Redfield revisited

1. Regulation of nitrate, phosphate, and oxygen in the ocean

Timothy M. Lenton and Andrew J. Watson
School of Environmental Sciences, University of East Anglia, Norwich, United Kingdom

Abstract. The ratio of phosphate and nitrate concentrations in the deep ocean matches closely the Redfield ratio required by phytoplankton growing in the surface ocean. Furthermore, the oxygen available from dissolution in ocean water is, on average, just sufficient for the respiration of the resulting organic matter. We review various feedback mechanisms that have been proposed to account for these remarkable correspondences and construct a model to test their effectiveness. The model’s initial steady state is close to the Redfield ratios and stable against instantaneous changes in the sizes of the nitrate and phosphate reservoirs. When classic flux estimates are adopted, nitrate responds to perturbation in 1000-2000 years and phosphate in 40,000-60,000 years. However, recently increased estimates of the input and output fluxes of nitrate and phosphate suggest that they respond more rapidly to perturbation, nitrate in 500-1000 years and phosphate in 10,000-15,000 years. Nitrogen fixation tends to maintain nitrate close to Redfield ratio with phosphate, while denitrification tends to keep nitrate as the proximate limiting nutrient and tie it in Redfield ratio to dissolved oxygen. Under increases in phosphorus input to the ocean, the relative responsiveness of nitrogen fixation and denitrification determine whether nitrate remains close to Redfield ratio to phosphate or to oxygen. If nitrogen fixation is strongly limited (e.g., by lack of iron), increasing phosphorus input to the ocean can cause phosphate to deviate above Redfield ratio to nitrate. Hence nitrogen dynamics can control phosphate behavior and nitrate can potentially be the ultimate limiting nutrient over geologic periods of time. When nitrate and phosphate are coupled together by responsive nitrogen fixation, negative feedbacks on organic and calcium-bound phosphorus burial stabilize their concentrations. If anoxia suppresses organic phosphorus burial, the resulting feedbacks on phosphate (positive) and oxygen (negative) improve regulation toward the Redfield ratios. Variants of the model are forced with a global record of phosphorus accumulation in biogenic sediments as a proxy for changes in phosphate input to the ocean over the past 40 Myr. Nitrate is generally regulated close to Redfield ratio to phosphate, despite large changes in phosphorus input. If nitrogen fixation is strongly limited, then there is one interval (~15 Myr ago) when a very rapid increase in phosphate input forces phosphate above Redfield ratio to nitrate. Decreases in phosphorus input cause phosphate and nitrate to quickly deviate below Redfield ratio with oxygen, removing anoxia from the ocean, while increases in phosphorus input rapidly increase anoxia. Hence we conclude that there appears to be an element of chance in observing today’s ocean “on the edge of anoxia” with nitrate, phosphate, and oxygen all close to the Redfield ratios.

1. Introduction

There is a well-known, striking correspondence between the requirements of marine organisms for P, N, and O₂ and the ratio of PO₄, NO₃, and O₂ dissolved in ocean water [Redfield, 1958]. The Redfield ratios describe the average composition of marine organic matter and the oxygen required to respire it; their classic values are P:N:C:O₂ = 1:16:106:138 [Redfield, 1934, 1958; Redfield et al., 1963].

The precise Redfield ratio values have recently been the subject of debate [Anderson and Sarmiento, 1994; Broecker et al., 1985; Peng and Broecker, 1987; Shaffer, 1987; Takahashi et al., 1985] with the current best estimates being P:N:C:O₂ = 1:16(+1):117(+14):170(+10) [Anderson and Sarmiento, 1994]. However, the classic values are still widely used, for example in modeling studies [Van Cappellen and Ingall, 1994]. The PO₄:NO₃ ratio of deep water is ~1:15, close to the 1:16 required by organisms, making nitrate, on average, the proximate limiting nutrient. The deep ocean concentration of nitrate thus determines the oxygen demand of respiration, which appears well matched over the whole ocean by the supply of oxygen dissolved in surface waters. For example, a simple calculation of the initial concentration of oxygen in the waters that ventilate the deep ocean, using the formula of Weiss [1970] and assuming they are at 2⁰C and have 35% salinity, yields a value of 331.5 μmol kg⁻¹. Taking

1Now at Institute of Terrestrial Ecology, Edinburgh Research Station, Bush Estate, Penicuik, Midlothian, United Kingdom.

Copyright 2000 by the American Geophysical Union.

Paper number 1999GD900065
0886-6236/00/1999GD900065$12.00
the average concentration of nitrate in the deep ocean as ~31 µmol kg⁻¹ (from analysis of the World Ocean Atlas dataset by T. Tyrrell, personal communication, 1998), the revised Redfield ratios [Andersson and Sarmento, 1994] suggest that this generates an oxygen demand of ~330 µmol kg⁻¹, remarkably similar to the calculated oxygen supply. When one turns to a plot of oxygen saturation with depth averaged annually and over the world ocean [Levitus, 1982], the correspondence is not so close, there is at least 50% excess oxygen at all depths. This discrepancy may be a result of incomplete nutrient utilization and the seasonality of new production versus more continuous ventilation. However, average oxygen concentrations on the oxygen minimum surface (Figure 1) [Levitus, 1982] indicate an ocean that is in some sense “on the edge of anoxia.” Anoxia appears at the ends of the oceanic “conveyor belt” and in regions of high productivity. Increases in the limiting nutrient relative to oxygen supply could readily extend these regions.

The remarkable correspondence between marine life’s requirements for nitrogen, phosphorus, and oxygen and the availability of these elements in ocean water begs an explanation. Redfield [1958] offered three possibilities: first it may simply be “a coincidence, dependent on the accidents of geochemical history.” Second, it could be the result of “adaptation on the part of the organism” to the prevailing oceanic conditions. Finally, the correspondence might arise from feedback mechanisms involving “organic processes which tend in some way to control the proportions of these elements in the water”. “Feedback” is defined as occurring when a change in an environmental variable triggers a response that affects that variable. Feedback is said to be “negative” when it tends to damp the initial change and “positive” when it tends to amplify it.

Given that the correspondence involves three elements, the probability of it being a coincidence is very low [Redfield, 1958]. It is also difficult to frame such an explanation as a falsifiable hypothesis. Regarding adaptation, Redfield [1958] noted that phytoplankton do have some ability to vary their elemental composition. Subsequent work has shown that phytoplankton can exhibit large variations in composition from the Redfield ratios when grown under phosphorus or nitrogen limited conditions and at low growth rates [Goldman, 1986; Goldman et al., 1979]. However, at high growth rates, phytoplankton composition approaches the Redfield ratios of C₁₆₆N₁₆P₁, even when the nutrient balance of the medium is far from these proportions [Goldman, 1986; Goldman et al., 1979]. Thus C₁₆₆N₁₆P₁ may be an optimum composition for phytoplankton biochemistry, independent of the composition of the growth medium. Furthermore, the correspondence of oxygen supply and demand relates to the balance of organic matter production and the chemical stoichiometry of respiration. There seems little scope for adaptation on the part of the heterotrophic, respiring organisms to circumvent chemical constraints, and there is no clear evolutionary reason why organisms in the surface ocean would adapt their elemental composition to suit the consumers below.

For these reasons, we follow Redfield [1958] in exploring to what degree realistic feedback mechanisms involving organisms can control the proportions of phosphate, nitrate, and oxygen in ocean water. We return at the end to consider the need to invoke adaptation or chance to explain the current correspondence. The candidate feedback hypotheses are summarized in Table 1 and referred to in the text by “Fn”. We construct a simple model to test their effectiveness, illustrated in Figure 2. The initial model (termed “M1”) is described in section 2, and its response to perturbation is examined in section 3. In section 4 we explore the implications of uncertainties in the residence times of nitrate and phosphate, and the functional responses of nitrogen fixation and phosphorus burial, by making independent variants of the model and comparing their responses to perturbation. In section 5, we force variants of the model with a proxy for phosphorus input to the ocean over the last 40 million years.

2. Feedback Model

The main features of the coupled N, P, and O₂ system can be captured in a simple model (Figure 2). This approach is appropriate to our limited understanding of many of the key processes we wish to incorporate, is easier to understand than a more complex model, including being more mathematically tractable (the equations can be solved analytically), and is computationally efficient (allowing us to perform 100 million year simulations and perform multiple sensitivity experiments).

We restrict the model to three reservoirs, deep ocean phosphate, deep ocean nitrate, and atmospheric oxygen equilibrated with the surface ocean. The “NO₃” reservoir represents all biologically available reactive forms of nitrogen, including ammonia, and is dominated by nitrate itself. Initial reservoir sizes are given in Table 2. The phosphate and nitrate reservoirs are expressed as the average concentration dissolved in the deep ocean in mol kg⁻¹. The oxygen reservoir is expressed as the concentration dissolved in high-latitude surface waters that ventilate the deep ocean, also in mol kg⁻¹. We assume that these ventilating waters remain at constant temperature (2°C) and salinity (35‰), and hence their oxygen concentration is proportional to the atmospheric partial pressure of oxygen (Henry’s law).

The model includes the key fluxes in the marine phosphorus, marine nitrogen, and oxygen cycles. The functional dependence and magnitude of many of these fluxes are poorly known. Rather than defending one particular formulation of each process, we explore the implications of these uncertainties by presenting the results of variants of the same basic model framework. In the initial formulation of the model we take conservative estimates of the magnitude of the input and output fluxes, expressed in mol yr⁻¹ and given in Table 2 (together with the remaining, necessary model constants). Where there are different suggestions in the literature for the functionality of a particular flux, we choose an intermediate formulation. These choices in turn determine the number and nature of the feedbacks. Where possible, we use functions in the literature to allow intercomparison of models. The following subsections review the key processes and feedback mechanisms incorporated in the model and explain the equations of the initial version (M1), which are summarized in Table 3.
Figure 1. Annual mean oxygen saturation (%) on the absolute oxygen minimum surface [Levitus, 1982]. Hatching indicates where gradients are too large to contour. We define the present anoxic fraction as those regions where annual mean oxygen saturation falls to <10%.
Table 1. Summary of Feedback Loops Considered in This Study

<table>
<thead>
<tr>
<th>Key Process Involved</th>
<th>Reservoir Affected</th>
<th>Sign</th>
<th>Limiting Nutrient</th>
<th>Operational Limits</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1 Nitrogen fixation</td>
<td>NO₂</td>
<td>-N</td>
<td>N</td>
<td>NO₅/16 &lt; PO₄</td>
<td>Broecker and Peng [1982], Piper and Codispoti [1975], Redfield [1934, 1938]</td>
</tr>
<tr>
<td>F2 Water-column denitrification</td>
<td>NO₃</td>
<td>-N</td>
<td>N</td>
<td>0 &lt; A &lt; 1</td>
<td>Piper and Codispoti [1975]</td>
</tr>
<tr>
<td>F3 Organic nitrogen burial</td>
<td>NO₅</td>
<td>-N</td>
<td>N</td>
<td>proposed in this work</td>
<td></td>
</tr>
<tr>
<td>F4 Organic phosphorus burial</td>
<td>PO₄</td>
<td>-P</td>
<td>P</td>
<td></td>
<td>Broecker [1971], Mach et al. [1987], Van Cappellen and Ingall [1994]</td>
</tr>
<tr>
<td>F5 Fe-P burial suppressed by anoxia</td>
<td>PO₃</td>
<td>+P</td>
<td>P</td>
<td>0 &lt; A &lt; 1</td>
<td>Holland [1994], Van Cappellen and Ingall [1994]</td>
</tr>
<tr>
<td>F6 Ca-P burial</td>
<td>PO₄</td>
<td>-P</td>
<td>P</td>
<td></td>
<td>Föllmi et al. [1993], Van Cappellen and Ingall [1994]</td>
</tr>
<tr>
<td>F7 Water-column denitrification</td>
<td>O₂</td>
<td>+N</td>
<td>N</td>
<td>0 &lt; A &lt; 1</td>
<td>proposed in this work</td>
</tr>
<tr>
<td>F8 Fe-P burial suppressed by anoxia</td>
<td>O₂</td>
<td>-P</td>
<td>P</td>
<td></td>
<td>Holland [1994], Van Cappellen and Ingall [1994]</td>
</tr>
<tr>
<td>F9 Org-P burial suppressed by anoxia</td>
<td>PO₃</td>
<td>+P</td>
<td>P</td>
<td></td>
<td>Ingall and Jahnke [1994], Ingall et al. [1993], Van Cappellen and Ingall [1994]</td>
</tr>
<tr>
<td>F10 Org P burial suppressed by anoxia</td>
<td>O₂</td>
<td>-P</td>
<td>P</td>
<td>0 &lt; A &lt; 1</td>
<td>Van Cappellen and Ingall [1996]</td>
</tr>
</tbody>
</table>

2.1. Weathering Forcing

We focus on the capacity of feedbacks within the ocean-atmosphere system to respond to perturbations on timescales <100 Myr. Therefore we do not include the tectonic recycling of sediments as a mass-balance approach, although this process has a stabilizing effect on atmospheric oxygen over timescales of hundreds of millions of years [Berner and Canfield, 1989; Van Cappellen and Ingall, 1996]. The model has a single (normalized, dimensionless) input parameter, termed "weathering," W. This determines the rate of uptake of oxygen due to oxidative weathering (section 2.5) and the rate of supply of bio-available phosphorus to the ocean due to chemical weathering (section 2.11). This coupling provides a natural compensatory mechanism, whereby the sink of oxygen is linked to the rate of supply of nutrient to the ocean and thus to the source of oxygen, organic carbon burial [Hettas and Holland, 1991; Garrels et al., 1976].

