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Biotic stoichiometric controls on the deep ocean N:P ratio[*]

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Abstract. We re-examine what controls the deep ocean N:P ratio in the light of recent findings that the C:N:P stoichiometry of phytoplankton varies with growth rate, nutrient and light limitation, species and phylum, and that N_2-fixation may be limited by Fe, temperature and/or light in large parts of the world ocean. In particular, we assess whether a systematic change in phytoplankton stoichiometry can alter the deep ocean N:P ratio. To do this we adapt recent models to include non-Redfieldian stoichiometry of phytoplankton and restriction of N_2-fixers to a fraction of the surface ocean. We show that a systematic change in phytoplankton C:N:P can alter the concentrations of NO_3 and PO_4 in the deep ocean but cannot greatly alter their ratio, unless it also alters the N:P threshold for N_2-fixation. This occurs if competitive dynamics set the N:P threshold for N_2-fixation, in which case it remains close to the N:P requirement of non-fixers (rather than that of N_2-fixers) and consequently so does the deep ocean N:P ratio. Then, even if N_2-fixers are restricted to a fraction of the surface ocean, they reach higher densities there, minimising variations in deep ocean N:P. Theoretical limits on the N:P requirements of phytoplankton suggest that whilst the deep ocean has been well oxygenated (i.e. since the Neoproterozoic, with the possible exception of Oceanic Anoxic Events), its N:P ratio is unlikely to have varied by more than a factor of two in either direction. Within these bounds, evolutionary changes in phytoplankton composition, and increased phosphorus weathering due to the biological colonisation of the land surface, are predicted to have driven long-term changes in ocean composition.

1 Introduction

There is a well-known correspondence between the average proportions of N and P in marine organic matter – the "Redfield ratio" of N:P∼16 – and the composition of the deep ocean with N:P∼15. Redfield (1934) suggested that an explanation "...may be sought in the activities of those bacteria which form nitrogenous compounds or liberate nitrogen in the course of the decomposition of organic matter" intuiting that "...in a world populated by organisms of these two types the relative proportion of phosphate and nitrate must tend to approach that characteristic of protoplasm in general..." In his later work, Redfield (1958) proposed that: "When living in an environment containing a deficiency of nitrate relative to phosphate, the growth and assimilation of the nitrogen-fixing organisms might tend continually to bring the proportions of nitrogen and phosphorus nearer to that characteristic of their own substance." Subsequent workers (Broecker and Peng, 1982; Tyrrell, 1999; Lenton and Watson, 2000) have expressed the mechanism in terms of competition between N_2-fixing organisms that are selected when N:P<16 and non-fixers that out-compete them when N:P>16. This mechanism assumes that under P-limiting conditions N_2-fixers have a lower growth rate than non-fixers, because of the high energy cost of N_2-fixation, whilst under sufficiently N-limiting conditions N_2-fixers out-compete non-fixers.

The canonical value of ∼16 for the N:P Redfield ratio represents an average for today's phytoplankton. It has long been known that the Redfield ratios of phytoplankton vary with growth rate (Goldman et al., 1979) and light regime (Goldman, 1986). Nutrient replete phytoplankton cultures (with consequently high growth rates) have a mean N:P of 10.1 across 34 studies, in contrast to marine particulate matter with a mean N:P of 16.4 across 27 studies (Geider and La Roche, 2002). It was thought that N:P∼16 might represent some kind of optimum for phytoplankton, but no theoretical basis has yet been found for this (Klausmeier et al., 2004).

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Instead, a model predicts that the optimum composition of phytoplankton under exponential growth is 8.2, whilst under light limitation it is 35.8, nitrogen limitation 37.4, and phosphorus limitation 45.0 (Klausmeier et al., 2004). Furthermore, different phyla or super-families of differing antiquity have different N:P, with older "greens" having higher N:P than younger "reds" (Quigg et al., 2003). This raises the question (Falkowski and Davis, 2004; Arrigo, 2005): Would a systematic shift in the Redfield ratios alter deep ocean composition?

The question provokes a deeper one: What sets the deep ocean N:P ratio? Some authors still make statements, which can be traced back to Redfield (1934), to the effect that the ratio of major nutrients N:P~15 in the deep ocean directly reflects the average Redfield ratio (N:P~16) of sinking organic matter being remineralised in the water column. However, the cycle of uptake in the surface ocean and remineralisation at depth only redistributes NO_3 and PO_4, it cannot directly alter their absolute or relative amounts in the ocean as a whole, which depend on net input to or removal from the ocean. The ocean mixing time ($<10^3$ yr) is shorter than the residence time of NO_3 ($\sim 3 \times 10^3$ yr) (Codispoti, 1995; Lenton and Watson, 2000), which is in turn shorter than that of PO_4 ($\sim 1.8 \times 10^4$ yr) (Ruttenberg, 1993; Lenton and Watson, 2000). Hence mixing tends to homogenize the concentrations of both nutrients. Furthermore, we can consider a timescale over which PO_4 is relatively constant but NO_3 can vary due to imbalances of input (primarily N_2-fixation) and output (primarily denitrification) processes. The essence of Redfield's mechanism is that N_2-fixation responds to any deficit of NO_3 relative to the N:P requirement of average phytoplankton (non-fixers), whilst denitrification tends to continually remove NO_3 and thus maintain a small N:P deficit and corresponding population of N_2-fixers.

Both N_2-fixation and denitrification processes need some elaboration in the light of recent discoveries. On the input side, although N_2-fixation is sometimes P-limited and suppressed by N-addition, there is also evidence for Fe-limitation (Berman-Frank et al., 2001; Mills et al., 2004), temperature-limitation (Breitbarth et al., 2007), light-limitation (Hood et al., 2004) and P and Fe co-limitation (Mills et al., 2004) of N_2-fixers. This raises the question: Given that N_2-fixers may be limited to restricted areas of the world ocean, can they still regulate deep ocean N:P? It has recently been inferred that nitrogen inputs and losses in the ocean are spatially coupled (Deutsch et al., 2007), which may alleviate the problem somewhat. On the output side, anaerobic ammonium oxidation ("anammox"; $NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$), in the ocean water column and sediments, has been found to be responsible for significant removal (up to 30–50%) of fixed nitrogen (Dalsgaard et al., 2003; Kuypers et al., 2003) and thus contributes to lowering deep ocean N:P. However, both processes occur under anaerobic conditions, and the nitrite (NO_2^-) used in the anammox reaction may be supplied by denitrification (of NO_3). Hence

there is no qualitative change to Redfield's mechanism and in the remainder of this article we take "denitrification" to also include anammox.

