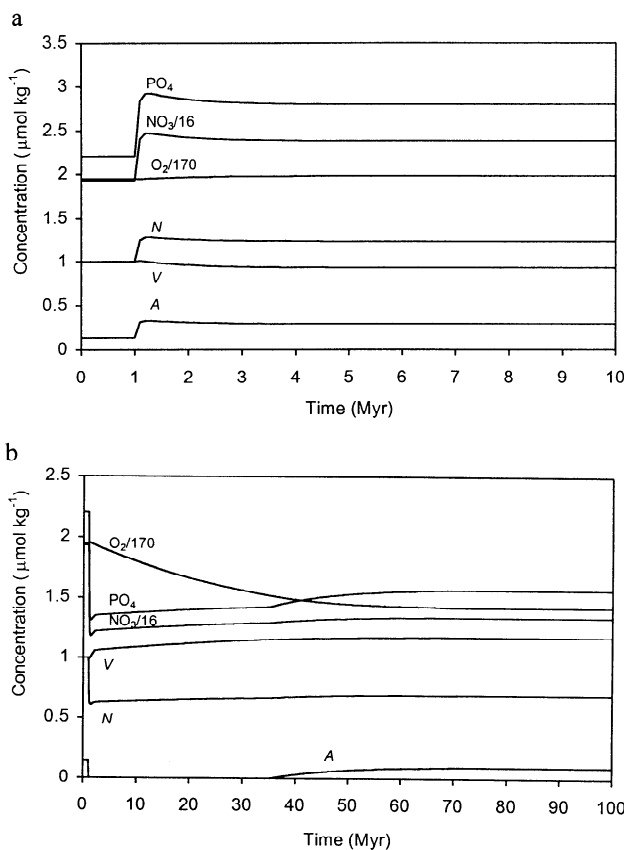


Figure 10. Vegetation feedback on phosphorus weathering (M8), response to (a) 50% increase in uplift and (b) 50% decrease in uplift.

Table 7. Sensitivity of Oxygen Regulation in the Final Model (M8) to the Formulation of Key Terrestrial Processes

Process	Alteration	Revised Equation / Constants	Final O ₂ , vol%	
			50% Increase in Uplift	50% Decrease in Uplift
Control (M8)	-	-	21.2	16.3
Biological amplification of phosphorus weathering	reduced to factor of 5	$F_{PW} = k_{11}U(0.2 + 0.8V)$	21.3	15.9
	reduced to factor of 2	$F_{PW} = k_{11}U(0.5 + 0.5V)$	21.4	14.3
Fire frequency dependence on oxygen	fuel moisture = 10%	$F = 56.04m_{O_2} - 10.77 *$	22.3	16.3
	fuel moisture = 0%	$F = 27.12m_{O_2} - 4.695 *$	22.7	16.3
Initial suppression of vegetation biomass by fire	decreased to ~1%	$V = \frac{100P}{F + 99}$	21.8	15.3
	increased to ~10%	$V = \frac{10P}{F + 9}$	21.1	17.6
Terrestrially-derived organic carbon burial flux	increased to $3.75 \times 10^{12} \text{ mol yr}^{-1}$	$k_{11} = 3.975 \times 10^{10} \text{ mol yr}^{-1}$ $k_{12} = 0.09434$ $k_2 = 7.5 \times 10^{12} \text{ mol yr}^{-1}$	21.2	17.9

*Linear approximation reasonable up to O₂ = 25 vol%.