2.2. Nutrient Limitation of New Production

There is an ongoing and unresolved debate over whether phosphorus or nitrogen (or even iron [Falkowski, 1997]) is the ultimate limiting nutrient over geologic timescales [Codispoti, 1989; Ryther and Dunstan, 1971; Smith, 1984; Tyrrell, 1999]. It has been common in the geochemical literature to assume that phosphorus is the limiting nutrient [Colman et al., 1997; Holland, 1984; Van Cappellen and Ingall, 1994, 1996] while biological oceanographers tend to favor nitrogen [Codispoti, 1989; Falkowski, 1997; McElroy, 1983]. Nitrogen is the proximate limiting nutrient in the ocean at present, but it may be phosphorus that determines productivity over geologic timescales [Tyrrell, 1999].

We model both nitrogen and phosphorus as potentially limiting nutrients of new production, N, adopting Redfield ratios of P:N:C:O₂ = 1:16:117:170 [Anderson and Sarmiento, 1994]:

\[
N = \min \left( \frac{117}{16} \cdot \text{NO}_3, 117 \cdot \text{PO}_4 \right). \tag{1}
\]

The model assumes that when water is upwelled from the deep ocean, the limiting nutrient is completely used up in the generation of new production exported from the photic zone. There is a switch of nutrient limitation between nitrogen and phosphorus. Nitrate limits new production when below Redfield ratio to phosphate (i.e., when NO₅/16 < PO₄), and phosphate limits new production when below Redfield ratio to nitrate (i.e., when PO₄ < NO₅/16). New production is expressed in terms of the concentration of organic carbon produced from the limiting nutrient in mol kg⁻¹.

2.3. Anoxic Fraction

The balance of oxygen supply and demand (from new production) determines the degree of anoxia in the ocean. We reduce this to a single variable for the world ocean, the "anoxic fraction," A, defined as the fraction of the surface area of the ocean where annual average oxygen concentration falls to <10% saturation at some point in the water column:

\[
A = 1 - k_i \text{O}_2 N_0 O_{\text{H}(0)} N. \tag{2}
\]

The anoxic fraction is estimated from Figure 1 [Levitus, 1982] to be 14% at present. This covers the known regions of water-column denitrification and is broadly intended to cover those regions likely to experience seasonal anoxia in the water column. We follow the proposal [Van Cappellen and Ingall, 1994] that the degree of anoxia in the ocean asymptotes toward unity with increases in new production (oxygen demand) over oxygen supply. If an increase in new production occurs in a region where there is already anoxia in
the water column, this will not alter the anoxic fraction, and, as the degree of anoxia increases, this is more likely to occur, hence the asymptotic function.

We also use the anoxic fraction to determine the degree of anoxia at the sediments. A small fraction of ocean sediments are in contact with anoxic waters, where an oxygen minimum in the water column intersects the slope or shelf of the sea bottom [Pedersen and Calvert, 1990]. Much of the total sedimentation occurs in these regions [Müller and Suess, 1979; Pedersen and Calvert, 1990]. If the extent of anoxia in

2.4. Organic Carbon Burial

The burial flux of marine organic carbon, $F_{\text{Org-C}}$, provides the only variable source of oxygen in the model and determines the removal of phosphorus and nitrogen to sediments. We initially take a low estimate of the present organic carbon burial flux of $3.75 \times 10^{12}$ mol C yr$^{-1}$ (Table 2), which gives atmospheric oxygen a residence time of ~10 Myr. Residence time is defined as the size of the reservoir divided by the total input or output flux at steady state. The marine organic carbon burial flux appears to be primarily determined by sedimentation rate [Betts and Holland, 1991]. In the open ocean, sedimentation is mostly new production. Sedimentation rate has been estimated to be proportional to primary production raised to a power of ~2.85 [Müller and Suess, 1979; Van Cappellen and Ingall, 1994], although this is thought to be biased by some data points from the highly productive Peru shelf, and the relation is closer to quadratic without these points [Van Cappellen and Ingall, 1994]. The rate of organic carbon burial below the zone of active early diagenesis has been estimated to be proportional to bulk sedimentation rate to the power 1.09 (i.e., close to linear) [Henrichs and Reeburgh, 1987]. This suggests that organic carbon burial is proportional to new production raised to the product of the powers, which lies in the range of 2-3 [Van Cappellen and Ingall, 1994]. We initially adopt a quadratic dependence:

$$F_{\text{Org-C}} = k_2 \left( \frac{N}{N_0} \right)^2.$$  (3)

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].

2.5. Oxidative Weathering

The oxidative weathering of reduced materials exposed in continental rocks provides the sink of oxygen. The oxidative weathering flux, $F_{\text{Ox-W}}$, is assumed to depend on bulk weathering rate, represented by the forcing parameter, $W$:

$$F_{\text{Ox-W}} = k_W W.$$  (4)

virtually all of the reduced material that is exposed gets oxidized and hence the rate of uptake of oxygen is assumed to be independent of the size of the atmospheric oxygen reservoir.

2.6. Nitrogen Cycling

Redfield [1934, 1958] first suggested that the activities of nitrogen fixing and denitrifying organisms may regulate the quantity of nitrate in the ocean in Redfield ratio with phosphate and that the absolute size of the nitrate reservoir is ultimately determined by the size of the phosphate reservoir. Recent estimates confirm that the dominant input and output
Table 2. Model Reservoirs, Fluxes and Constants

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Description</th>
<th>Initial Size, mol</th>
<th>Concentration, µmol kg⁻¹</th>
<th>Model Constant</th>
<th>Reference(s) and Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO₄</td>
<td>phosphate in the deep ocean</td>
<td>3.1 x 10¹⁴</td>
<td>2.2</td>
<td>PO₄(0)</td>
<td>from analysis of the World Ocean Atlas dataset (T. Tyrrell, personal communication, 1998)</td>
</tr>
<tr>
<td>NO₃</td>
<td>biologically available nitrogen in the deep ocean</td>
<td>4.35 x 10¹⁶</td>
<td>30.9</td>
<td>NO₃(0)</td>
<td>from analysis of the World Ocean Atlas dataset (T. Tyrrell, personal communication, 1998)</td>
</tr>
<tr>
<td>O₂</td>
<td>oxygen in the atmosphere and the concentration dissolved in water ventilating the deep ocean</td>
<td>3.7 x 10¹⁰</td>
<td>331.5</td>
<td>O₂(0)</td>
<td>reservoir from Betts and Holland [1991], concentration assuming ventilating waters are at 2°C and 35% salinity from Leventis [1982] using the formula of Weiss [1970]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flux</th>
<th>Description</th>
<th>Magnitude, mol yr⁻¹</th>
<th>Model Constant</th>
<th>Reference and Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{Org-C}$</td>
<td>organic carbon (Org-C) burial</td>
<td>3.1 x 10¹²</td>
<td>$k_2$</td>
<td>Froelich et al. [1982]</td>
</tr>
<tr>
<td>$F_{Ox-W}$</td>
<td>oxidative weathering</td>
<td>3.75 x 10¹²</td>
<td>$k_2$</td>
<td>for steady state</td>
</tr>
<tr>
<td>$F_{Nix}$</td>
<td>nitrogen fixation</td>
<td>8.7 x 10¹²</td>
<td>$k_3$</td>
<td>for steady state</td>
</tr>
<tr>
<td>$F_{Den-N}$</td>
<td>denitrification</td>
<td>8.0 x 10¹³</td>
<td>$k_3$</td>
<td>Codispoti and Christensen [1985]</td>
</tr>
<tr>
<td>$F_{Org-N}$</td>
<td>organic nitrogen (Org-N) burial</td>
<td>0.1 x 10¹²</td>
<td>(C/N)_burial = 37.5</td>
<td>Ingall et al. [1993]</td>
</tr>
<tr>
<td>$F_{r-r}$</td>
<td>riverine bioavailable phosphorus input</td>
<td>3.6 x 10¹⁰</td>
<td>$k_4$</td>
<td>Froelich et al. [1982]</td>
</tr>
<tr>
<td>$F_{Fe-P}$</td>
<td>iron-sorbed phosphorus (Fe-P) burial</td>
<td>0.6 x 10¹⁰</td>
<td>$k_5$</td>
<td>Van Cappellen and Ingall [1994]</td>
</tr>
<tr>
<td>$F_{Org-P}$</td>
<td>organic phosphorus (Org-P) burial</td>
<td>1.5 x 10¹⁰</td>
<td>(C/P)_burial = 250</td>
<td>Froelich et al. [1982], Van Cappellen and Ingall [1994]</td>
</tr>
<tr>
<td>$F_{Ca-P}$</td>
<td>calcium-bound phosphorus (Ca-P) burial</td>
<td>1.5 x 10¹⁰</td>
<td>$k_7$</td>
<td>Van Cappellen and Ingall [1994]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Constant</th>
<th>Description</th>
<th>Value</th>
<th>Reference and Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>P:N:C:O₂</td>
<td>Redfield ratios</td>
<td>1.16:117.17:1</td>
<td>Anderson and Sarmiento [1994]</td>
</tr>
<tr>
<td>$N_0$</td>
<td>initial value of new production</td>
<td>226.0 x 10⁶ mol kg⁻¹</td>
<td>organic carbon concentration estimated from Figure 1</td>
</tr>
<tr>
<td>$A_0$</td>
<td>initial anoxic fraction</td>
<td>0.14</td>
<td>(1 - Aₐ) for nitrate and phosphate</td>
</tr>
<tr>
<td>$k_8$</td>
<td>initial oxic fraction</td>
<td>0.86</td>
<td>for nitrate and phosphate</td>
</tr>
<tr>
<td>$k_9$</td>
<td>conversion factor from deep sea reservoir size to average concentration</td>
<td>7.1 x 10⁻²² kg⁻¹</td>
<td>for nitrate and phosphate</td>
</tr>
<tr>
<td>$k_6$</td>
<td>conversion factor from oxygen atmospheric reservoir size to concentration dissolved in surface waters ventilating the deep ocean</td>
<td>8.96 x 10⁻²⁴ kg⁻¹</td>
<td>temperature and salinity of ventilating waters is assumed constant</td>
</tr>
</tbody>
</table>
Table 3. Equations of the Basic Model (M1)

<table>
<thead>
<tr>
<th>Weathering ((W))</th>
<th>New production ((N))</th>
<th>Anoxic fraction ((A))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N = \min\left(\frac{117}{16}NO_3, 117PO_4\right))</td>
<td>(A = 1 - k_1\frac{O_2}{O_2^{(0)}})</td>
<td>(k_2W)</td>
</tr>
</tbody>
</table>

**Oxygen** \((O_2)\)  

\[ F_{O_2-C} = k_2 \left(\frac{N}{N_0}\right)^2 \]  

\[ F_{O_2-W} = k_2W \]  

\[ F_{De-N} = k_4 \left(1 + \frac{A}{A_0}\right) \]  

\[ F_{O_2} = \frac{F_{O_2-C}}{37.5} \]