Our aims in this paper are to elucidate the controls on the deep ocean N:P ratio by adapting two existing, simple models (Tyrrell, 1999; Lenton and Watson, 2000) and conducting a series of "What if...?" thought experiments. Section 2 introduces the models and Sect. 3 presents the results. First we examine what controls deep ocean N:P by decoupling the N:P ratio of phytoplankton from the N:P threshold that triggers N_2-fixation, and varying each independently. Having established which exerts the greatest control on deep ocean N:P, we couple these ratios through the common assumption that competitive dynamics set the N:P threshold for N_2-fixation, and we maintain this assumption for the remainder of the Results. We examine the relative influences of the N:P ratios of non-fixers and of N_2-fixers on the deep ocean N:P ratio. Then we consider what happens if N_2-fixers are limited to a fraction of the surface ocean. The effects of changes in the N:P ratio of the phytoplankton (and corresponding changes in the N:P threshold of N_2-fixation) on long-term steady state deep ocean N:P are estimated. Then the effect of variations in weathering rate are examined. Finally we make an estimate of the combined effects of changes in N:P of the phytoplankton and changes in weathering. Section 4 discusses the findings and Sect. 5 concludes.

2 Methods

Here we introduce the two models adapted for this study (Fig. 1–2). For further explanation and justification of their formulation, including the values chosen for various constants, see Lenton and Watson (2000) (henceforth LW) and Tyrrell (1999) (henceforth TT). Those readers familiar with one or both models may skip the corresponding section(s). Both are simple box models, LW is essentially a 1-box model, TT is a 2-box model and we extend it to 3 boxes. LW include N, P, C and O_2 cycling and concentrate on the feedback mechanisms in the system, but have no explicit biological populations. TT includes N and P cycling and explicit competition between N_2-fixers and non-fixers, but has no C or O_2 cycling hence the effects of changes in C:P or C:N ratios cannot be addressed. Table 1 lists the key parameters varied in this study and all other model constants.

2.1 LW model

Lenton and Watson (2000) model (Fig. 1) reservoirs of nitrate (NO_3, actually available nitrogen) and phosphate (PO_4) expressed as deep ocean concentrations, and a reservoir of atmospheric oxygen (O_2) expressed as the concentration in water ventilating the deep ocean. Here we generalize the original model (M1) of LW to allow independent variation of the C:N and C:P Redfield ratios of new production, denoted

Table 1. Model parameters varied in this study and all remaining model constants.

| Model	Class	Label	Description	Value
LW	Parameters	W	Normalised weathering forcing	1
		$r_{C:N}$	C:N Redfield ratio	117/16
		$r_{C:P}$	C:P Redfield ratio	117
		$r_{N:P}$	N:P Redfield ratio	16
		$r_{N:P,Fix}$	N:P threshold below which N_2-fixation occurs	16
	Constants	$b_{C:N}$	Organic C:N burial ratio	37.5
		$b_{C:P}$	Organic C:P burial ratio	250
		$PO_{4(0)}$	Initial deep ocean phosphate concentration	$2.2\,\mu\text{mol kg}^{-1}$
		$NO_{3(0)}$	Initial deep ocean nitrate concentration	$30.9\,\mu\text{mol kg}^{-1}$
		$O_{2(0)}$	Initial oxygen concentration in ventilating water	$331.5\,\mu\text{mol kg}^{-1}$
		C_0	Initial carbon concentration due to new production in surface waters	$226.0\,\mu\text{mol kg}^{-1}$
		k_P	Initial PO_4 surplus in surface waters after NO_3 removal	$0.26875\,\mu\text{mol kg}^{-1}$
		A_0	Initial anoxic fraction	0.14
		k_1	Initial oxic fraction	0.86
		k_2	Initial organic carbon burial flux	$3.75\times10^{12}\,\text{mol C yr}^{-1}$
		k_3	Initial nitrogen fixation flux	$8.7\times10^{12}\,\text{mol N yr}^{-1}$
		k_4	Half of initial denitrification flux	$4.3\times10^{12}\,\text{mol N yr}^{-1}$
		k_5	Initial bio-available phosphorus input flux	$3.6\times10^{10}\,\text{mol P yr}^{-1}$
		k_6	Initial iron-sorbed phosphorus burial flux	$0.6\times10^{10}\,\text{mol P yr}^{-1}$
		k_7	Initial calcium-bound phosphorus burial flux	$1.5\times10^{10}\,\text{mol P yr}^{-1}$
		k_8	Conversion factor from deep ocean reservoir size to concentration	$7.1\times10^{-22}\,\text{kg}^{-1}$
		k_9	Conversion factor from atmospheric reservoir size to concentration	$8.96\times10^{-24}\,\text{kg}^{-1}$
TT	Parameters	R_{NF}	N:P Redfield ratio of N_2-fixers	16
		R_O	N:P Redfield ratio of other phytoplankton	16
		f_A	Fraction of surface ocean where N_2-fixers can grow	1
		f_B	Fraction of surface ocean where N_2-fixers cannot grow	0
	Constants	P_H	Half-saturation constant for growth on PO_4	$3\times10^{-5}\,\text{mol P m}^{-3}$
		N_H	Half-saturation constant for growth on NO_3	$5\times10^{-4}\,\text{mol N m}^{-3}$
		μ'_{NF}	Maximum growth rate for N_2-fixers	$87.6\,\text{yr}^{-1}$
		μ'_O	Maximum growth rate for other phytoplankton	$91.25\,\text{yr}^{-1}$
		M	Mortality	$73\,\text{yr}^{-1}$
		SD	Depth of the surface layer	$500\,\text{m}$
		DD	Depth of the deep layer	$3230\,\text{m}$
		K	Mixing coefficient between the surface and the deep	$3.0\,\text{m yr}^{-1}$
		SR	Fraction of total primary productivity regenerated in the surface layer	95%
		DN	Fraction of total N uptake that is converted to N_2 via denitrification	1.5%
		DR	Fraction of total primary productivity regenerated in the deep layer	4.8%
		RP	River input of P	$2.0\times10^{-4}\,\text{mol P m}^{-2}\,\text{yr}^{-1}$
		RN	River input of N	$6.0\times10^{-3}\,\text{mol N m}^{-2}\,\text{yr}^{-1}$
		AN	Atmospheric input of N	$7.5\times10^{-3}\,\text{mol N m}^{-2}\,\text{yr}^{-1}$

$r_{C:N}$ and $r_{C:P}$, and the N:P threshold below which N_2-fixation occurs, denoted $r_{N:P,Fix}$.