5.3. Sensitivity Analysis

We have tested the robustness of our results by varying the formulation of key terrestrial processes in the final model (M8), as summarized in Table 7. Reducing the biological amplification factor for phosphorus weathering only slightly affects the regulation against increasing oxygen but significantly impairs the regulation against declining oxygen. Alternative functions for the dependence of fire frequency on oxygen mixing ratio were derived by fitting the 10 and 0% fuel moisture curves in Figure 1 and normalizing the equations to 1 at 21% oxygen. The sensitivity of fire frequency to increases in oxygen above 21% gets progressively weaker for drier fuel, but even for tinder dry fuel the regulation against increasing oxygen is impressive. Altering the fire frequency function has no effect on the response to a 50% decrease in uplift because oxygen stabilizes at a level (16.3%) that prevents fires in all cases. If the amount by which fires limit vegetation biomass is <5% at present, then this implies slightly weaker oxygen regulation. (Conversely, if it is >5%, this implies stronger oxygen regulation.) Finally, if we take an upper estimate for the terrestrially derived organic carbon burial flux, equal to the marine-derived flux, this significantly improves the regulation against declining oxygen. Overall, the strong oxygen regulation generated by negative feedback on the biological amplification of phosphorus weathering is a robust result.

6. Oxygen Over the Past 40 Myr

We now make a historical case study of the past 40 Myr, the period of Himalayan uplift and the growth of continental ice sheets. This interval is chosen because a growing range of paleo-oceanographic records and proxies for chemical weathering exist. These records bring us to the present (where

we know the sizes of the nitrate, phosphate, and oxygen reservoirs), and thus we can constrain model simulations to being consistent with the observed state of the Earth system. The impacts of Himalayan uplift and ice sheet growth on atmospheric carbon dioxide and climate have been much discussed [Caldeira *et al.*, 1993; France-Lanord and Derry, 1997; Raymo, 1994; Raymo and Ruddiman, 1993, 1992; Raymo *et al.*, 1988; Volk, 1993], but the implications for atmospheric oxygen have received relatively little consideration [Derry and France-Lanord, 1996]. The case study highlights contradictions between different proxy records, makes testable predictions, and allows us to evaluate particular hypotheses for the regulation of oxygen.

6.1. Proxies for Weathering Rates

A range of proxies have been interpreted as indicating an increase in the rate of chemical weathering over the past 40 million years [Delaney and Boyle, 1988; Raymo and Ruddiman, 1992], although this is much debated [Caldeira *et al.*, 1993; Raymo and Ruddiman, 1993; Volk, 1993]. The ⁸⁷Sr/⁸⁶Sr ratio of seawater [Edmond, 1992] has risen particularly steeply over the last 40 million years, concomitant with the uplift of the Tibetan plateau [Richter *et al.*, 1992]. This could be due to an increased flux of dissolved strontium from rivers originating in the Himalaya-Tibet region because these comprise a significant fraction of the global riverine strontium flux and are particularly rich in radiogenic strontium. The dashed line in Figure 11 is an estimate of the changes in the global river flux of strontium that would be required to produce the seawater strontium isotope curve [Raymo, 1994; Richter *et al.*, 1992]. The inferred flux increases at the time of the collision of India with Asia, and the rate of increase is a maximum from ~20 to ~15 Myr ago, a time of exceptionally high erosion [Richter *et al.*

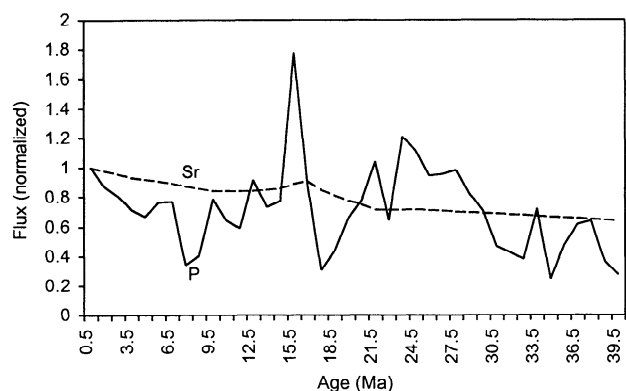


Figure 11. Alternative proxies for chemical weathering rates over the past 40 Myr. The dashed line is the strontium river flux inferred from the seawater strontium isotope record, assuming hydrothermal strontium flux changes in proportion to seafloor spreading rates and that riverine $^{87}\text{Sr}/^{86}\text{Sr} = 0.713$ [Raymo, 1994; Richter *et al.*, 1992]. The solid line is the global, geometric mean phosphorus accumulation rate in biogenic sediments [Föllmi, 1995].

al., 1992]. However, increases in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the river water draining the Himalaya-Tibetan plateau, particularly since the late Miocene (~15 Myr ago) [Quade *et al.*, 1997], could equally have caused the rise in seawater $^{87}\text{Sr}/^{86}\text{Sr}$. This would tend to reduce the inferred changes in the river flux and weathering rates.