**Nitrate** \((NO_3)\)  

\[ F_{N-Fix} = k_3 \left(\frac{PO_4 - NO_3}{PO_4(0)}\right) \]  

\[ F_{NO_3} = k_4 \left(\frac{N}{N_0}\right)^2 \]

**Phosphate** \((PO_4)\)  

\[ F_{P-in} = k_5W \]  

\[ F_{P-Fe} = \frac{k_6}{k_7} \left(1 - A\right) \]  

\[ F_{Ca,P} = k_8 \left(\frac{N}{N_0}\right)^2 \]

\[ \frac{dO_2}{dt} = k_0 \left(F_{O_2-C} - F_{O_2-W}\right) \]  

\[ \frac{dNO_3}{dt} = k_0 \left(F_{N-Fix} - F_{De-N} - F_{NO_3}\right) \]  

\[ \frac{dPO_4}{dt} = k_0 \left(F_{P-in} - F_{P-Fe} - F_{Ca,P}\right) \]

Fluxes of bio-available nitrogen to the ocean are biogenic nitrogen fixation of 2.85-14.3 x 10^{12} mol N yr^{-1} [Galloway et al., 1995] and denitrification of 8.6-17.85 x 10^{12} mol N yr^{-1} [Christensen et al., 1987; Codispoti et al., 1985; Codispoti and Christensen, 1985; Devol, 1991; Galloway et al., 1995]. Preindustrial river input of nitrogen to the coastal zone was ~1 x 10^{12} mol N yr^{-1} in dissolved form and ~1.5 x 10^{12} mol N yr^{-1} as particulate organic nitrogen [Galloway et al., 1995]. However, most of this river input is thought to have been denitrified or stored in sediments in the coastal zone and hence did not reach the open ocean [Galloway et al., 1995]. Preindustrial atmospheric transfers of nitrogen between the land and the ocean are estimated to have been roughly in balance at ~1 x 10^{12} mol N yr^{-1}, suggesting that there was no net input of bio-available nitrogen via the atmosphere [Galloway et al., 1995]. We initially adopt intermediate estimates of the major nitrogen fluxes (Table 2) that give nitrate a residence time of 5000 years in the ocean.

### 2.7. Nitrogen Fixation

The major nitrogen fixing organisms in the marine plankton are cyanobacteria in the genus Trichodesmium [Capone et al., 1997]. Although nitrogen fixation has also been measured in floating Rhizosolenia diatom mats [Martinez et al., 1983]. Temperature restricts the growth of Trichodesmium spp., such that they are physiologically inactive below 20°C and have an optimum for growth of around 30°C [Carpenter, 1983]. Hence, nitrogen fixation by Trichodesmium spp. is concentrated in tropical and subtropical regions of the oceans [Capone et al., 1997].

Nitrogen fixation potentially provides a negative feedback (F1) linking nitrate in Redfield ratio to phosphate [Redfield, 1958]. For example, if phosphate is forced above Redfield ratio to nitrate, this should give nitrogen fixing organisms an increasing selective advantage, thus increasing the inventory of nitrate [Broecker and Peng, 1982; Redfield, 1958]. This is a relatively fast feedback because nitrogen fixation responds to deficiencies in nitrate at the source of new production, the surface ocean [Codispoti, 1989]. Nitrogen fixation is thermodynamically very demanding, requiring a large energy input [Delwiche, 1970]. Therefore if phosphate falls below Redfield ratio to nitrate, nitrogen fixing should be selected against, while denitrification will tend to reduce nitrate until nitrate has returned sufficiently below Redfield ratio to phosphate for nitrogen fixation to balance denitrification.

We assume that the deficit of nitrate below Redfield ratio to phosphate determines the selective advantage of nitrogen fixation and the resultant flux into the reservoir of available nitrogen, \(F_{N-Fix}\):

\[ F_{N-Fix} = k_3 \left(\frac{PO_4 - NO_3}{PO_4(0) - NO_3(0)}\right) \]

The relationship between nitrate deficit and nitrogen fixation is initially assumed to be linear. A more physiologically explicit modeling approach yields qualitatively similar results [Tyrrell, 1999].

### 2.8. Denitrification

Denitrification liberates almost as much energy as conventional respiration, in contrast to the thermodynamic constraints on nitrogen fixation, and it readily occurs wherever oxygen has fallen below ~0.05 mL L^{-1}, and there is an adequate supply of nitrate [Delwiche, 1970]. There are numerous types of denitrifying bacteria (~17 genera) and
direct evidence for water-column denitrification in three areas of high new production relative to oxygen supply; the eastern tropical North Pacific Ocean [Thomas, 1966], the Arabian Sea [Mantoura et al., 1993], and the eastern tropical South Pacific [Codispoti and Christensen, 1985]. These are also highlighted as areas of denitrification by the quasiconservative tracer $N^2$ [Gruber and Sarmiento, 1997]. Sedimentary denitrification appears to occur more widely and has been measured in both deep sea and continental shelf sediments, with the majority in the shelf and slope sediments [Christensen et al., 1987]. Sedimentary denitrification alters water-column nutrient concentrations in the Bering Sea and near the continental shelves of the east and west coasts of North America [Gruber and Sarmiento, 1997]. The total flux of denitrification appears to be roughly equally divided between the water column and the sediments [Codispoti and Christensen, 1985].

Denitrification potentially provides a negative feedback (F2) that tends to maintain nitrate as the limiting nutrient and tie it in Redfield ratio to oxygen [Codispoti, 1989; Piper and Codispoti, 1975], thus maintaining the ocean on the edge of anoxia. Increases in nitrate fuel increases in new production, and consequently anoxia in the water-column, thus stimulating increased denitrification. Correspondingly, decreases in nitrate trigger a reduction in anoxia and hence in denitrification. This self-limitation of denitrification (F2) is a slow negative feedback relative to nitrogen fixation (F1) in that the effect of changes in denitrification in the water column or sediments will not be felt as changes in nitrate at the surface of the ocean until the denitrified water has been circulated, which may take 1000 years [Codispoti and Christensen, 1985]. Furthermore, the denitrification feedback mechanism can be readily overwhelmed over short timescales [Codispoti and Christensen, 1985]. For example, there appear to be globally significant changes in the regional denitrification rate off Peru over several-month to several-year timescales [Codispoti et al., 1986]. Over longer timescales, the exposure and reflooding of continental shelves may have forced large changes in the sedimentary denitrification rate that could have contributed to glacial-interglacial changes in atmospheric carbon dioxide and climate [Christensen et al., 1987; Shaffer, 1990].

We model two components of denitrification, $F_{\text{De-N}}$, water column and sedimentary, and these are initially assumed to be of equal magnitude:

$$F_{\text{De-N}} = F_{\text{Org-N}}.$$  \hspace{1cm} (6)

Water-column denitrification is assumed to vary linearly with the anoxic fraction; that is, denitrification occurs wherever oxygen falls sufficiently low. The present anoxic fraction covers the regions where there is direct evidence for water-column denitrification. Sedimentary denitrification is assumed to be 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. We ignore any limitation of denitrification due to lack of nitrate.

2.9. Organic Nitrogen Burial

Organic nitrogen burial potentially provides a negative feedback on the size of the nitrate reservoir (F3), which is not linked to the Redfield ratios. For example, if an increase in nitrate increases new production and the supply of organic matter to the sediments then, all else being equal, more organic nitrogen will be buried. However, the magnitude of this sink of nitrogen is small relative to the denitrification flux. The burial flux of organic nitrogen in sediments can be estimated from a C/N burial ratio in the range of 10.6-38 [Ingall et al., 1993; Mackenzie et al., 1993] and an organic carbon burial flux of 3.75-10 x 10^{-12} mol yr^{-1} [Hett et al. and Holland, 1991; Van Cappellen and Ingall, 1994] to be in the range of 0.1-1 x 10^{-12} mol yr^{-1}.

We model organic nitrogen burial, $F_{\text{Org-N}}$, as a function of the organic carbon burial flux and the C/N burial ratio:

$$F_{\text{Org-N}} = \frac{F_{\text{Org-C}}}{37.5}.$$ \hspace{1cm} (7)

A C/N burial ratio of 37.5 is used initially, from analysis of the New Albany Shale, where it was found to be independent of anoxia [Ingall et al., 1993]. This gives an initial value of the organic nitrogen burial flux that is at the low end of the range of estimates.

A related negative feedback has been proposed to counteract high-nitrate anomalies in “red tide” situations of coastal eutrophication, involving the synthesis of nitrogen-rich saxitoxins [Wyatt, 1990]. However, the model study suggests that such high-nitrate anomalies cannot readily occur at a global scale.

2.10. Phosphorus Cycling

Redfield [1958] saw phosphorus as “the master element which controls the availability of the others” and argued that the phosphorus concentration of the deep sea is ultimately controlled by the low solubility of phosphate in the ocean. This thermodynamic equilibrium view of phosphorus in the ocean [Redfield, 1958; Sillén, 1961, 1967a,b] was later abandoned with the recognition that inorganic, homogeneous precipitation of calcium phosphate is predicted to take millions of years [Froelich et al., 1982]. The observation that interstitial phosphate concentrations in sediments are much higher than in ocean water [Froelich et al., 1982] suggested instead a kinetic model for the control of phosphorus [Broecker, 1971]. Control of the size of the oceanic phosphate reservoir is thought to rest on feedback on the removal of phosphate.

Phosphorus enters the open ocean mostly via rivers [Meybeck, 1982], in which it is carried in dissolved form (as phosphate), adsorbed to particles, and incorporated in organic matter. A natural phosphate buffer mechanism exists in estuarine waters, whereby considerable amounts of reactive phosphorus are desorbed from particles [Froelich, 1988]. In the ocean, each phosphorus atom is cycled through photosynthesis and regenerated to inorganic form in the water column an average of 280 times before reaching the sediments [Volk, 1998]. Phosphorus reaches the sediments primarily as organic phosphorus from sinking organic matter. In the sediments, phosphorus is subject to diagenesis by the benthic community of heterotrophic organisms [Tromp et al., 1995]. Initially, pore water phosphate is generated, which may subsequently be released to the water column or incorporated in calcium minerals or bound to iron oxides.
Thus phosphorus leaving the ocean has been characterized in three major forms; organic phosphorus (Org-P), calcium-bound phosphorus (Ca-P), and iron-sorbed phosphorus (Fe-P) [Filippelli and Delaney, 1996]. Classic estimates of the sizes of the total phosphorus input [Meybeck, 1982] and burial fluxes [Froelich et al., 1982] are both \( \sim 3.6 \times 10^{10} \) mol yr\(^{-1}\) (Table 2) suggesting that phosphorus has a residence time of \( \sim 86,000 \) years in the ocean. We adopt these fluxes initially for comparison with existing models [Van Cappellen and Ingall, 1994, 1996] but consider revised estimates [Delaney, 1998; Filippelli and Delaney, 1996; Rutenberg, 1993; Wheat et al., 1996] in section 4.2.

### 2.11. Phosphorus Input

The input flux of bio-available phosphorus to the ocean, \( F_{P_{\text{in}}} \), depends on the rate of release of phosphorus from the chemical weathering of continental rocks. This in turn is assumed to depend on bulk weathering rate, represented by the forcing parameter, \( W \).

\[
F_{P_{\text{in}}} = k_4 W.
\]

### 2.12. Organic Phosphorus Burial

Organic phosphorus (Org-P) burial comprises material that has either escaped diagenesis or has been reincorporated in the bodies of organisms in the sediment. Broecker [1971] first proposed that increases in river input of phosphate may be counteracted by two coupled negative feedbacks on organic-phosphorus burial. First, the resultant rise in phosphate concentration may provoke an increase in the level of new production, sedimentation, and hence phosphorus burial. Subsequently, a rise in new production should generate increased anoxia at the sediments and may thus enhance the preservation of phosphorus. The second mechanism was later abandoned [Broecker, 1974; Broecker and Peng, 1982] and is now contradicted by evidence of enhanced organic phosphorus regeneration under anoxic conditions [Ingall and Jahnke, 1994; Ingall et al., 1993]. The first mechanism is consistent with the organic phosphorus content of marine sediments being a constant fraction (\( \sim 100 \) ppm), independent of the organic carbon content [Froelich et al., 1982]. In this case, phosphorus is buried in linear proportion to the amount in the ocean, providing a relatively weak negative feedback. However, the same data were later reinterpreted to suggest that for organic carbon-rich (>2%) sediments the \( (P/C)_{\text{org}} \) ratio is nearly constant (at 1/490 atomic ratio) and the concentration of organic phosphorus is thus proportional to the concentration of organic carbon [Mach et al., 1987]. This implies stronger negative feedback on phosphate (F4) because of the highly nonlinear relation between new production and organic carbon burial [Henrichs and Reeburgh, 1987; Müller and Suess, 1979; Van Cappellen and Ingall, 1994] (section 2.4).