The limiting nutrient in water up-welled to the surface ocean is assumed to be completely used up, generating a corresponding concentration ($\mu\text{mol kg}^{-1}$) of carbon due to new production in the surface layer, denoted C here instead of N (to avoid confusion with Tyrrell's N):

$$C = \min\left(r_{C:N}NO_3, r_{C:P}PO_4\right) \qquad (1)$$

N_2-fixation (N-Fix) is assumed to depend on the deficit of $NO_3/r_{N:P,Fix}$ below PO_4:

$$F_{\text{N-Fix}} = \frac{k_3}{k_P}\left(PO_4 - \frac{NO_3}{r_{N:P,Fix}}\right) \qquad (2)$$
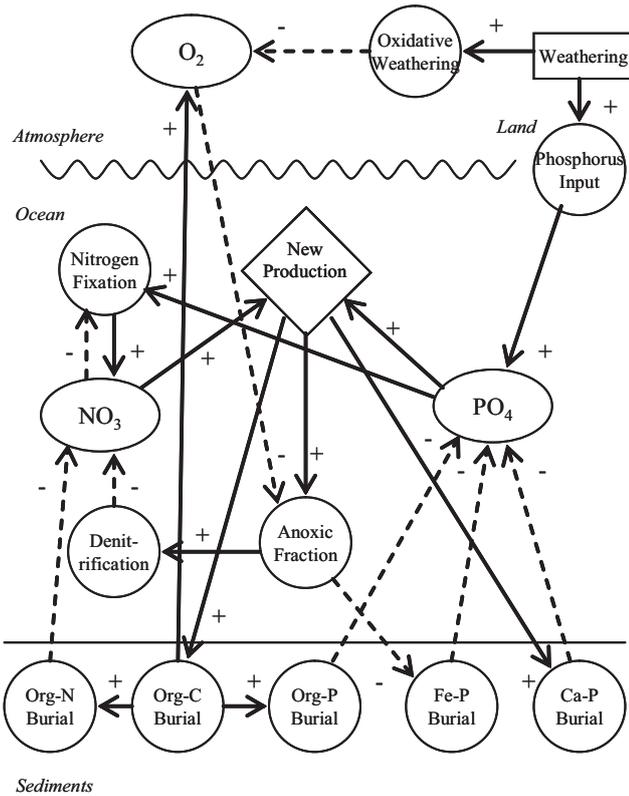
Fig. 1. Feedback diagram of the LW model where arrows indicate causal relationships. Ovals indicate reservoirs, circles indicate dependent variables, the diamond indicates a switch – new production is determined by either NO_3 or PO_4 – and the rectangle indicates the single input parameter, weathering. A solid arrow with a plus sign indicates a direct relationship, e.g. increased nitrogen fixation increases NO_3. A dashed arrow with a minus sign indicates an inverse relationship, e.g. increased NO_3 decreases nitrogen fixation. In this example, a negative feedback loop is closed. All closed loops of arrows that can be traced around the diagram represent feedbacks. If there are an odd number of inverse relationships in a loop it is a negative feedback, whereas those containing none or an even number are positive feedbacks.

where F denotes a flux. All constants are retained including the initial N_2-fixation flux $k_3=8.7\times10^{12}$ mol N yr^{-1} and the initial average deep ocean nutrient concentrations of $PO_{4(0)}=2.2\,\mu$mol kg^{-1} and $NO_{3(0)}=30.9\,\mu$mol kg^{-1} from World Ocean Atlas data. The derived constant $k_P=PO_{4(0)}-NO_{3(0)}/16=0.26875\,\mu$mol kg^{-1} represents the average surplus PO_4 remaining in surface waters after NO_3 has been removed by new production. N_2-fixation provides negative feedback on nitrate that tends to couple it to phosphate, e.g. increased NO_3 suppresses N_2-fixation, counteracting the initial change.

The anoxic fraction of the ocean (A) depends on the balance of oxygen supply via ocean mixing and oxygen demand

due to respiration of sinking new production:

$$A = 1 - k_1 \frac{O_2}{O_{2(0)}} \frac{C_0}{C} \qquad (3)$$

The initial oxic fraction $k_1=0.86$ and the initial anoxic fraction $A_0=0.14$ are derived from data for the present ocean. The initial oxygen concentration for water ventilating the deep ocean $O_{2(0)}=331.5\,\mu$mol kg^{-1} is based on a temperature of 2°C. The initial average carbon concentration due to new production in surface waters $C_0=226.0\,\mu$mol kg^{-1} is derived from $NO_{3(0)}$ and the present value of $r_{C:N}$.

Denitrification (De-N) comprises a fixed sedimentary flux and a variable water column flux that depends on anoxia:

$$F_{De-N} = k_4 \left(1 + \frac{A}{A_0}\right) \qquad (4)$$

where $k_4=4.3\times10^{12}$ mol N yr^{-1} is the initial size of each flux. The dependence of water column denitrification on anoxia provides negative feedback on nitrate that tends to couple nitrate to oxygen, e.g. increased NO_3 increases new production, anoxia, and denitrification, thus counteracting the initial change.

A further minor sink of nitrate is organic nitrogen (Org-N) burial, which occurs with the burial of organic carbon and a C:N burial ratio $b_{C:N}=37.5$:

$$F_{Org-N} = \frac{k_2}{b_{C:N}} \left(\frac{C}{C_0}\right)^2 \qquad (5)$$

where the initial organic carbon burial flux $k_2=3.75\times10^{12}$ mol C yr^{-1}, hence organic nitrogen burial is initially 0.1×10^{12} mol N yr^{-1}. Organic nitrogen burial provides a small additional negative feedback on nitrate, e.g. increased NO_3 increases new production and Org-N burial, thus counteracting the initial change.