The global (geometric mean) phosphorus accumulation record in biogenic sediments [Föllmi, 1995], shown by the solid line in Figure 11, offers an alternative proxy for the input of bio-available phosphorus to the ocean and the rate of continental weathering. Phosphorus has a much shorter residence time in the ocean ($1.5\text{--}8.5 \times 10^4$ years) than strontium ($\sim 3 \times 10^6$ years) giving a much finer resolution proxy. This may in part account for the much larger variations observed in phosphorus accumulation rate than in inferred strontium river flux (Figure 11). Phosphorus accumulation appears to have increased significantly over the last 40 Myr, and this could have been driven by progressive glaciation [Föllmi, 1995, 1996]. The largest peak in the phosphorus accumulation record, at 15 Ma, roughly coincides with the main peak in the inferred riverine flux of strontium (allowing for the uncertainty in dating the records), suggesting a major peak in continental weathering at this time. However, the data for phosphorus accumulation [Föllmi, 1996] are limited in being biased toward the deep sea [Mallinson and Compton, 1997], missing large phosphorite deposits on the continental shelves [Ruttenberg, 1993] and phosphorus burial in deltaic and other near-shore sediments. Furthermore, the large fluctuations in phosphorus burial suggested in Figure 11 may be an artifact of the interpretation of the data set [Föllmi, 1995, 1996], which shows considerable scatter.

Seawater $^{187}\text{Os}/^{186}\text{Os}$ has increased from 3.2 at 58 Ma to ~8.6 today, which could be explained by increased weathering of the crust which is particularly rich in ^{187}Os [Pegram *et al.*, 1992]. The changes correlate well with the $^{87}\text{Sr}/^{86}\text{Sr}$ evolution of seawater [Pegram *et al.*, 1992]. However, an increase in the $^{187}\text{Os}/^{186}\text{Os}$ of rivers due to the

weathering of rhenium-rich Himalayan black shales may also have contributed [Pegram *et al.*, 1992]. Germanium and silicon have similar geochemical behavior in the ocean, and the Ge/Si ratio recorded in diatoms has declined from 35 Ma to the present. This could be explained by an increase in the dissolved river flux of silicon by up to a factor of 3.5 [Shemesh *et al.*, 1989]. However, this estimate is highly sensitive to a number of assumptions, and the increase may have been as little as 10% [Delaney and Filippelli, 1994]. A slight increase in the Sr/Ca ratio of marine carbonates has been attributed to a decrease in the hydrothermal Ca flux, assuming the riverine Sr/Ca ratio remained constant [Graham *et al.*, 1982], but this does not constrain absolute river fluxes [Delaney and Boyle, 1988]. A significant increase in the calcium carbonate compensation depth is consistent with increasing dissolved river fluxes during the Cenozoic [Delaney and Boyle, 1988].