We initially model organic phosphorus burial, \( F_{\text{Org-P}} \), as linearly dependent on organic carbon burial [Mach et al., 1987] and independent of anoxia [Colman et al., 1997]:

\[
F_{\text{Org-P}} = \frac{F_{\text{Org-C}}}{250}.
\]

A \( (P/C)_{\text{org}} \) burial ratio of 250, slightly larger than that suggested by Mach et al. [1987], relates the organic carbon and phosphorus burial fluxes [Van Cappellen and Ingall, 1994]. In reality, \( (P/C)_{\text{org}} \) may vary with sedimentation rate [Ingall and Van Cappellen, 1990] or bottom water anoxia [Ingall and Jahnke, 1994; Ingall et al., 1993] (and the latter is considered in section 4.4).

#### 2.13. Iron-sorbed Phosphorus Burial

The iron-sorbed phosphorus (Fe-P) sink includes phosphorus sorbed to iron oxides formed from reduced iron that enters the ocean via hydrothermal vents [Berner, 1973], phosphorus associated with iron- and manganese-rich coatings of foraminiferal carbonate ooze [Sherwood et al., 1987], and reactive phosphorus buried with iron oxides in rapidly depositing near shore sediments [Berner et al., 1993]. Much of the iron-sorbed phosphorus buried in coastal shelf regions is delivered by rivers as detritus and thus does not represent a true sink of reactive phosphorus from the ocean [Berner et al., 1993]. Phosphorus may also be scavenged by wind blown, iron rich detritus [Berner et al., 1993].

Iron-sorbed phosphorus burial has been proposed to provide a positive feedback (F5) on phosphorus-limited new production [Holland, 1994; Van Cappellen and Ingall, 1994]. The burial flux of iron-sorbed phosphorus is dependent on the degree of anoxia in bottom water and the supply of soluble ferrous iron. At the oxia/anoxia horizon, soluble ferrous iron precipitates out as insoluble ferric iron (oxy)hydroxides. If the horizon is in the sediment, where phosphate concentrations are high, then the iron hydroxides adsorb phosphate as they form. However, if the oxia/anoxia horizon is in the water column, relatively little phosphate will be adsorbed. An increase in phosphate, new production, and deep anoxia generates a decrease in the area where the precipitation of ferric (oxy)hydroxides occurs in the sediments. This reduces the sink of phosphorus by iron adsorbed burial, tending to amplify the rise in phosphate.

Iron-sorbed phosphorus burial, \( F_{\text{Fe-P}} \), is assumed to vary inversely with bottom water anoxia [Holland, 1994], which is in turn taken to vary in proportion to water-column anoxia, the anoxic fraction [Van Cappellen and Ingall, 1994]:

\[
F_{\text{Fe-P}} = \frac{k_6}{k_1} (1 - A).
\]

Bottom waters are unlikely to all be anoxic when there is anoxia throughout the oxygen minimum of the water column, hence the formulation adopted may be too responsive. Furthermore, iron oxides are hard to dissolve, even under anoxic conditions, unless reducing agents are present. The burial function is almost certainly more complex than suggested in equation (10), but it captures the first-order control [Colman and Holland, 1999]. The supply of reactive iron is assumed to be constant.

#### 2.14. Calcium-Bound Phosphorus Burial

The majority of calcium-bound phosphorus (Ca-P) that is buried appears to be incorporated in authigenic calcium minerals, especially carbonate fluorapatite (francolite), produced in the sediments (hence, in the literature it is also
referred to as "authigenic P"). Authigenic apatite is distinct from detrital apatite, which does not represent a true sink of oceanic phosphate [Berner et al., 1993; Ruttenberg and Berner, 1993]. The "Ca-P" category also includes skeletal debris and phosphate incorporated in calcium carbonate [Berner et al., 1993].

Authigenic calcium-bound phosphorus burial has been estimated to be the most important contemporary phosphorus sink [Ruttenberg, 1993]. "Sink switching" [Froelich et al., 1982] from more labile forms (e.g., organic) to authigenic phosphorus has been observed with increasing sediment depth, leaving it as the dominant form [Delaney, 1998; Filippelli and Delaney, 1996; Ruttenberg and Berner, 1993]. Examination of the nonlinearities in phosphogenesis (the formation of phosphorus-rich sediments) and phosphorus-carbon coupling led to the proposal that phosphogenesis provides a highly responsive negative feedback (h6) against rises in phosphate that is more responsive to changes in new production than organic carbon burial [Föllmi et al., 1993]. A certain fraction of phosphorus taken up in new production is recycled in the sediment. As production increases so too does the concentration of phosphate in sedimentary pore waters, encouraging the formation of authigenic calcium phosphate minerals [Föllmi et al., 1993]. A weaker version of this feedback has also been proposed, which assumes that calcium-bound phosphorus burial and organic carbon burial are equally responsive [Van Cappellen and Ingall, 1994] because authigenic P derives from phosphorus supplied to the sediment in organic matter.

We initially adopt this formulation, assuming that calcium-bound phosphorus burial, \( F_{Ca-P} \), is quadratically dependent on new production (the same power relation as organic carbon burial):

\[
F_{Ca-P} = k_7 \left( \frac{N}{N_0} \right)^2.
\]

This is a quantitatively very similar simplification of the formulation suggested by Van Cappellen and Ingall [1994]. The nonlinearity is meant to imply that as new production increases, a greater fraction of it is buried in shelf and slope environments, where pore water phosphate concentration can rise sufficiently for the formation of authigenic calcium phosphate minerals.

### 2.15. Differential Equations

The rate of change of size of each model reservoir is determined by the net flux into or out of that reservoir:

\[
\frac{dO_2}{dt} = k_9 (F_{O_x-C} - F_{O_x-W})
\]

\[
\frac{dNO_3}{dt} = k_9 (F_{N_{-FIX}} - F_{O_x-N} - F_{O_x-N})
\]

\[
\frac{dPO_4}{dt} = k_9 (F_{P_{-in}} - F_{P_{-e}} - F_{O_x-P} - F_{Ca-P})
\]

\( k_9 \) converts the deep ocean nutrient reservoirs from sizes in mol to average concentrations in mol kg\(^{-1}\). \( k_9 \) converts from the atmospheric oxygen reservoir size in mol to the concentration of oxygen dissolved in the waters that ventilate the deep ocean, in mol kg\(^{-1}\).

### 2.16. Oxygen Feedbacks

Two feedbacks on oxygen are implicit in the preceding discussion and have implications for the maintenance of the Redfield ratio of limiting nutrient (oxygen demand) to oxygen supply. Oxygen concentration affects the anoxic fraction and thus influences denitrification and iron-sorbed phosphorus burial. Both of these processes may alter the level of new production and thus the flux of organic carbon burial, which provides the source of oxygen in the model.

Changes in denitrification potentially provide a positive feedback on oxygen (F7). For example, a decrease in oxygen generates an increase in the anoxic fraction and water-column denitrification. This tends to reduce the level of nitrate, new production, and organic carbon burial, thus reducing the source of oxygen and amplifying its fall. Equally, there can be amplification of a rise in oxygen, but this depends on some anoxia remaining in the ocean. The positive feedback tends to maintain nitrate in Redfield ratio to oxygen (changes in oxygen force corresponding changes in nitrate) but tends to destabilize oxygen.

Changes in iron-sorbed phosphorus burial potentially provide a negative feedback on oxygen (F8) by triggering compensatory changes in organic phosphorus and organic carbon burial [Colman et al., 1997; Holland, 1994]. This provides an example of phosphorus sink switching [Froelich et al., 1982]. An increase in oxygen causes a decrease in the anoxic fraction and an increase in iron-sorbed phosphorus burial that tends to decrease phosphate. This tends to lower new production, either directly if phosphate is limiting or indirectly if nitrate is limiting, by reducing nitrogen fixation. This in turn reduces organic carbon burial and thus tends to counteract the initial change in oxygen. Equally, a decrease in oxygen and an increase in anoxia triggers decreased iron-sorbed phosphorus burial but increased organic phosphorus and organic carbon burial [Colman et al., 1997; Holland, 1994]. This feedback tends to force phosphate and oxygen away from Redfield ratio because changes in oxygen force opposing changes in phosphate, but it tends to stabilize oxygen. We develop the model to consider in detail what regulates the oxygen content of the atmosphere in the companion paper [Lenton and Watson, this issue].

### 3. Testing the Basic Model (M1)

The regulatory capacity of the feedback mechanisms described above are now tested by subjecting the model to internal perturbations involving doubling or halving the size of the nitrate or phosphate reservoirs then subjecting the model to external perturbations involving doubling or halving the forcing parameter, weathering. The results are presented so as to show the proximity of phosphorus, nitrogen, and oxygen in the ocean to the Redfield ratios. The deep ocean nitrate concentration is divided by the Redfield ratio requirement of photosynthesizers (16 mol N / mol P). The oxygen concentration dissolved in surface waters that ventilate the deep ocean is divided by the Redfield ratio requirement of respirers (170 mol O\(_2\) / mol P). These are plotted together with the deep ocean phosphate concentration. The anoxic fraction of the ocean is plotted on the same scale but is dimensionless (and can only vary between 0 and 1).
The size of the atmosphere-ocean oxygen reservoir is proportional to the oxygen concentration.

3.1. Results

The differing residence times of nitrate, phosphate, and oxygen simplify the behavior of the model system. Feedbacks on nitrate respond to perturbation on a timescale of hundreds of years, over which phosphate cannot vary considerably. Thus nitrate remains close to steady state over the timescale that phosphate varies (thousands to tens of thousands of years). Similarly, perturbations of phosphate are redressed on a timescale of tens of thousands of years, over which atmospheric oxygen cannot vary considerably. Thus phosphate and nitrate are close to steady state over the timescale that atmospheric oxygen varies (millions of years).

![Figure 3](image.png)

**Figure 3.** Response of the basic model (M1) to (a) doubling of the phosphate reservoir and (b) halving of the phosphate reservoir. The diagrams show the proximity of phosphorus, nitrogen, and oxygen to the Redfield ratio requirements of marine organisms during the simulations. “PO₄” is the average deep ocean phosphate concentration, “NO₃/16” is the average deep ocean nitrate concentration, divided by the Redfield ratio requirement of photosynthesizers (16 mol N / mol P). “O₂/170” is the oxygen concentration dissolved in surface waters that ventilate the deep ocean, divided by the Redfield ratio requirement of respirers (170 mol O₂ / mol P). “O₂/170” 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.

![Figure 4](image.png)

**Figure 4.** Response of the basic model (M1) to (a) doubling of the phosphate reservoir and (b) halving of the phosphate reservoir.

In response to instantaneous changes in their size, the nitrate (Figure 3) and phosphate (Figure 4) reservoirs tend to return toward their initial sizes, close to the Redfield ratios. Perturbations of the nitrate reservoir are redressed over a ~10^3 year timescale by direct feedbacks on nitrate (Figure 3). Under a doubling of nitrate (Figure 3a), nitrogen fixation is switched off and denitrification increased to a new constant level. This (plus a little organic nitrogen burial) reduces the size of the nitrate reservoir, until nitrate becomes limiting again and the flux of nitrogen fixation increases to match the declining denitrification flux. Under a halving of nitrate (Figure 3b), anoxia disappears from the water column, switching off denitrification there, while nitrogen fixation increases, forcing up nitrate. As nitrate rises, nitrogen fixation declines. When some anoxia returns to the water column, this increases denitrification until nitrate returns to the original steady state. Nitrate responds faster than its residence time would suggest (Table 4) because there are negative feedbacks on both nitrate input and output giving a nonlinear response of the net flux. The response to a reduction in nitrate below Redfield ratio to phosphate is especially fast because the effective residence time of nitrate is halved by halving the reservoir size.