The overall rate of change of nitrate is given by:

$$\frac{dNO_3}{dt} = k_8 \left(F_{N-Fix} - F_{De-N} - F_{Org-N}\right) \qquad (6)$$

where $k_8=7.1\times10^{-22}$ kg^{-1} converts from reservoir size in mol to average concentration. The overall balance of feedbacks is such that nitrate tracks any variations in phosphate.

Normalized weathering, W, represents the only external forcing parameter for the model (i.e. $W=1$ at present day). Weathering drives phosphorus input to the ocean (P-in), via rivers:

$$F_{P-in} = k_5 W \qquad (7)$$

with initial flux $k_5=3.6\times10^{10}$ mol P yr^{-1}. Phosphorus is removed from the ocean via burial in sediments, which occurs in three main forms:

Burial of phosphorus with iron oxides (Fe-P) is initially $k_6=0.6\times10^{10}$ mol P yr^{-1} and is inversely dependent on anoxia:

$$F_{Fe-P} = \frac{k_6}{k_1} (1 - A) \qquad (8)$$
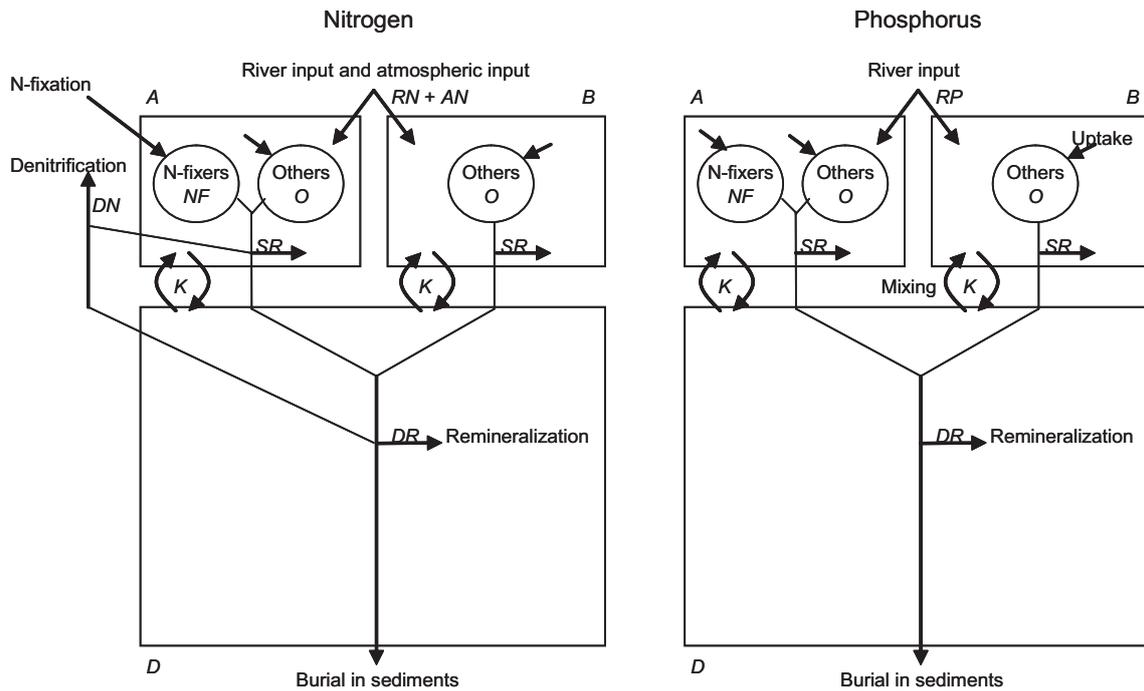
Fig. 2. Schematics of the nitrogen and phosphorus cycles in the extended TT model, where arrows indicate fluxes. The model has two surface ocean boxes (A, B) and a deep ocean box (D). Within box A there are populations of nitrogen fixers and other phytoplankton. Within box B there are only other phytoplankton. Where possible, fluxes are labelled and model variables and constants are indicated in italics. Mixing (K) occurs between each surface box and the deep box but not between the two surface boxes. N enters the surface boxes from rivers (RN) and atmospheric deposition (AN). P enters from rivers (RP). Biological uptake of nutrient is indicated by an arrow from within a surface box to a population. N is also fixed from outside the system directly into the N_2-fixers. Mortality is represented by lines leaving the populations, forming sinking fluxes of nutrients. For both nutrients, a fraction (SR) of the sinking flux is remineralised in the surface layer and a fraction (SD) in the deep box. For N, a fraction (DN) is also lost by denitrification. The remaining sinking fluxes of nutrients leave the system as burial in sediments.

This provides a positive feedback on phosphate, e.g. increased PO_4 tends to increase NO_3, new production and anoxia, decreasing Fe-P burial and tending to further increase PO_4.

Organic phosphorus (Org-P) burial is initially 1.5×10^{10} mol P yr^{-1} and occurs with the burial of organic carbon in a C:P burial ratio $b_{C:P}=250$:

$$F_{\mathrm{Org-P}} = \frac{k_2}{b_{C:P}} \left(\frac{C}{C_0} \right)^2 \qquad (9)$$

The dependence on new production provides negative feedback on phosphate, e.g. increased PO_4 tends to increase NO_3, new production and Org-P burial, thus counteracting the initial change.

Calcium-bound (Ca-P) phosphorus burial is also initially $k_7=1.5 \times 10^{10}$ mol P yr^{-1} and is largely authigenic (it forms in sediments). The phosphorus buried as Ca-P is supplied via new production hence it has the same functional dependence on new production as Org-P burial:

$$F_{\mathrm{Ca-P}} = k_7 \left(\frac{C}{C_0} \right)^2 \qquad (10)$$

This provides further negative feedback on phosphate.

The overall rate of change of phosphate is given by:

$$\frac{d\mathrm{PO_4}}{dt} = k_8 \left(F_{\mathrm{P-in}} - F_{\mathrm{Fe-P}} - F_{\mathrm{Org-P}} - F_{\mathrm{Ca-P}} \right) \qquad (11)$$

The overall feedback is negative tending to buffer variations in phosphate, e.g. those driven by changes in weathering. This is because feedbacks on Org-P and Ca-P are both negative, they comprise $\approx$83% of the present P burial flux, and the functional dependence of their burial on productivity is quadratic (i.e. non-linear). In contrast, the positive feedback on Fe-P burial comprises $\approx$17% of P burial and has a simple inverse dependence on productivity.