6.2. Methodology

We use the inferred strontium river flux and the global phosphorus accumulation flux in biogenic sediments (Figure 11) as alternative proxies to force uplift in the basic ocean model (M1) and the extended model with biological amplification of phosphorus weathering (M8). Both records are averaged at 1 Myr intervals, and we retain this resolution, changing uplift once every 1 Myr in the model (while the model time step remains 100 yr). The normalized phosphorus burial record is a good proxy for forcing phosphorus weathering. Even when phosphorus weathering is also affected by vegetation (M8), there is only a slight discrepancy between the predicted phosphorus burial and the actual record. Neither phosphorus or strontium records may be appropriate proxies for forcing oxidative weathering. However, if we decouple phosphorus weathering and oxidative weathering, this forces large variations in oxygen [Lenton, 1998b]. The modeling effort involves trial-and-error manual iteration in an attempt to predict what the sizes of the oxygen reservoir must have been 40 Myr ago in order to arrive at the current value. Changes in forcing are generally of sufficient magnitude to prevent oxygen from remaining in

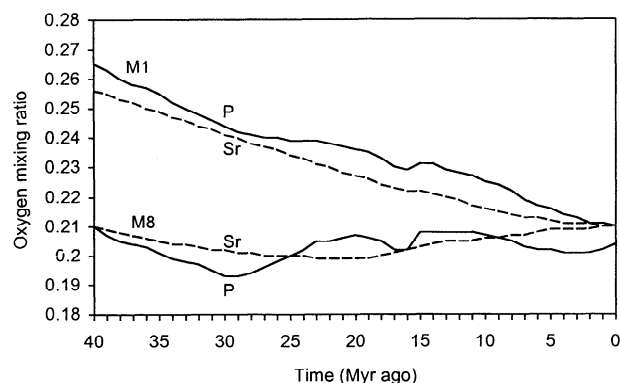


Figure 12. Histories of atmospheric oxygen predicted from the basic ocean model (M1) and the extended model with biological amplification of phosphorus weathering (M8) using either inferred Sr river flux or P accumulation rate as proxies for uplift.

steady state, suggesting that a steady state modeling approach [Berner and Canfield, 1989] to this period is inappropriate. The model cannot be run backwards in time because changes in the oxygen reservoir generally lag changes in forcing by 2-3 Myr.

6.3. Basic Ocean Model (M1)

In the basic ocean model (M1), under a given decrease in uplift, organic carbon burial declines more than oxidative weathering generating a net removal of oxygen from the atmosphere. Therefore if the rate of uplift has been less than at present for most of the last 40 Myr, then the model demands that the oxygen reservoir must have been larger than now 40 Myr ago.

Taking the inferred strontium river flux as a proxy for uplift the model predicts that the oxygen reservoir was 4.8×10^{19} mol, 40 Myr ago, amounting to 25.6% of the atmosphere (Figure 12). The ocean is predicted to have been fully oxic until 9 Myr ago, with anoxia rising steadily since then (Figure 13a). When terrestrial vegetation is included as a variable dependent on oxygen but with no resulting feedback effects, it is predicted to have been only 33% of its present biomass 40 Myr ago. Marine new production is predicted to have risen from 71% of its present value 40 Myr ago, as a consequence of increasing phosphorus input to the ocean.

Forcing the model with the phosphorus burial record generates a similar prediction of a larger oxygen reservoir of 5.02×10^{19} mol, 40 Myr ago, corresponding to 26.5% of the