Perturbations of the phosphate reservoir are redressed over a ~10^3 year timescale, by triggering corresponding changes in
Table 4. Response Times of Nitrate and Phosphate Reservoirs to Perturbation

<table>
<thead>
<tr>
<th>Model Variant</th>
<th>Description</th>
<th>Reservoir</th>
<th>Resilience* Against Doubling of Reservoir, years</th>
<th>Resilience* Against Halving of Reservoir, years</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>basic model</td>
<td>NO₃</td>
<td>2,300</td>
<td>900</td>
</tr>
<tr>
<td>M2</td>
<td>larger nitrogen fluxes</td>
<td>NO₃</td>
<td>1,100</td>
<td>450</td>
</tr>
<tr>
<td>M3</td>
<td>basic model</td>
<td>PO₄</td>
<td>38,500</td>
<td>66,000</td>
</tr>
<tr>
<td>M4</td>
<td>larger nitrogen fluxes</td>
<td>PO₄</td>
<td>46,500</td>
<td>91,500</td>
</tr>
<tr>
<td>M5</td>
<td>larger burial fluxes</td>
<td>PO₄</td>
<td>9,000</td>
<td>15,500</td>
</tr>
<tr>
<td>M6</td>
<td>weak nitrogen fixation</td>
<td>PO₄</td>
<td>179,000</td>
<td>86,000</td>
</tr>
<tr>
<td>M7</td>
<td>Org-P burial suppressed by anoxia</td>
<td>PO₄</td>
<td>55,000</td>
<td>73,000</td>
</tr>
</tbody>
</table>

*Defined as the time for the perturbation to be reduced to \(1/e\) (37%) of its initial value [Pimm, 1984].

nitrate, new production, and phosphorus burial (Figure 4). Doubling of phosphate (Figure 4a) triggers a spike of nitrogen fixation that increases nitrate close to Redfield ratio to phosphate. This drives increased new production, organic phosphorus burial, and calcium-bound phosphorus burial, tending to decrease phosphate. In contrast, halving of phosphate (Figure 4b) triggers reduced new production and organic and calcium-bound phosphorus burial. It also switches off nitrogen fixation and water-column denitrification, leaving sedimentary denitrification (and organic nitrogen burial) to reduce nitrate until it is just below Redfield ratio to phosphate. Phosphate responds faster to perturbation than its residence time would suggest (Table 4), but, in contrast to nitrate, the response is faster against a doubling of phosphate than a halving.

In response to perturbations of weathering rates, the nutrients remain close to Redfield ratio, while oxygen (which has a much slower response time) converges toward them (Figure 5). Under a sustained 50% increase in weathering (Figure 5a), the increase in phosphorus input to the ocean forces up phosphate, stimulating increases in nitrogen fixation, nitrate, new production, organic carbon burial, organic phosphorus burial, and calcium-bound phosphorus burial until the total phosphorus burial flux increases by 50% to match the river input (this takes ~0.3 Myr). Iron-sorbed phosphorus burial is suppressed by increased anoxia, hence organic carbon burial increases proportionately more than total phosphorus burial, exceeding the imposed increase in oxidative weathering and causing oxygen to rise (over millions of years). Rising oxygen forces a gradual decline in anoxia, which causes an increase in iron-sorbed phosphorus burial, that tends to remove phosphate and thus reduce nitrogen fixation but also causes a countering decline in denitrification, such that nitrate varies very little. When oxygen rises to the point that anoxia is removed from the ocean water column (after ~44 Myr), the two feedbacks on oxygen switch off, and the remainder of the system is locked in steady state, with oxygen rising indefinitely.

A sustained 50% decrease in weathering and phosphorus input (Figure 5b) forces a decline in phosphate, nitrogen fixation, nitrate, and new production until phosphorus removal matches input. The resultant drop in carbon burial exceeds the imposed reduction in oxidative weathering, causing oxygen to decline. Once oxygen reaches Redfield ratio with the limiting nutrient and ocean anoxia returns (after ~23 Myr), then all three reservoirs tend to diverge from the Redfield ratios. Increasing anoxia triggers a decrease in iron-sorbed phosphorus burial and a rise in phosphate and nitrogen fixation but also an increase in denitrification. The net result is a very gradual rise in nitrate, new production, and carbon burial, providing a slight overall negative feedback on the fall of oxygen and (via organic and calcium-bound phosphorus burial) the rise of phosphate. A new steady state is achieved after over 100 Myr.

Steady state analytical solutions for the three reservoirs as functions of weathering are derived in the appendix and

Figure 5. Response of the basic model (M1) to (a) 50% increase in weathering and (b) 50% decrease in weathering.
shown in Figure 6. The oxygen reservoir stabilizes at a new steady state under large decreases in weathering but only under increases in weathering of up to 16.3% (derviation in appendix). This upper limit is determined by the ocean becoming totallyoxic. Phosphate, nitrate, and oxygen all diverge from Redfield ratio under moderate decreases in weathering.

3.2. Implications

The dynamic response of the model is generally consistent with the hypothesis that nitrate is maintained close to Redfield ratio to phosphate by self-regulating feedbacks, involving organic processes. Under internal perturbation, the feedbacks on nitrate (F1, F2) are effective at regulating nitrate just below Redfield ratio to phosphate, while the negative feedbacks on phosphate (F4, F6) regulate the coupled nutrient concentrations. However, under external forcing over longer timescales, contradictions appear between the mechanisms tending to tie nitrate in Redfield ratio to phosphate (nitrogen fixation) and in Redfield ratio to oxygen (denitrification). Nitrogen fixation feedback (F1) tends to couple nitrate to phosphate, while denitrification feedback (F2) tends to couple nitrate to oxygen. In general, nitrogen fixation exerts dynamic control, and this enhances the stability of the whole system. In such cases, while nitrate is always the proximate limiting nutrient, phosphate is the ultimate, determining nutrient. However, where denitrification has control (e.g., Figure 5b), phosphate can deviate significantly above Redfield ratio to nitrate. In this scenario, nitrate becomes the ultimate limiting nutrient over geologic timescales.

Oxygen regulation is poor in the model because negative feedback on oxygen via changes in iron-sorbed phosphorus burial (F8) [Holland, 1994] is counteracted by positive feedback on oxygen via changes in denitrification (F7). For example, under a 50% decrease in weathering, oxygen stabilizes at ~9% of the atmosphere. Furthermore, under increases in weathering, it takes only a small increase in oxygen relative to the limiting nutrient to make the model ocean completely oxic, thereby removing any feedback on oxygen and leaving oxygen rising indefinitely (Figure 5b). The inclusion of rapid sediment recycling [Berner and Canfield, 1989], which would expose the organic carbon-rich sediments being generated to oxidative weathering, within millions of years, could damp the rise of oxygen, but the majority of sediments are recycled over a ~100 Myr timescale. The negative feedback on oxygen (F8) [Holland, 1994] tends to shift oxygen and phosphate away from Redfield ratio, for example, a fall in oxygen forces a rise in phosphate. In contrast, the positive feedback on oxygen (F7) tends to keep nitrate and oxygen in Redfield ratio, for example, a fall in oxygen forces a decrease in nitrate. Hence there may be a contradiction between the requirements of oxygen regulation and those of maintaining the Redfield ratio of oxygen supply and demand, which is explored further in the companion paper [Lenton and Watson, this issue].

4. Testing Alternative Hypotheses

We now focus on a selection of topical areas of debate or recent insight that have implications for the regulation of nitrate, phosphate, and oxygen in the ocean. A series of independent variants of the basic model (M2-M5) are presented and tested with the same standard perturbations.

4.1. Larger Nitrogen Fluxes (M2)

The global denitrification flux has recently been revised upward to 17.85 x 10^{12} mol yr^{-1} [Codispoti, 1995], suggesting that the residence time of nitrate in the ocean is only ~2500 years. An upper estimate of global nitrogen fixation of 14.3 x 10^{12} mol yr^{-1} [Galloway et al., 1995] falls short of the estimate of denitrification. This begged the question: Is the ocean losing nitrate? [Codispoti, 1995]. A larger estimate of organic nitrogen burial, from a C/N burial ratio of 12.5 [Mackenzie et al., 1993], adds to the deficit. The revised nitrate fluxes are summarized in Table 5 and included in variant M2 of the model. A constant river input of bioavailable nitrogen is assumed to balance the nitrate budget in the model:

\[ F_{\text{N-in}} = k_{11}. \]  

(15)

Where \( k_{11} = 3.85 \times 10^{12} \text{ mol yr}^{-1}. \) However, massive nitrogen fixation fluxes in oceanic gyres may be sufficient to balance the nitrate budget in the real ocean [Michaels et al., 1996]. The extra initial denitrification flux is all assumed to be a function of anoxia:

\[ F_{\text{De-N}} = k_4 + k_{10} \frac{A}{A_0}. \]  

(16)

This replaces equation (6) and \( k_{10} = 13.55 \times 10^{12} \text{ mol yr}^{-1}. \) It allows us to examine further whether denitrification feedback (F2) can dominate over nitrogen fixation feedback (F1). The revised differential equation for the nitrate reservoir, replacing equation (13), is:

\[ \frac{d\text{NO}_3}{dt} = k_6(F_{\text{N-in}} + F_{\text{N-Fix}} - F_{\text{De-N}} - F_{\text{Org n}}). \]  

(17)

The larger nitrate fluxes (Table 5) reduce the response of nitrate to 450-1100 years (Table 4), i.e., more rapid
regulation toward the Redfield ratios, because there is a greater net flux to or from the nitrate reservoir under a given perturbation. Conversely, the response time of phosphate is increased (Table 4) because a greater fraction of total denitrification is assumed to be dependent on anoxia, which thereby ties nitrate more strongly to oxygen. The steady state size of the phosphate reservoir deviates further from Redfield ratio to nitrate and oxygen under a given change in weathering (Figure 7 and appendix) because nitrate is more strongly tied to oxygen by denitrification.

It has previously been assumed that nitrate responds to perturbation over a timescale of ~10^4 years [McElroy, 1983], but the revised model predicts that nitrate can respond to perturbation over hundreds of years. This implies that (1) the ocean may be better able to buffer the increased input of bioavailable nitrogen due to human activities [Galloway et al., 1995], (2) increases in shelf area and sedimentary denitrification at glacial termination [Christensen et al., 1987] may be able to force a reduction in the size of the oceanic nitrate reservoir and a resultant increase in atmospheric carbon dioxide over hundreds rather than thousands of years [McElroy, 1983; Shaffer, 1990], and (3) if the ocean is presently losing nitrate [Codispoti, 1995], it may not continue for longer than a few centuries because the feedbacks on nitrate can achieve steady state over that timescale.

4.2. Larger Phosphorus Burial Fluxes (M3)

The total phosphorus burial flux and each of its components (Org-P, Fe-P, Ca-P) have recently been revised upward, implying a shorter residence time for phosphate in the ocean [Delaney, 1998; Filippelli and Delaney, 1996; Ruttenberg, 1993; Wheat et al., 1996]. For example, a total phosphorus burial flux of 17.2 x 10^10 mol yr^-1 (including burial in shelf and slope sediments) implies a phosphate residence time of only ~18,000 years [Ruttenberg, 1993]. Increased estimates of pelagic phosphorus burial fluxes may imply an even shorter residence time of ~15,000 years [Filippelli and Delaney, 1996]. However, such a large net output flux of phosphorus (~2 x 10^10 mol yr^-1) demands a similarly large input flux of phosphate desorbing from organic and inorganic particulate matter, which is difficult to match with present estimates [Froelich, 1988].

Ruttenberg's [1993] revised phosphorus burial fluxes are summarized in Table 6 and included in variant M3 of the model, excluding the flux of loosely sorbed P because it is not clear whether this is involved in any feedback on phosphate. Increased phosphorus burial fluxes demand correspondingly larger organic carbon and organic nitrogen burial fluxes (Table 6 and references therein). Consequently, larger phosphorus input, oxidative weathering, and nitrogen fixation fluxes are required for steady state (Table 6), and the oxygen residence time is reduced to ~3.6 Myr.