Organic carbon (Org-C) burial provides the net source of atmospheric oxygen and depends quadratically on new production:

$$F_{\mathrm{Org-C}} = k_2 \left(\frac{C}{C_0} \right)^2 \qquad (12)$$

Although Org-C burial has no direct dependence on oxygen, the dependence of Fe-P burial on anoxia provides a negative feedback on atmospheric oxygen, e.g. increased O_2

decreases anoxia, increasing Fe-P burial, decreasing PO_4, tending to decrease new production and Org-C burial, thus counteracting the initial change.

Oxidative weathering (Ox-W) provides the net sink of atmospheric oxygen and is forced by W:

$$F_{Ox-W} = k_2 W \tag{13}$$

All reduced material that is exposed is assumed to be oxidized, thus making oxygen consumption independent of oxygen level.

The overall rate of change of oxygen is given by:

$$\frac{dO_2}{dt} = k_9 \left(F_{Org-C} - F_{Ox-W} \right) \tag{14}$$

where $k_9 = 8.96 \times 10^{-24}$ kg^{-1} converts from atmospheric oxygen reservoir size in mol to concentration dissolved in surface waters ventilating the deep ocean. Atmospheric oxygen has a much longer response time to perturbations ($\approx 10^7$ yr) than either of the nutrient reservoirs. Hence the steady state response to variations in W is achieved over a much longer timescale than the steady state response to variations in $r_{C:N}$, $r_{C:P}$ or $r_{N:P,Fix}$, none of which affect O_2.

The system was solved analytically for steady state following the method in the Appendix of LW but for an unknown limiting nutrient, yielding:

$$\frac{C}{C_0} = W^{\frac{1}{2}} \tag{15}$$

$$\frac{O_2}{O_{2(0)}} = W^{\frac{3}{2}} \tag{16}$$

$$A = 1 - k_1 W \tag{17}$$

$$PO_4 = \frac{NO_3}{r_{N:P,Fix}} + k_P (4.025 - 3.025W) \tag{18}$$

Steady state for O_2 is lost when $A \rightarrow 0$, which from Eq. (17) gives an upper limit on W=1.163 (above this, O_2 increases monotonically). From Eqs. (1) and (15):

$$\min (r_{C:N} NO_3, r_{C:P} PO_4) = C_0 W^{\frac{1}{2}} \tag{19}$$

which determines the value of the limiting nutrient and the other nutrient is found from Eq. (18). When NO_3 is limiting:

$$NO_3 = \frac{C_0 W^{\frac{1}{2}}}{r_{C:N}} \tag{20}$$

$$PO_4 = \frac{C_0 W^{\frac{1}{2}}}{r_{C:N} r_{N:P,Fix}} + k_P (4.025 - 3.025W) \tag{21}$$

When PO_4 is limiting:

$$PO_4 = \frac{C_0 W^{\frac{1}{2}}}{r_{C:P}} \tag{22}$$

$$NO_3 = r_{N:P,Fix} \left(\frac{C_0 W^{\frac{1}{2}}}{r_{C:P}} - k_P (4.025 - 3.025W) \right) \tag{23}$$

LW took $r_{C:N}$=117/16=7.3125 and $r_{C:P}$=117 from nutrient data analysis (Anderson and Sarmiento, 1994) and assumed $r_{N:P,Fix}=r_{C:P}/r_{C:N}$=16, hence NO_3 was always limiting. This corresponds to a steady state PO_4=2.2 μmol kg^{-1} and NO_3=30.9 μmol kg^{-1}, i.e. deep ocean N:P=14.0 (a little below observations).

2.2 Extended TT model

Tyrrell (1999) models nitrate and phosphate in two boxes, the surface and deep ocean, and includes explicit competition between N_2-fixing and non-fixing organisms in the surface ocean. Here we extended the TT model (Fig. 2) in two ways: First, nitrogen-fixers and other phytoplankton are given different N:P stoichiometry (R_{NF} and R_O respectively). Second, the surface layer of the ocean is split into two boxes, a fraction where nitrogen-fixers can grow (f_A) and a fraction where they cannot ($f_B=1-f_A$), due to limitation by e.g. iron, temperature or light. These two boxes are not directly coupled, but both exchange nutrients and dead biomass with the deep layer. The subscripts A, B and D refer to the two surface boxes and the deep box, respectively. NF is the standing stock of N_2-fixers and O that of other phytoplankton. P and N are the concentrations of PO_4 and NO_3, respectively. All other symbols and parameter values are as in Tyrrell (1999).

The dynamics of each population is determined by a balance of nutrient uptake and mortality, described by:

$$\frac{dNF_A}{dt} = \mu'_{NF} \times \frac{P_A}{P_A + P_H} \times NF_A - M \times NF_A \tag{24}$$

$$\frac{dO_A}{dt} = \mu'_O \times \min \left(\frac{P_A}{P_A + P_H}, \frac{N_A}{N_A + N_H} \right) \times O_A - M \times O_A \tag{25}$$

$$\frac{dO_B}{dt} = \mu'_O \times \min \left(\frac{P_B}{P_B + P_H}, \frac{N_B}{N_B + N_H} \right) \times O_B - M \times O_B \tag{26}$$

where net primary production of nitrogen fixers is limited only by P, following Michaelis-Menten kinetics with a half-saturation constant, $P_H = 3 \times 10^{-5}$ mol P m^{-3} and maximum growth rate, μ'_{NF}=87.6 yr^{-1}. Other phytoplankton can be limited by either N or P, with half-saturation constant for growth on N of $N_H = 5 \times 10^{-4}$ mol N m^{-3}, and a higher maximum growth rate of μ'_O=91.25 yr^{-1}. Mortality for both types of plankton, M=73 yr^{-1}.

N_2-fixers are given a lower maximum growth rate on P because of the energy demands of N_2-fixation. Thus if P is limiting they are out-competed, but this removes a source of N to the system, and N drops until the system settles into an N-limited state. In that state, there is negative feedback on changes in N – should N increase, N_2-fixers will tend to be out-competed by other plankton, conversely, should N drop, N_2-fixers tend to make up a larger fraction of the population.