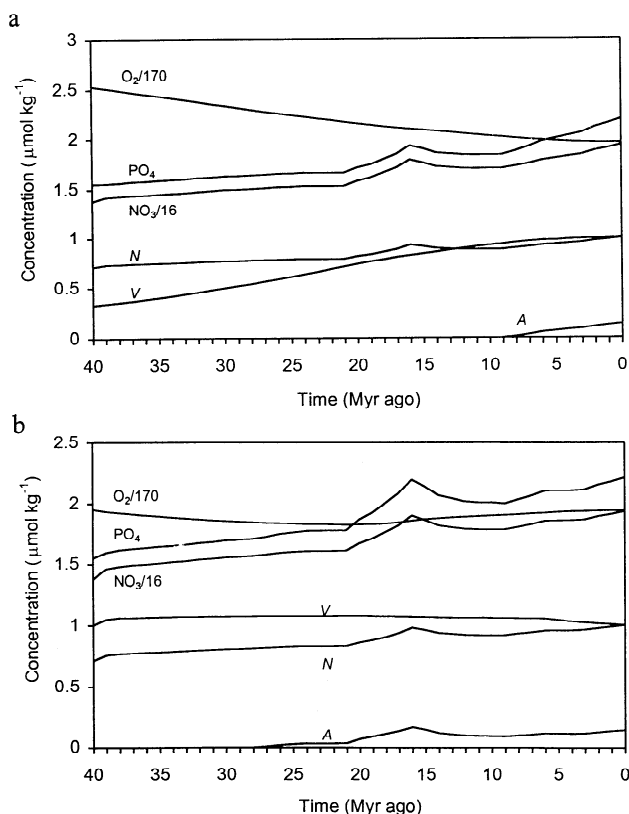


Figure 13. Inferred strontium river flux forcing of (a) basic ocean model (M1) and (b) extended model with biological amplification of phosphorus weathering (M8).

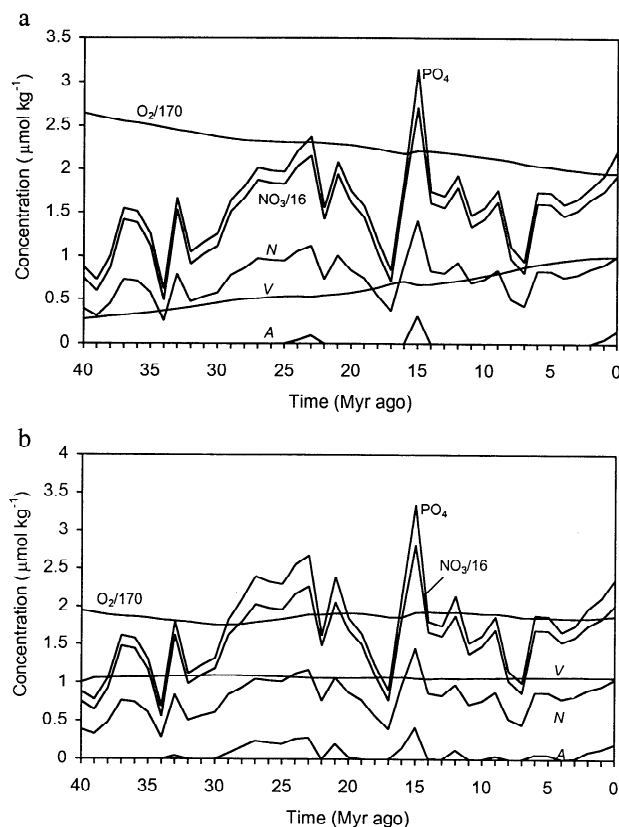


Figure 14. Phosphorus accumulation flux forcing of (a) basic ocean model (M1) and (b) extended model with biological amplification of phosphorus weathering (M8).

atmosphere (Figure 12). The ocean is predicted to have lacked anoxia for most of the last 40 Myr, with only brief intrusions ~23 Myr ago, 15 Myr ago, and over the last 2 Myr (Figure 14a). The high oxygen level is predicted to have suppressed terrestrial vegetation to only 27% of its present biomass 40 Myr ago, while reduced phosphorus input to the ocean restricted marine new production to ~35% of its present level.

6.4. Biological Amplification of Phosphorus Weathering (M8)

When the extended model with vegetation feedback on phosphorus weathering (M8) is forced with the strontium derived proxy for uplift (Figure 13b), the rate of change of uplift is slow enough and the model is responsive enough for oxygen to remain close to steady state with uplift. Under decreases in uplift, oxygen tends to decline, but this triggers a slight increase in terrestrial vegetation, phosphorus weathering, and reduced transfer of phosphorus to the ocean, counteracting the change in oxygen. Oxygen is predicted to have varied slightly over a range of 19.9-21.0% during the past 40 Myr (Figure 12). The ocean is predicted to have been fully oxic from 40 to 28 Myr ago and to have contained some anoxia since then (Figure 13b). The changes in terrestrial biomass necessary for effective feedback are small. However, reduced phosphorus input to the ocean suppresses marine new production to 71% of its present level, 40 Myr ago.