Increased phosphorus burial fluxes reduce the response time of phosphate to internal perturbation to only 9000-15,500 years (Table 4). This more rapid regulation toward Redfield ratio with oxygen occurs because there is an increased imbalance in input and output fluxes under a given perturbation. The response time of oxygen to changes in weathering is also significantly reduced, causing it to converge more rapidly toward Redfield ratio with the nutrients. However, the final steady state of the system is not significantly altered (see appendix).

A phosphate response time of order 10^4 rather than 10^5 years, with a high proportion of phosphorus being buried on continental shelves, implies that changes in the phosphate reservoir may play a more dynamic role than previously thought in glacial-interglacial CO2 changes [Ruttenberg, 1993].

4.3. Limited Nitrogen Fixation (M4)

Redfield's [1958] view that nitrogen fixation is able to automatically redress any lack of nitrate relative to phosphate triggered a long-standing debate over whether nitrogen or phosphorus is the ultimate limiting nutrient in the ocean [Codispoti, 1989; Ryther and Dunstan, 1971; Smith, 1984; MacKenzie et al., 1993].

**Table 5. Larger Steady State Nitrogen Fluxes (M2)**

<table>
<thead>
<tr>
<th>Flux</th>
<th>Description</th>
<th>Magnitude, mol yr^-1</th>
<th>New and Altered Constants</th>
<th>Reference and Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>F_{in}</td>
<td>river input</td>
<td>3.85 x 10^11</td>
<td>k_n = 3.85 x 10^11 mol yr^-1</td>
<td>for steady state</td>
</tr>
<tr>
<td>F_{fix}</td>
<td>nitrogen fixation</td>
<td>14.3 x 10^10</td>
<td>k_n = 14.3 x 10^10 mol yr^-1</td>
<td>Galloway et al. [1995]</td>
</tr>
<tr>
<td>F_{dri}</td>
<td>denitrification</td>
<td>17.85 x 10^12</td>
<td>k_n = 13.55 x 10^12 mol yr^-1</td>
<td>Codispoti [1995]</td>
</tr>
<tr>
<td>F_{or}</td>
<td>organic nitrogen burial</td>
<td>0.3 x 10^10</td>
<td>(C/N)_{or} = 12.5</td>
<td>Mackenzie et al. [1993]</td>
</tr>
</tbody>
</table>

**Figure 7.** The effect of altering nitrogen fluxes (M2) and weakening nitrogen fixation (M4) on the steady state size of the phosphate reservoir. The steady state nitrate and oxygen reservoirs are unaltered from Figure 6.
Table 6. Larger Steady State Burial Fluxes and Corresponding Input Fluxes (M3)

<table>
<thead>
<tr>
<th>Flux</th>
<th>Description</th>
<th>Magnitude, mol yr$^{-1}$</th>
<th>Altered Constant</th>
<th>Reference and Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{Fe-P}$</td>
<td>imm-carb. phosphorus (Fe-P) burial</td>
<td>4.0 $\times 10^{10}$</td>
<td>$k_s$</td>
<td>Rutterhorgen [1993]</td>
</tr>
<tr>
<td>$F_{Ca-P}$</td>
<td>organic phosphorus (Ox-P) burial</td>
<td>4.1 $\times 10^{10}$</td>
<td>$k_s$</td>
<td>Rutterhorgen [1993]</td>
</tr>
<tr>
<td>$F_{Ca-P}$</td>
<td>calcium-bound phosphorus (Ca-P) burial</td>
<td>9.1 $\times 10^{10}$</td>
<td>$k_s$</td>
<td>Rutterhorgen [1993]</td>
</tr>
<tr>
<td>$F_{Fe-P}$</td>
<td>riverine input of bio-available phosphorus</td>
<td>1.72 $\times 10^{10}$</td>
<td>$k_s$</td>
<td>for steady state</td>
</tr>
<tr>
<td>$F_{Fe-C}$</td>
<td>organic carbon (Org-C) burial</td>
<td>1.025 $\times 10^{10}$</td>
<td>$k_s$</td>
<td>from (C/P)$_{burial}$ = 7.50</td>
</tr>
<tr>
<td>$F_{Fe-Fe}$</td>
<td>oxidative weathering</td>
<td>1.025 $\times 10^{10}$</td>
<td>$k_s$</td>
<td>for steady state</td>
</tr>
<tr>
<td>$F_{Fe-N}$</td>
<td>organic nitrogen (Org-N) burial</td>
<td>2.75 $\times 10^{10}$</td>
<td>-</td>
<td>from (C/N)$_{burial}$ = 37.5</td>
</tr>
<tr>
<td>$F_{Fe-N}$</td>
<td>nitrogen fixation</td>
<td>8.873 $\times 10^{10}$</td>
<td>$k_s$</td>
<td>for steady state</td>
</tr>
</tbody>
</table>

Tyrrell, 1999]. It is now recognized that a situation in which phosphate is available and nitrates is limiting is necessary but not a sufficient condition for the onset of nitrogen fixation [Codispoti, 1989], there being other potentially limiting factors. For example, nitrogen fixing organisms have a much higher iron requirement than other phytoplankton, iron being required for electron transfer in the nitrogen fixing enzyme, nitrogenase [Falkowski, 1997]. Iron additions have been shown to stimulate nitrogen fixation in Trichodesmium spp. [Pierl et al., 1994], and the "iron hypothesis"[de Baar, 1994] has thus been extended to tropical and subtropical, oligotrophic (low-nitrate, low chlorophyll) regions of the ocean that are often characterized by Trichodesmium blooms [Falkowski, 1997; Pierl et al., 1994]. Appropriate oxygen depleted microhabitats and a supply of organic matter are required for nitrogen fixation and may also be limiting in areas of the ocean [Pierl and Carlton, 1988; Paulsen et al., 1991].

To explore the implications of strong limitation of nitrogen fixation [Codispoti, 1989; Falkowski, 1997; Pierl et al., 1994], without explicitly including the limiting factors (e.g., iron) in the model, we simply assume a weaker functional dependence of nitrogen fixation on the deficit of nitrate below Redfield ratio to phosphate:

$$F_{N-Fix} = k_3 \ln \left[ \frac{117(PO_4) - NO_3}{16} \right]$$

$$= k_3 \ln \left[ \frac{117(PO_4) - NO_3}{16} \right]$$

if $117(PO_4) - NO_3 > 16$. (18)

This replaces equation (5). The natural logarithmic function is chosen to make the functional dependence very weak. The multiplication factor of 117 converts the nitrate deficit to units of potential carbon concentration and means that nitrogen fixation goes to zero when nitrate is only 0.4% below Redfield ratio to phosphate.

Weakening nitrogen fixation in the model (M4) causes nitrate to become more strongly coupled to oxygen via denitrification than to phosphate. This greatly increases the response time to an instantaneous doubling of phosphate from ~40,000 to ~180,000 years (Table 4) because nitrate remains well below Redfield ratio to phosphate (rising by only 23% in response to the 100% increase in phosphate), thus suppressing new production and phosphorus burial. In this scenario, the residence time of phosphate (~85,000 years) is irrelevant to its response.

Weak nitrogen fixation allows increases in the river input of phosphate to generate large excursions of phosphate above Redfield ratio to nitrate (Figure 8a). Under a 50% increase in weathering, phosphate rises to more than double Redfield ratio to nitrate (and oxygen) because it takes a large rise in phosphate to force up nitrogen fixation, nitrate, and new production to the point that phosphorus output matches, then

Figure 8. Response with limited nitrogen fixation (M4) (a) 50% increase in weathering and (b) 50% decrease in weathering.
exceeds its input. It takes 20 Myr before phosphate has returned reasonably close to the Redfield ratios. In response to a 50% decrease in weathering (Figure 8b), once some anoxia returns to the water column, nitrate is tied down to oxygen by denitrification, while increasing anoxia forces a decline in iron sorbed phosphorus burial and a steep rise in phosphate. This stimulates some nitrogen fixation and a slight rise in nitrate, new production, organic phosphorus, calcium-bound phosphorus, and organic carbon burial, but it is insufficient to prevent phosphate rising to very high concentrations. Steady state solutions (Figure 7) confirm that phosphate becomes extremely sensitive to decreases in weathering.

This theoretical experiment demonstrates that if denitrification has more control over nitrate concentrations than nitrogen fixation, then nitrate becomes tied to oxygen and phosphate can deviate far above the Redfield ratio under changes in forcing, causing nitrate to become the ultimate limiting nutrient over geological time periods. Whether this could have occurred under more realistic forcing is explored in section 5.

4.4. Organic Phosphorus Burial Suppressed by Anoxia (M5)

Anoxic environments may provide a less effective phosphorus sink than oxic environments and thereby provide scope for the burial of large quantities of organic matter without sequestering the phosphorus needed to sustain further new production [Ingall et al., 1993]. Organic C/P ratios as low as 150 have been found for ancient bioturbated shales, deposited under oxic conditions while organic C/P ratios as high as 3900 have been found for the corresponding laminated shales deposited under anoxic conditions [Ingall et al., 1993]. Studies of contemporary sediments support such values [Ingall and Jahnke, 1994]. A positive feedback on organic phosphorus burial (F9) has thus been proposed [Ingall and Jahnke, 1994] and quantitatively modeled [Van Cappellen and Ingall, 1994] together with the negative feedback on organic phosphorus burial via changes in organic carbon burial (F4). If phosphorus is the ultimate limiting nutrient, then an increase in phosphate increases new production and deep water anoxia, enhancing the recycling of organic phosphorus to the water column and thus increasing (C/P)org (F9). However, increased new production also drives increased organic carbon burial, carrying organic phosphorus with it (F4). It has been suggested that the net effect of an increase in phosphorus-limited new production is a decrease in organic phosphorus burial, assuming (C/P)org, anoxic = 4000 and (C/P)org, oxic = 200 [Van Cappellen and Ingall, 1994]. However, authigenic phosphorus burial may be counteractingly increased, leading to little change in the total C/P burial ratio with bottom water anoxia [Delaney, 1998]. Here we explore the implications of an organic phosphorus burial function of the same form as that proposed by Van Cappellen and Ingall [1994]:

\[ F_{\text{Org-P}} = F_{\text{Org-C}} \left( \frac{1 - A}{k_{\text{oxic}}} + \frac{A}{k_{\text{anoxic}}} \right). \]  

This replaces equation (9). We use values of \( k_{\text{oxic}} = (C/P)_{\text{oxic}} = 217 \) and \( k_{\text{anoxic}} = (C/P)_{\text{anoxic}} = 4340 \) in order to maintain an initial organic phosphorus flux of 1.5x10^{10} mol yr^{-1}. These differ slightly from those of Van Cappellen and Ingall [1994] because we adopt a smaller initial value for the anoxic fraction.

In the revised model (M5), the overall feedback on organic phosphorus burial remains negative in response to internal perturbation. For example, a doubling of phosphate generates an approximate doubling of organic phosphorus burial (organic carbon burial is quadrupled while \( P/C_{\text{org}} \) is approximately halved). The response time of phosphate to internal perturbation is slowed (Table 4) because the negative feedback on total phosphorus burial is weakened.

Changes in organic phosphorus burial related to the anoxia of bottom waters have also been proposed to provide a negative feedback on oxygen (F10) [Van Cappellen and Ingall, 1996], closely analogous to the mechanism involving iron-sorbed phosphorus burial (F8) [Colman et al., 1997; Holland, 1994]. For example, a decrease in oxygen causes an increase in anoxic fraction and a decrease in organic phosphorus burial that tends to increase phosphate, new production, and organic carbon burial, thus counteracting the initial change in oxygen (F10) [Van Cappellen and Ingall, 1996]. The two negative feedbacks on oxygen (F8 and F10) have been combined in a previous model [Van Cappellen and Ingall, 1996].