The model schematic (Fig. 2) illustrates the key fluxes of both nutrients. N and P are removed from the surface boxes by biological uptake, but for both nutrients, $SR=95\%$ of total primary productivity is regenerated in the surface layer. Atmospheric N_2 exchanges with seawater where it is fixed directly into N_2-fixers, and enters box A as available N via their mortality and remineralisation. N is removed from the system by denitrification, with $DN=1.5\%$ of total N uptake converted to N_2 via denitrification, 75% of this in the surface layer. Mixing of water ($K=3.0\,\mathrm{m\,yr^{-1}}$) with the deep box provides a net input of nutrients to each surface box. N also enters the surface boxes from rivers ($RN=6.0\times10^{-3}\,\mathrm{mol\,N\,m^{-2}\,yr^{-1}}$) and atmospheric deposition ($AN=7.5\times10^{-3}\,\mathrm{mol\,N\,m^{-2}\,yr^{-1}}$), whilst P enters only from rivers ($RP=2.0\times10^{-4}\,\mathrm{mol\,P\,m^{-2}\,yr^{-1}}$). All these fluxes determine the rate of change of nutrient concentrations in the surface ocean boxes, described by:

$$\begin{aligned}\frac{dP_A}{dt} = &-\mu'_{NF} \times \frac{P_A}{P_A+P_H} \times \frac{NF_A}{R_{NF}} \\ &-\mu'_O \times \min\left(\frac{P_A}{P_A+P_H}, \frac{N_A}{N_A+N_H}\right) \times \frac{O_A}{R_O} \\ &+M \times SR \times \frac{NF_A}{R_{NF}} + M \times SR \times \frac{O_A}{R_O} \\ &+\frac{K\times(P_D-P_A)}{SD} + \frac{RP}{SD}\end{aligned} \quad (27)$$

$$\begin{aligned}\frac{dN_A}{dt} = &-\mu'_O \times \min\left(\frac{P_A}{P_A+P_H}, \frac{N_A}{N_A+N_H}\right) \times O_A \\ &+M \times (SR-0.75\times DN) \times NF_A \\ &+M \times (SR-0.75\times DN) \times O_A \\ &+\frac{K\times(N_D-N_A)}{SD} + \frac{(RN+AN)}{SD}\end{aligned} \quad (28)$$

$$\begin{aligned}\frac{dP_B}{dt} = &-\mu'_O \times \min\left(\frac{P_B}{P_B+P_H}, \frac{N_B}{N_B+N_H}\right) \times \frac{O_B}{R_O} \\ &+M \times SR \times \frac{O_B}{R_O} + \frac{K\times(P_D-P_B)}{SD} + \frac{RP}{SD}\end{aligned} \quad (29)$$

$$\begin{aligned}\frac{dN_B}{dt} = &-\mu'_O \times \min\left(\frac{P_B}{P_B+P_H}, \frac{N_B}{N_B+N_H}\right) \times O_B \\ &+M \times (SR-0.75\times DN) \times O_B \\ &+\frac{K\times(N_D-N_B)}{SD} + \frac{(RN+AN)}{SD}\end{aligned} \quad (30)$$

where $SD=500\,\mathrm{m}$ is the depth of the surface layer.

Nutrients enter the deep ocean via remineralisation with $DR=4.8\%$ of total primary productivity regenerated in the deep layer (leaving 0.2% to leave the system via burial in sediments). Denitrification (25% of DN) removes some N from the sinking flux. There is also a net removal of both nutrients from the deep box due to mixing with the surface boxes. These fluxes determine the rate of change of nutrient concentrations in the deep ocean, given by:

$$\begin{aligned}\frac{dP_D}{dt} = &M \times DR \times \frac{NF_A}{R_{NF}} \times \frac{f_A\times SD}{DD} \\ &+M \times DR \times \frac{O_A}{R_O} \times \frac{f_A\times SD}{DD} \\ &+M \times DR \times \frac{O_B}{R_O} \times \frac{f_B\times SD}{DD} \\ &-\frac{K\times(P_D-f_A P_A-f_B P_B)}{DD}\end{aligned} \quad (31)$$

$$\begin{aligned}\frac{dN_D}{dt} = &M \times (DR-0.25\times DN) \times NF_A \times \frac{f_A\times SD}{DD} \\ &+M \times (DR-0.25DN) \times O_A \times \frac{f_A\times SD}{DD} \\ &+M \times (DR-0.25DN) \times O_B \times \frac{f_B\times SD}{DD} \\ &-\frac{K\times(N_D-f_A N_A-f_B N_B)}{DD}\end{aligned} \quad (32)$$

where $DD=3230\,\mathrm{m}$ is the depth of the deep layer.

Denitrification and N burial remove a constant fraction of the N taken up in net primary production from the system, providing a linear negative feedback on changes in N. P burial provides an equivalent linear negative feedback on changes in P.

Setting $f_A=1$ and $R_{NF}=R_O=16$ (=R_{ORG}) recovers the original TT model. These equations were solved numerically with a Fortran program and using Mathematica software.

2.3 Application of the models

We use the two models in a complementary fashion. In the LW model, the distinction between the N:P ratio of the phytoplankton and the N:P threshold that triggers N_2-fixation allows us to first independently examine their influences on deep ocean N:P. These ratios are then equated in the LW model for the remainder of the Results. This assumes that competitive dynamics set the N:P threshold for N_2-fixation, which is implicit in the TT model. Under this assumption, we use both models to examine the effect of changes in phytoplankton N:P on deep ocean N:P. We use the extended TT model to further examine the relative impact of independently varying the N:P ratios of N_2-fixers and non-fixers, and the effect of restricting N_2-fixers to a progressively smaller fraction of the surface ocean. Then we use the LW model to examine the effects of changes in C:P and C:N as well as N:P ratios of the phytoplankton, and the effect of changes in weathering. In all cases we concentrate on the steady state solutions of the models, rather than their transient responses. In response to changes in phytoplankton stoichiometry and/or the N:P threshold that triggers N_2-fixation, steady state is achieved over 10^4-10^5 yr, whereas in response to changes in weathering it takes 10^6-10^7 yr.