When forced with the phosphorus-derived proxy for uplift, oxygen is maintained within the range 19.3-21.0% (Figure 12) throughout the past 40 Myr by feedback involving small changes in terrestrial vegetation (Figure 14b). Marine new production varies over a range of 29-145% of its present value due to variations in phosphorus input to the ocean. Interestingly, when the initial size of the oxygen reservoir 40 Myr ago is altered, this does not affect its final size. Feedback against increases in oxygen above 21% atmospheric fraction, via fire frequency effects on land plants, is so strong that even when oxygen is started at ~25%, within 10 million years it is brought back to 21%.

6.5. Comparison With Other Records and Models

The differences between the two proxies of weathering flux adopted makes little difference to the first-order predictions of oxygen reservoir size in the two model variants. For both records, the basic ocean model (M1) predicts high oxygen mixing ratio (>25%) 40 Myr ago, while the extended model with vegetation feedback on phosphorus weathering (M8) predicts oxygen mixing ratio close to the present level (within 19-21%) throughout the past 40 Myr. The differing oxygen predictions allow us to evaluate the two models against historical records. The basic ocean model (M1) predicts raging fires and terrestrial vegetation suppressed to ~30% of its present biomass 40 Myr ago. An oxygen atmospheric fraction of 25% 40 Myr ago has also been predicted from a geochemical mass-balance model [Berner and Canfield, 1989]. There are no signs of fire catastrophe in the historical record. Indeed, the charcoal content of Pacific deep-sea cores has risen over the past 25 Myr [Herring, 1985]. This observation is inconsistent with the predictions of the basic ocean model (M1) or the model of Berner and Canfield [1989] but is consistent with the slight increase in oxygen predicted with vegetation feedback on phosphorus weathering (M8), coupled with a drying of the climate [Frakes, 1979].

Past changes in oxygen inferred from the marine $\delta^{13}\text{C}$ record [Shackleton, 1987] are poorly constrained due to uncertainty in the mean isotopic fractionation between carbonate and organic matter being eroded, and until this is better constrained, even the sign of any overall change remains uncertain [Raymo, 1997]. Both an overall decline in the sedimentary organic carbon reservoir, implying shrinkage of the oxygen reservoir [Compton and Mallinson, 1996; Raymo, 1994; Shackleton, 1987], and an overall increase, implying growth of the oxygen reservoir [Derry and France-Lanord, 1996], have been inferred. Our basic ocean model (M1) predicts an overall shrinkage of the sedimentary organic carbon reservoir, while the extended model with vegetation feedback on phosphorus weathering (M8) predicts little net change.

6.6. Climate and Carbon Dioxide Effects

Our model simulations assume that climate remains constant, whereas it has cooled and probably dried over the last 40 Myr [Frakes, 1979]. Both climate cooling and drying should have tended to reduce chemical weathering rates with time, as they are linearly dependent on precipitation and exponentially dependent on temperature [White and Blum, 1995]. Cooling will also have increased the solubility of

oxygen in the ocean and tended to reduce the anoxic fraction. Hence, if global temperature change were included in the model, it would tend to predict more anoxia in the past, implying more scope for anoxia-mediated negative feedback on oxygen. A wetter climate 40 Myr ago might have allowed oxygen to rise slightly above 21% mixing ratio, without increasing fire frequency. However, in order to maintain the same probability of ignition under ~25% oxygen, an increase in fuel moisture content from 20 to 35% is required, and wood fibres saturate at ~30% moisture content [Watson, 1978]. Climate cooling over the past 40 Myr may have been caused by a decline in atmospheric carbon dioxide [Berner, 1994], which would have tended to directly suppress chemical weathering and increase the Warburg effect, suppressing C_3 photosynthesis and the biological amplification of weathering. This could have forced a decline in oxygen by reducing the input of phosphorus from rock weathering (as well as causing a direct negative feedback on atmospheric carbon dioxide). However, C_4 plants have proliferated in the last ~7 Myr [Cerling *et al.*, 1993], tending to prevent any decline in global productivity by out-competing C_3 plants in warmer environments under lower CO_2 .