Figure 9. Response with organic phosphorus burial suppressed by anoxia (M5) to (a) 50% increase in weathering and (b) 50% decrease in weathering.
Oxygen reaches a new steady state in response to a 50% increase in weathering (Figure 9a), while in previous variants of the model, oxygen rose indefinitely under this perturbation. Initially, both organic and total phosphorus burial increase, i.e., there is negative feedback on phosphate. This stabilizes phosphate and subsequently nitrate, new production, and organic carbon burial at a level that generates a rise in oxygen. However, as oxygen rises and anoxia declines, this forces increases in organic and iron-sorbed phosphorus burial that tend to draw down phosphate over longer timescales. This forces a decline in nitrate, new production, and organic carbon burial until oxygen reaches a new steady state, close to the Redfield ratios. Oxygen changes in the opposite direction to the model of Van Cappellen and Ingall [1996] because it included a fictitious, long-residence time holding reservoir for riverine phosphorus that allowed an increase in oxidative weathering to generate a decrease in oxygen.

In response to a 50% decrease in weathering (Figure 9b), the system stabilizes more rapidly than before (compare to Figure 5b) and comes to steady state closer to the Redfield ratios, with the oxygen reservoir about half its initial size, indicating improved oxygen regulation. Initially, phosphate falls further because it is subject to less negative feedback and this generates a more rapid drop in oxygen. Once some anoxia returns to the ocean, this forces a decrease in organic and iron-sorbed phosphorus burial, triggering phosphate to rise. This in turn forces up nitrate, new production, and organic carbon burial stabilizing both oxygen and phosphate.

Suppression of organic phosphorus burial by anoxia improves regulation toward the Redfield ratios. At steady state, for a given change in weathering, the oxygen and phosphate reservoirs are closer to Redfield ratio to nitrate (Figure 10). Furthermore, oxygen stabilizes under greater increases in weathering of up to ~87% (see appendix).

5. Historical Forcing for the Past 40 Myr

Thus far, somewhat arbitrary, instantaneous perturbations, coupled with steady state analyses, have allowed us to explore and compare the sensitivity of the model systems. This type of approach is common in the geochemical literature [Betts and Holland, 1991; Colman et al., 1997; Van Cappellen and Ingall, 1996] and is useful for assessing the potential effects of different processes and feedback mechanisms. However, it does not tell us about what actually happened in the past, what might happen in the future, or how the feedback mechanisms respond to more realistic forcing.

Here we make a case study of the past 40 Myr, by forcing variants of the model with a proxy for changes in the input of biologically available phosphorus in the open ocean (Figure 11) [Föllmi, 1995, 1996]. During this period, the Himalaya were uplifted and continental ice sheets appeared and grew. We test whether nitrate, phosphate, and oxygen in the ocean could have been maintained close to the Redfield ratios during this period under such forcing, focusing on the implications of uncertainties in the responsiveness of nitrogen fixation by comparing the results of the original model (M1) with those for limited nitrogen fixation (M4).

5.1. Phosphorus Accumulation Record

Over timescales significantly longer than its residence time in the ocean, the total output of phosphorus must closely match the total input. Therefore a record of the accumulation of bio-available phosphorus in marine sediments provides a proxy for the input of bio-available phosphorus to the ocean. Phosphorus input in turn depends upon the flux of phosphorus weathered from continental rocks. Thus phosphorus accumulation potentially offers a proxy for chemical weathering rates, of much finer resolution than the more commonly used changes in the strontium isotope composition of sea water because phosphorus has a much shorter residence time in the ocean (1.5-8.5 x 10^9 years) than strontium (~3 x 10^6 years).

A compilation of all meaningful data from the Deep Sea Drilling Project and the Ocean Drilling Program has recently been used to extract a 100 Myr marine burial record of
biogenic phosphorus (together with a 160 Myr marine burial record of total phosphorus) [Fölmi, 1995]. This record does not include phosphorus burial in deltaic and other nearshore sediments, hence it is not a complete proxy for phosphorus input to the ocean or phosphorus weathering rates, but it is the nearest proxy available. Other studies of phosphorus accumulation [Delaney and Filippelli, 1994; Filippelli and Delaney, 1994; Moody et al., 1988] have focused on specific areas where current burial fluxes of phosphorus are large. Drill sites in the Eastern and Western Equatorial Pacific show correlated changes in phosphorus accumulation over the last 50 Myr, with a number of peaks in the last 16 Myr [Delaney and Filippelli, 1994; Filippelli and Delaney, 1994], but there is little correlation with the global record [Fölmi, 1996]. In contrast, the combined Atlantic and Indian Ocean phosphorus accumulation records correlate well with the global record and are often anticorrelated with the Pacific Ocean record over the last 25 Myr [Fölmi, 1996]. It appears that interocean fractionation of phosphorus burial has occurred over million year timescales, meaning that global inferences made from the Equatorial Pacific data set would not be reliable.

Over the last 40 Myr, the global biogenic phosphorus burial flux (Figure 11), inferred from the geometrical mean of the data [Fölmi, 1995], has roughly quadrupled and has fluctuated widely. Such large changes are difficult to explain and may be an artifact of the incomplete data set or its interpretation. Progressive glaciation plausibly drove increasing phosphorus weathering over the past ~30 Myr because both mechanical and chemical weathering rates are enhanced in glacial environments, and over this period increasing phosphorus accumulation is correlated with declining sea level (a measure of the build-up of continental ice sheets) [Fölmi, 1995, 1996]. An overall increase in the rate of chemical weathering has been inferred from other proxies [Delaney and Boyce, 1988; Pegram et al., 1997; Richter et al., 1992; Shemesh et al., 1989], but these can also be interpreted as suggesting little or no increase in chemical weathering rates [Kump and Arthur, 1997]. Climate cooling and drying should have tended to reduce chemical weathering rates over this time because they are linearly dependent on precipitation and exponentially dependent on temperature [White and Blum, 1995]. The rate of chemical weathering is also amplified by biological activity, and this is included as a factor affecting phosphorus supply to the ocean in the companion paper [Lenton and Watson, this issue]. Given these reservations, the record in Figure 11 should be viewed as an upper limit on the likely rapidity of historical changes in phosphorus input to the ocean and hence provides an extreme test of the model.

5.2. Methodology

The normalized record of phosphorus accumulation in biogenic sediments (Figure 11) [Fölmi, 1995] is used to force both phosphorus input to the ocean and oxidative weathering in the model. The record is averaged at 1 Myr intervals, and we retain this resolution, changing weathering once every 1 Myr (while the model time step remains 10 yr). Model predicted phosphorus burial rates match the record used to force phosphorus input very closely, confirming that phosphorus burial is a valid proxy for phosphorus input over million year timescales. It may not be a good proxy for oxidative weathering rates, but decoupling oxidative weathering and phosphorus input can generate unrealistically large variations in oxygen [Lenton, 1998b]. The modeling effort involves trial-and-error manual iteration (the “shooting method”), in an attempt to predict what the reservoir sizes of phosphate, nitrate, and oxygen must have been 40 Myr ago in order to arrive at today’s values. Phosphate and nitrate generally remain close to steady state with the forcing, reducing the problem to one of estimating the oxygen reservoir size 40 Myr ago.

5.3. Basic Model (M1)

Nitrate is effectively regulated just below Redfield ratio to phosphate under the large changes in phosphorus input over the last 40 Myr (Figure 12a). However, oxygen is generally well above Redfield ratio to the limiting nutrient, hence the ocean water column is predicted to have been fully oxic for most of the last 40 Myr, with only brief intrusions of anoxia at ~23 Myr ago, ~15 Myr ago, and from 2 Myr ago to the present. This lack of regulation occurs because both phosphate and nitrate adjust to changes in phosphorus input over a timescale of ~10,000 years, while oxygen only responds over millions of years. If the input of phosphorus to the ocean has increased over the past 40 Myr, then the oceanic reservoirs of phosphate and nitrate must have also

![Figure 12. Forcing (a) the basic model (M1) and (b) weak nitrogen fixation (M4), with the proxy for phosphorus input to the ocean over the last 40 Myr shown in Figure 11.](image-url)
increased. The assumption that weathering has been less than the present rate throughout most of the last 40 Myr implies a lower rate of organic carbon burial than oxidative weathering and therefore shrinking of the oxygen reservoir from an initial size corresponding to 26.5% of the atmosphere 40 Myr ago. Thus the ocean is predicted to have converged upon its present state on the edge of anoxia. The lack of anoxia throughout most of the model run implies no feedback on oxygen.

5.4. Limited Nitrogen Fixation (M4)

Limitation of nitrogen fixation does not generally impair the regulation of nitrate to Redfield ratio with phosphate, with the exception of one high phosphate anomaly predicted at ~15 Myr ago (Figure 12b). This is caused by an inferred ~5-fold increase in phosphorus input to the ocean over a 2 million year period (whether this actually occurred is open to question; it may be an artifact of the incomplete phosphorus burial record). The inability of nitrogen fixation to trigger a matching increase in nitrate generates an excess of phosphate; at peak there is almost twice as much phosphate as can be utilized (according to the Redfield ratio), and nitrate is clearly the limiting nutrient for ~2 million years. However, this peak in phosphate is less pronounced than might be expected on the basis of the previous perturbation studies; because the oxygen concentration in the ocean is high, there is little anoxia, and therefore there is relatively little water-column denitrification holding down nitrate. For most of the model run (Figure 12b) the ocean is predicted to be fully oxic, and nitrate is closer to Redfield ratio to phosphate than when there is some water-column anoxia. This is because there is no water-column denitrification, and therefore the deficit of nitrate below phosphate does not have to be so great to trigger sufficient nitrogen fixation to balance the sedimentary denitrification flux.

5.5. Changes in Oxygen

The predicted decline in the size of the oxygen reservoir over the last 40 Myr (Figure 12) should be viewed with caution because potentially important stabilizing feedbacks on oxygen are missing from the model. These can maintain nearly constant oxygen throughout the past 40 Myr under the same forcing [Lenton and Watson, this issue], without significantly altering the predicted changes in nitrate and phosphate. The length of time that the ocean is predicted to be fully oxic is then reduced, but the anoxic fraction still varies widely in response to changes in nutrients and new production.

Past changes in oxygen inferred from the marine δ13C record [Shackleton, 1987] are also poorly constrained. Both an overall decline in the sedimentary organic carbon reservoir, implying shrinkage of the oxygen reservoir [Compton and Millinn, 1996; Raymo, 1994; Shackleton, 1987], and an overall increase, implying growth of the oxygen reservoir [Derry and France-Lanord, 1996], have been inferred. The difference is principally 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].

6. Conclusion

A new model of the coupled biogeochemical cycles of nitrogen, phosphorus, carbon, and oxygen has been constructed. The model exhibits robust regulation of deep ocean nitrate just below Redfield ratio with phosphate under a wide range of forcing, owing to feedback mechanisms involving nitrogen fixing and denitrifying organisms. This supports the hypothesis that the correspondence of P/Al(NO3) in ocean waters and marine organisms' P:N requirement is the result of self-regulating feedbacks involving organic processes [Redfield, 1958]. There is no need to invoke adaptation on the part of the organisms to explain the correspondence; rather the feedback mechanisms unconsciously adapt the environment to suit the organisms. Nitrogen fixation responds to increases of phosphate relative to nitrate, while denitrification tends to keep the deep-ocean nitrate concentration just below Redfield ratio to the phosphate concentration, maintaining nitrate as the proximate limiting nutrient. With the nutrients thus tied together, negative feedbacks on organic and calcium-bound phosphorus burial reduce their coupled variation. When a weakly responsive function for nitrogen fixation is adopted (model variant “M4”) arbitrary, instantaneous perturbations in phosphorus input can force the deep-ocean phosphate concentration far above Redfield ratio to nitrate. However, when the model ocean is forced with a proxy suggesting large fluctuations in phosphorus input, there is only one interval at ~15 Ma, where phosphate deviates significantly above Redfield ratio to nitrate. We conclude that the correspondence of nitrate and phosphate in the ocean to the organisms' requirements is a robust property of the present Earth system.

In the variants of the model explored, the concentrations of the limiting nutrient (which determines oxygen demand) and oxygen in the ocean are not generally regulated toward Redfield ratio with one another. This is because both phosphate and nitrate tend to track changes in phosphorus input on ~10,000 year timescales. In contrast, oxygen can only respond on million year timescales, and where oxygen regulation is effective, by definition it tends not to respond. If phosphorus input was less than now 40 Myr ago, the nutrient reservoirs would have been smaller, while the initial model predicts that the oxygen reservoir was larger, and hence there were long periods where the ocean was completely oxic. Predictions of total ocean oxia are potentially falsifiable with evidence of widespread laminated sediments from these periods or of high δ15N indicating significant water column denitrification. Even if we assume that the oxygen reservoir has grown over the last 40 Myr [Derry and France-Lanord, 1996], the rapid changes in ocean nutrient inventories suggested by records of phosphorus accumulation [Falkem, 1996] would have caused oxygen demand to vary much faster than oxygen supply. Furthermore, when changes in anoxia are predicted, positive feedbacks on iron-sorbed and organic phosphorus burial tend to amplify them. We conclude that there is an element of chance in our observing today's ocean on "the edge of anoxia."