3 Results

3.1 What controls deep ocean N:P?

From the analytical solution of the LW model for steady state (Sect. 2.1) (valid for normalised weathering forcing $0\leq W\leq1.163$), we find the following solutions for the ratio of available nitrogen (NO_3) and phosphorus (PO_4) in the deep ocean. When NO_3 is limiting:
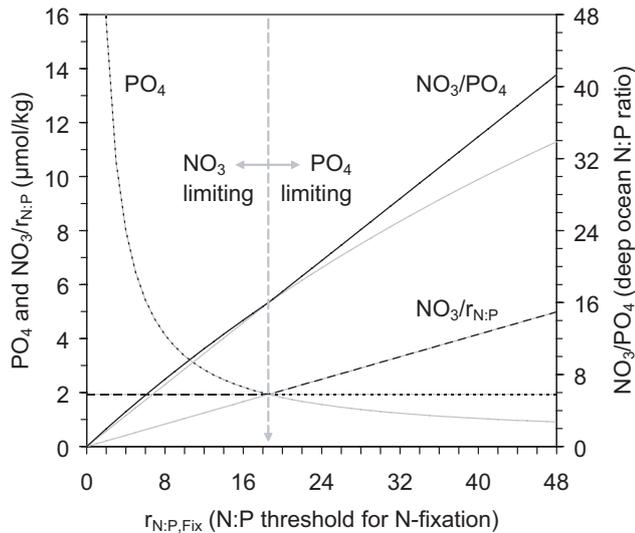
$$\frac{NO_3}{PO_4} = \left(\frac{1}{r_{\mathrm{N:P,Fix}}} + \frac{r_{\mathrm{C:N}}k_P}{C_0 W^{\frac{1}{2}}}(4.025-3.025W)\right)^{-1} \quad (33)$$

When PO_4 is limiting:

$$\frac{NO_3}{PO_4} = r_{\mathrm{N:P,Fix}}\left(1 - \frac{r_{\mathrm{C:P}}k_P}{C_0 W^{\frac{1}{2}}}(4.025-3.025W)\right) \quad (34)$$

The condition for NO_3 to be limiting is:

$$\frac{1}{r_{\mathrm{C:P}}} - \frac{1}{r_{\mathrm{C:N}}r_{\mathrm{N:P,Fix}}} \leq \frac{k_P}{C_0 W^{\frac{1}{2}}}(4.025-3.025W) \quad (35)$$

Fig. 3. Analytic solutions for the dependence of steady state PO_4 (dotted line), $NO_3/r_{N:P}$ (dashed line), and deep ocean N:P ratio (solid line) on the N:P threshold for N_2-fixation ($r_{N:P,Fix}$), in the LW model. Here the N:P Redfield ratio (i.e. the composition of all phytoplankton) is fixed at $r_{N:P}$=16. We plot $NO_3/r_{N:P}$ rather than NO_3 to visually indicate whether PO_4 or NO_3 is limiting. The pale grey solid lines show the solutions for both NO_3 limiting and PO_4 limiting conditions throughout. However, for a given value of $r_{N:P,Fix}$, only one set of solutions is valid and self-consistent. The space divides into two regimes, one where NO_3 is limiting and the other where PO_4 is limiting (when $r_{N:P,Fix} \geq 18.6$).

For the default parameter values, NO_3 is limiting. However, if the N:P threshold that triggers N_2-fixation ($r_{N:P,Fix}$) and the N:P Redfield ratio ($r_{N:P}$) can be decoupled, then PO_4 limitation can be triggered by increasing $r_{N:P,Fix}$, or by decreasing $r_{N:P}$ (by either decreasing $r_{C:P}$ or by increasing $r_{C:N}$).

Figures 3 and 4 show, for present day weathering W=1, the effects of independently varying $r_{N:P,Fix}$, $r_{C:P}$, or $r_{C:N}$ on $NO_3/r_{N:P}$, PO_4, and the deep ocean N:P ratio. With fixed W=1, atmospheric oxygen, new production, and ocean anoxia are constant at their initial values (from Eqs. 15–17).

Deep ocean N:P is primarily controlled by the N:P threshold that triggers N_2-fixation, $r_{N:P,Fix}$ (Fig. 3). Considering Eqs. (33) and (34), k_P=0.26875 μmol kg^{-1} is small, therefore deep ocean N:P is set modestly below $r_{N:P,Fix}$, whether N or P is limiting. In mechanistic terms, denitrification in the water column and sediments, plus a small amount of organic nitrogen burial, continually remove N from the ocean, thus lowering deep ocean N:P and supporting a counterbalancing flux of N_2-fixation. For the default parameter values shown, in the N-limiting regime, deep ocean N:P tends toward $r_{N:P,Fix}$ as $r_{N:P,Fix}$ tends to zero. When $r_{N:P,Fix}$ is increased, this tends to transiently increase N_2-fixation, NO_3, new production, Org-P and Ca-P burial until steady state is restored with lower PO_4, identical NO_3 and consequently higher deep ocean N:P. When $r_{N:P,Fix} \geq 18.6$, a switch to P-

limitation occurs. Now as $r_{N:P,Fix}$ is increased further, increases in N_2-fixation increase steady-state NO_3 (because it is no longer limiting) without affecting PO_4 (which remains constant). Thus deep ocean N:P=0.86$r_{N:P,Fix}$ increases linearly.

When the N:P threshold triggering N_2-fixation is fixed at $r_{N:P,Fix}$=16, varying the N:P Redfield ratio – by varying either C:P or C:N – has little effect on the deep ocean N:P ratio (Fig. 4), although the concentrations of NO_3 and PO_4 can be substantially altered.

When varying $r_{C:P}$ with fixed $r_{C:N}$=7.3125 (Fig. 4a), if the system is in the N-limiting regime, deep ocean N:P ratio remains constant at 14.04 ($r_{C:P}$ does not appear in Eq. 33). Indeed the concentrations of both nutrients are constant (Eqs. 20–21) because changes in C:P do not alter any of the controlling fluxes when N is limiting and C:N is constant. If $r_{C:P} \leq 102.7$ (corresponding to $r_{N:P} \leq 14.04$), a switch to P-limitation occurs. Further decreases in $r_{C:P}$ transiently reduce new production, Org-P burial, Ca-P burial, Org-N burial, anoxia and denitrification until steady state is restored with higher concentrations of both NO_3 and PO_4. Deep ocean N:P increases linearly with decreasing $r_{C:P}$, tending toward $r_{N:P,Fix}$=16 as $r_{C:P}$ tends toward zero.