7. Coupled Regulation of Redfield Ratios

Regulation of atmospheric oxygen is not completely consistent with regulation of the nitrate, phosphate and oxygen contents of the ocean toward the Redfield ratios [Lenton and Watson, this issue]. The regulation of oxygen involves the absolute amount in the atmosphere, assuming the mass of the remainder of the atmosphere is constant. In contrast, regulation toward the Redfield ratios involves the proportions of phosphate, nitrate, and oxygen in the ocean. Simultaneous regulation of (1) the size of the atmospheric oxygen reservoir, (2) the deep ocean nitrate and phosphate reservoirs toward Redfield ratio, and (3) oxygen demand and availability in the ocean toward Redfield ratio would demand that the phosphate and nitrate reservoirs in the ocean are regulated toward fixed sizes, corresponding to their initial steady state values. Such coupled regulation is difficult to achieve because changes in uplift force the nutrient reservoirs, which must adjust such that carbon burial comes to match oxidative weathering for the system to return to a steady state.

In response to increases in uplift, the size of the nutrient reservoirs are initially increased, and the systems then adjust such that organic carbon burial comes to match the increased oxidative weathering. If there is effective regulation of the oxygen reservoir, then the limiting nutrient and oxygen demand must remain above Redfield ratio to oxygen supply (e.g., Figures 4a, 7a, and 10a). In response to decreases in uplift, oceanic negative feedbacks rely on forcing up nutrients and new production to stabilize declining oxygen. In some cases (e.g., Figures 4b and 10b), there is regulation of both deep ocean $\text{PO}_4:\text{NO}_3$ toward Redfield ratio and $\text{NO}_3:\text{O}_2$ (oxygen demand and supply) toward Redfield ratio, but this is at the expense of oxygen regulation. If atmospheric oxygen were more effectively regulated, the oxygen content of the ocean would remain above Redfield ratio to the nutrients, removing anoxia.

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Hence, there appears to be a trade off between the strength of atmospheric oxygen regulation and the regulation of

oxygen supply and demand in the ocean. Simulations of the last 40 Myr confirm that the phosphate and nitrate contents of the ocean tend to track changes in phosphorus input and only close to the present rate of uplift are they near Redfield ratio to the oxygen content of the ocean. There is little evidence regarding the balance of oxygen supply and demand in the past, except for ocean anoxia events (~90 and ~110 Myr ago) where demand clearly exceeded supply [Holland, 1984]. If the ocean was ever fully oxic, the shift in $\delta^{15}\text{N}$ of oceanic nitrate due to denitrification would have been much less than today, and this should be recorded in the $\delta^{15}\text{N}$ of marine organic matter. Hence our predictions of changes in ocean anoxia are potentially testable with a $\delta^{15}\text{N}$ record for the past 40 Myr. We conclude from the present study and existing evidence that there is an element of chance in our observing today's ocean on "the edge of anoxia," while oxygen regulation and regulation of the deep ocean nitrate to phosphate ratio are more robust properties of the Earth system.

8. Conclusion

Hypotheses for the regulation of the oxygen content of the atmosphere have been tested with a new model of the coupled biogeochemical cycles of nitrogen, phosphorus, carbon, and oxygen. In the basic ocean-only model, negative feedback involving the suppression of iron-sorbed phosphorus by anoxia buffers declining oxygen [Holland, 1994], but it is counteracted by a positive feedback from enhanced denitrification [Lenton and Watson, this issue]. Suppression of organic phosphorus burial by anoxia provides a further negative feedback improving oxygen regulation [Van Cappellen and Ingall, 1996], as does any weak enhancement of organic carbon burial efficiency under anoxic conditions [Betts and Holland, 1991]. However, increases in atmospheric oxygen that remove anoxia from the ocean can remove any ocean-based feedback, leaving oxygen rising.