Our model is geophysiological [Loveland, 1986, 1995; Whitfield, 1981] in that it focuses on the tight coupling of organisms and their material environment and the resulting feedback mechanisms that are somewhat analogous to the
Appendix

Here we present, for each model system, derivations of the steady state PO₄, NO₃ and O₂ reservoir sizes as functions of the (normalized, dimensionless) forcing parameter, weathering ($W$). In essence, NO₃ is determined by steady state for O₂, O₂ is determined by steady state for PO₄ given NO₃, and PO₄ is determined by steady state for NO₃ given NO₃ and O₂. Derivations of the upper limit of $W$ at which oxygen can reach steady state are also given. PO₄(0), NO₃(0) and O₂(0) are constants (initial sizes of the three reservoirs for $W = 1$) used in the equations to convert the reservoirs to normalized, dimensionless form. Nitrate (NO₃) is assumed to be the limiting nutrient throughout, on the basis that it remains so in the dynamic studies; therefore we can substitute for new production ($N$) in the equations:

$$N = \frac{117}{16} \text{NO}_3 \quad \text{and} \quad \frac{N}{N_0} = \frac{\text{NO}_3}{\text{NO}_3(0)} .$$

A1. Basic Model (M1)

The variables and constants of the basic model and their units are defined in Table 2. From the equations in Table 3 the following are given:

$$\frac{d\text{PO}_4}{dt} = k_8 \left[ k_5 W - k_4 \left( \frac{\text{NO}_3}{\text{NO}_3(0)} \right)^2 \right] - k_6 \frac{\text{NO}_3(0)}{\text{O}_2(0)} \text{NO}_3$$

$$\frac{d\text{NO}_3}{dt} = k_8 \left[ k_4 \left( \frac{1 + \frac{1}{14} - \frac{k_1 \text{NO}_3(0)}{\text{O}_2(0)} \text{NO}_3}{37.5} \right) \frac{\text{PO}_4 - \text{NO}_3}{\text{PO}_4(0) - \text{NO}_3(0)} \right] - k_7 \frac{\text{NO}_3}{37.5} \left( \frac{\text{NO}_3}{\text{NO}_3(0)} \right)^2$$

$$\frac{d\text{O}_2}{dt} = k_9 \left[ k_2 \left( \frac{\text{NO}_3}{\text{NO}_3(0)} \right)^2 - k_2 W \right]$$

From \( \frac{d\text{NO}_3}{dt} = 0 \),

$$\text{NO}_3 = \text{NO}_3(0) W^{1/2} . \quad (A4)$$

From \( \frac{d\text{PO}_4}{dt} = 0 \),

$$\text{PO}_4 = \frac{\text{PO}_4(0) - \text{NO}_3(0) W^{1/2}}{16} \left( \frac{k_4 \left( 1 + \frac{1}{14} - \frac{k_1 \text{NO}_3(0)}{\text{O}_2(0)} \text{NO}_3}{37.5} \right) \frac{\text{PO}_4 - \text{NO}_3}{\text{PO}_4(0) - \text{NO}_3(0)} \right)$$

Substituting the formula (A4) for NO₃ gives

$$\text{O}_2^* = \text{O}_2(0) \left( \frac{k_5 W - k_2 W}{250} \right)^{1/2} . \quad (A5)$$

The constants cancel one another, leaving

$$\text{O}_2^* = \text{O}_2(0) W^{1/2} .$$

From \( \frac{d\text{NO}_3}{dt} = 0 \),

$$\text{PO}_4 = \frac{\text{PO}_4(0) - \text{NO}_3(0) W^{1/2}}{16} \left( \frac{k_4 \left( 1 + \frac{1}{14} - \frac{k_1 \text{NO}_3(0)}{\text{O}_2(0)} \text{NO}_3}{37.5} \right) \frac{\text{PO}_4 - \text{NO}_3}{\text{PO}_4(0) - \text{NO}_3(0)} \right)$$

Substituting the formulae for NO₃ (A4) and O₂ (A5) yields

$$\text{PO}_4 = \frac{\text{NO}_3(0) W^{1/2} + \left( \text{PO}_4(0) - \text{NO}_3(0) \right) W^{1/2}}{16} \left( \frac{k_4 \left( 1 + \frac{1}{14} - \frac{k_1 \text{NO}_3(0)}{\text{O}_2(0)} \text{NO}_3}{37.5} \right) \frac{\text{PO}_4 - \text{NO}_3}{\text{PO}_4(0) - \text{NO}_3(0)} \right)$$

$$\text{PO}_4 = \frac{\text{NO}_3(0) W^{1/2} + \left( \text{PO}_4(0) - \text{NO}_3(0) \right) W^{1/2}}{16} \left( \frac{k_4 \left( 1 + \frac{1}{14} - \frac{k_1 \text{NO}_3(0)}{\text{O}_2(0)} \text{NO}_3}{37.5} \right) \frac{\text{PO}_4 - \text{NO}_3}{\text{PO}_4(0) - \text{NO}_3(0)} \right)$$

The maximum increase in uplift at which steady state for oxygen can be achieved is determined by the anoxic fraction tending to zero:

$$A = 1 - \frac{k_1 \text{O}_2(0) \text{NO}_3(0)}{\text{O}_2(0) \text{NO}_3} = 0 .$$

This yields

$$\frac{\text{O}_2}{\text{NO}_3} = -12.471 . \quad (A7)$$
Substituting the formulae for NO₃ (A4) and O₂ (A5) yields
\[
\frac{O_{2}(0)}{NO_{3}(0)} = 12.471
\]
\[
W = 1.163
\]

The steady state solutions (for 0 < W < 1.163) are presented in Figure 6.

**A2. Model Variants**

The steady state equation for nitrate (A4) is identical throughout because we do not consider changes in the functional form of the oxygen differential equation (A3). In the cases where the differential equation for phosphate (A1) is unaltered, steady state for oxygen (A5) remains the same.

**A3. Larger Nitrate Fluxes (M2)**

New formulae and constants in Table 5 give
\[
dNO_{3} \over dt = k_{8} \left[ k_{3} \left( \frac{PO_{4} - NO_{3}}{PO_{4}(0) - NO_{3}(0)} \right) + k_{11} - k_{4} \right]
\]
\[
- \frac{k_{10}}{0.14} \left[ 1 - k_{1} \frac{NO_{3}(0)}{O_{2}(0) - NO_{3}} - \frac{k_{2}}{12.5} \left( \frac{NO_{3}}{NO_{3}(0)} \right)^{2} \right]
\]

Let \( dNO_{3} \over dt = 0 \):

\[
PO_{4} = \frac{NO_{3}}{16} + \left( \frac{PO_{4}(0) - NO_{3}(0)}{16} \right) \frac{1}{k_{3}} \times
\]
\[
k_{4} + \frac{k_{10}}{0.14} \left[ 1 - k_{1} \frac{NO_{3}(0)}{O_{2}(0) - NO_{3}} \right] + \frac{k_{2}}{12.5} \left( \frac{NO_{3}}{NO_{3}(0)} \right)^{2} - k_{11}
\]

Substituting the formulae for NO₃ (A4) and O₂ (A5) gives
\[
PO_{4} = \frac{NO_{3}(0)}{16} W^2/2 + \left( \frac{PO_{4}(0) - NO_{3}(0)}{16} \right) \times
\]
\[
\left( \frac{1}{k_{3}} \left( k_{4} + \frac{k_{10}}{0.14} - k_{11} \right) + \frac{k_{2}}{12.5 - k_{1}k_{10}/0.14} W \right)
\]
\[
PO_{4} = \frac{NO_{3}(0)}{16} W^2/2 + \left( \frac{PO_{4}(0) - NO_{3}(0)}{16} \right) (6.8 - 5.8W)
\]

This is presented in Figure 7.

**A4. Larger Phosphorus Burial Fluxes (M3)**

Altered constants in Table 6 do not affect the steady state for NO₃ or O₂ (because the revised O₂ and PO₄ input and output flux constants cancel one another). Following the derivation for PO₄ as in the basic model (M1), but inserting the new values for the flux constants yields:
\[
PO_{4} = \frac{NO_{3}(0)}{16} W^2/2 + \left( \frac{PO_{4}(0) - NO_{3}(0)}{16} \right) (3.946 - 2.946W)
\]

This is little different from the basic model.

**A5. Weaker Nitrogen Fixation (M4)**

The altered formulae are
\[
F_{N-Fix} = k_{12} \ln \left[ 117 \left( \frac{PO_{4} - NO_{3}}{16} \right) \right]
\]

if \( 117 \left( PO_{4} - NO_{3} \right) > 1 \)

where \( k_{12} = \frac{k_{1}}{\ln \left( 117 \left( PO_{4}(0) - NO_{3}(0) \right) / 16 \right)} \)

\[
\frac{dNO_{3}}{dt} = k_{8} \left[ k_{4} \left( 1 + \frac{1}{0.14} - k_{1} \frac{NO_{3}(0)}{O_{2}(0) - NO_{3}} \right) \right]
\]
\[
- \frac{k_{2}}{37.5} \left( \frac{NO_{3}}{NO_{3}(0)} \right)^{2}
\]

This gives an altered steady state for phosphate from
\[
\frac{dNO_{3}}{dt} = 0
\]

\[
PO_{4} = \frac{NO_{3}}{16}
\]
\[
+ \frac{1}{117} \exp \left[ \frac{k_{4} \left( 1 + \frac{1}{0.14} - k_{1} \frac{NO_{3}(0)}{O_{2}(0) - NO_{3}} \right) \right]
\]
\[
+ \frac{1}{k_{12}} \exp \left[ \frac{k_{4} \left( 1 + \frac{1}{0.14} - k_{1} \frac{NO_{3}(0)}{O_{2}(0) - NO_{3}} \right) \right]
\]
\[
+ \frac{k_{2}}{37.5} \left( \frac{NO_{3}}{NO_{3}(0)} \right)^{2}
\]

Substituting the formulae for NO₃ (A4) and O₂ (A5) gives:
\[
PO_{4} = \frac{NO_{3}(0)}{16} W^2/2 + \frac{1}{117} \exp \left[ 13.878 - 10.43W \right]
\]

This is presented in Figure 7.

**A6. Organic Phosphorus Burial Suppressed by Anoxia (M5)**

The altered formulae are
\[
F_{Org-P} = k_{2} \left( \frac{NO_{3}}{NO_{3}(0)} \right)^{2} \left( \frac{1 - A}{217} + \frac{A}{4340} \right)
\]

\[21\]
which yields the solution

\[ W = 1.872. \]

New solutions for \( O_2 \) and \( PO_4 \) are presented in Figure 9.

Acknowledgments. We thank J. E. Lovelock, M. Whitfield and P. S. Liss for many stimulating discussions and K. B. Follmi for providing phosphorus burial flux data. T. M. L. thanks the University of East Anglia for a research studentship; Plymouth Marine Laboratory for hosting him during much of this work, and Gaia Charities for additional funding. Many of the central ideas were first discussed at “Gaia in Oxford: The self-regulating Earth” meeting in April 1994.

References


Redfield, A.C., The biological control of chemical factors in the environment, Am. Sci., 46, 205-221, 1958.


Sillén, L.G., The ocean as a chemical system, Science, 156, 1189-1197, 1967b.


Volk, I., Gaia's Body - Toward a Physiology of the Earth, Copernicus, New York, 1998.


T. M. Lenton, Institute of Terrestrial Ecology, Edinburgh Research Station, Bush Estate, Penicuik, Midlothian EH26 0QB, United Kingdom. (tlen@ite.ac.uk)
A. J. Watson, School of Environmental Sciences, University of East Anglia, Norwich NR4 7JG, United Kingdom.

(Received September 16, 1998; revised July 26, 1999; accepted August 9, 1999)