The frequency of fires is extremely sensitive to any increase in the mixing ratio of atmospheric oxygen above 21%, and this also directly suppresses photosynthesis. If oxygen increases from 21 to 25% of the atmosphere, we predict that vegetation biomass will be drastically reduced unless the climate gets much wetter. Ocean-based feedback mechanisms cannot prevent atmospheric oxygen rising to levels that would decimate the land biota. Changes in plant growth and terrestrial biomass affect the distribution of phosphorus between the land and the ocean providing negative feedback against increases in oxygen [Kump, 1988], but the effect appears to be too weak to explain the past stability of oxygen. A new proposal, which is that changes in plant growth alter the rate of weathering of phosphorus from rocks, provides the most effective regulatory feedback on oxygen of any of the systems considered.

In simulations of the past 40 million years, when a model with plant-mediated feedback on phosphorus weathering (M8) is subject to large changes in uplift inferred from strontium isotope or phosphorus accumulation records, oxygen is regulated close to 21%. In contrast, in a model with only ocean-based feedback on oxygen (M1), oxygen is predicted to have been >25% 40 million years ago and with the ocean lacking anoxia, there is no feedback on oxygen for much of

the past 40 million years. Negative feedback on carbon burial, mediated by fire frequency effects on land plants, appears necessary to simulate a plausible history of atmospheric oxygen. Furthermore, regulation against rises in oxygen above 21% is so strong that we predict only wet periods can have oxygen exceeding 25%. Our model feedback system has a "set point" for oxygen regulation of 21%. We suggest that changes in the wetness of climate may adjust this set point, under a drier climate toward a minimum of ~18% (the level at which completely dry fuel is most sensitive to increasing oxygen), while a wetter climate might increase it toward 25%.

Regulation against declining oxygen is generally less effective than regulation against increasing oxygen in our model systems. One potentially important effect we have not quantified is that of oxygen mixing ratio on the amount of secondary respiration. If secondary respiration is suppressed at low oxygen levels, because large bodied herbivores cannot metabolize effectively, this may leave more carbon for burial and thus act as a negative feedback on oxygen. As organic carbon burial presently represents the tiny difference between two very large fluxes of net primary production and secondary respiration, any sensitivity of this balance to oxygen mixing ratio could provide strong feedback. A further negative feedback would occur if decreases in oxygen caused decreases in oxidative weathering, but the effect is thought to be weak [Holland, 1978] and might be counteracted by increases in the biological amplification of oxidative weathering.

We conclude that atmospheric oxygen can be regulated within approximate bounds of 18-25% by realistic feedback mechanisms involving a combination of organic and inorganic processes. Such feedback mechanisms operate more rapidly than sediment recycling [Berner and Canfield, 1989]. Mass-balance approaches demonstrate that crustal overturn only buffers oxygen over hundreds of millions of years [Van Cappellen and Ingall, 1996]. By enhancing phosphorus input through amplifying rock weathering and suppressing phosphorus output through preferential recycling from sediments, different organisms increase the amount of phosphorus in circulation in the Earth system, while other nitrogen-fixing organisms help maintain nitrogen at equivalent, biologically available levels to phosphate. Thus the potential for new photosynthetic production in the Earth system is increased. Inorganic processes, tightly coupled to organic processes in feedback loops, contribute to a self-regulating overall system. The ratio of nitrate and phosphate concentrations in the deep ocean and the oxygen mixing ratio of the atmosphere appear to be maintained in preferable states for life, by feedbacks involving organic processes. This supports Redfield's insight into the biological control of chemical factors in the environment [Redfield, 1958; Whitfield, 1981] and Lovelock's Gaia theory [Lenton, 1998a; Lovelock, 1995].

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