When varying $r_{C:N}$ with fixed $r_{C:P}$=117 (Fig. 4b), in the N-limiting regime, deep ocean N:P ratio shows a weak sensitivity to $r_{C:N}$ (Eq. 33). As $r_{C:N}$ is decreased (corresponding to increasing $r_{N:P}$), deep ocean N:P tends toward $r_{N:P,Fix}$. As $r_{C:N}$ is increased, transient increases in new production, Org-P burial, Ca-P burial, Org-N burial, anoxia and denitrification give rise to a new steady state with lower concentrations of both NO_3 and PO_4. If $r_{C:N} \geq 8.49$ (corresponding to $r_{N:P} \leq 13.77$), a switch to P-limitation occurs. In this regime, $r_{C:N}$ has no effect on either NO_3 or PO_4 (Eqs. 22–23) and deep ocean N:P is constant at 13.77.

Thus, a systematic change in phytoplankton C:N:P stoichiometry can alter the concentrations of NO_3 and PO_4 in the deep ocean but cannot greatly alter their ratio, unless it also alters the N:P threshold for N_2-fixation. This is a useful insight from the model, particularly if in reality $r_{N:P}$ and $r_{N:P,Fix}$ can be decoupled. However, it may be of limited applicability to the real ocean, because (as we will assume for the remainder of the Results section) changes in the N:P requirement of the phytoplankton are expected to alter the N:P threshold for N_2-fixation. In particular, it is implicit in Redfield's (1958) mechanism that the N:P level triggering N_2-fixation cannot be decoupled from the N:P ratio of the phytoplankton because the latter sets the threshold below which N_2-fixers are selected and N_2-fixation occurs. This can be explained in terms of competitive dynamics (Schade et al., 2005): If the N:P supply ratio in the water is below the N:P requirement of non-fixers, then they will use up all the N and leave some P remaining. N_2-fixers can utilise this P and in so doing add fixed N to the system. This will continue until the N:P supply ratio approaches the N:P requirement of the non-fixers, at which point the N_2-fixers tend to
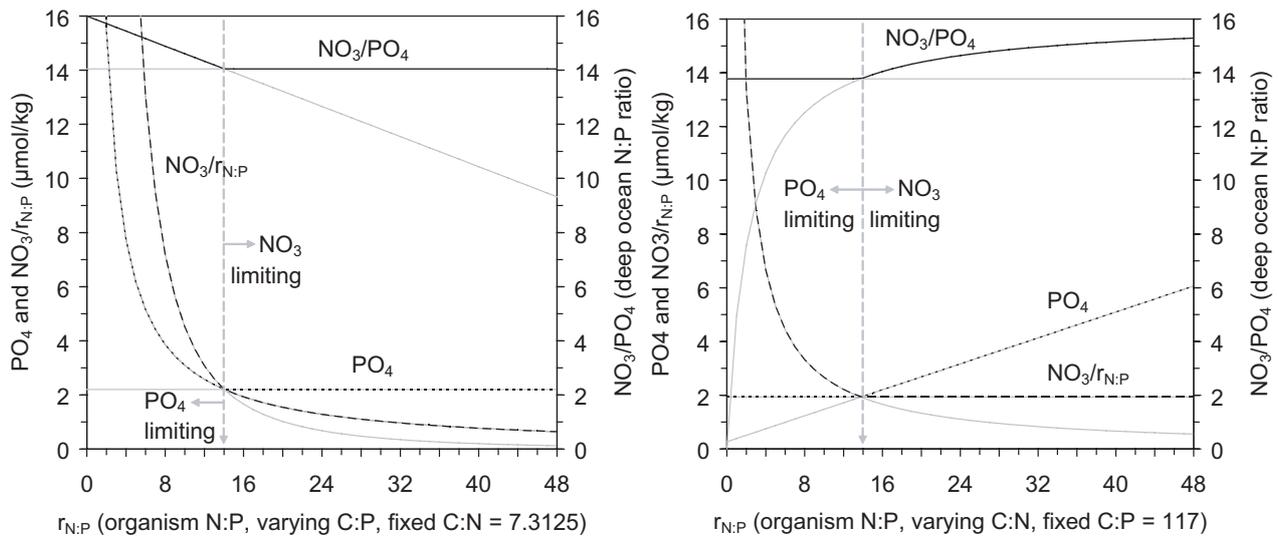
Fig. 4. Analytic solutions for the dependence of steady state PO_4 (dotted line), $NO_3/r_{N:P}$ (dashed line), and deep ocean N:P ratio (solid line) on the N:P Redfield ratio ($r_{N:P}$), when the N:P threshold for N_2-fixation is fixed at $r_{N:P,Fix}=16$, in the LW model. (a) Fixing the C:N Redfield ratio at $r_{C:N}=117/16=7.3125$. Here in the N-limiting regime, deep ocean N:P=14.04, and a switch to PO_4 limitation occurs when $r_{N:P}\leq14.04$. (b) Fixing the C:P Redfield ratio at $r_{C:P}=117$. Here the switch to PO_4 limitation occurs when $r_{N:P}\leq13.77$, and this regime has deep ocean N:P=13.77. Other details are as in Fig. 3.

be out-competed because N_2-fixation is an energy demanding process.

## 3.2 Assuming competitive dynamics set the N:P threshold for N_2-fixation

In the LW model, if we assume that the average N:P ratio of the phytoplankton is the N:P ratio that triggers N_2-fixation (i.e. $r_{N:P,Fix}=r_{C:P}/r_{C:N}=r_{N:P}$), then $NO_3=C_0/r_{C:N}$ is always limiting, $PO_4=(C_0/r_{C:P})+k_P$ and deep ocean N:P:

$$\frac{NO_3}{PO_4} = r_{N:P}\left(\frac{1}{1+r_{C:P}k_P/C_0}\right) \quad (36)$$

In the original TT model this assumption is implicit because competition between N_2-fixers and non-fixers is made explicit. They have identical N:P ratios ($r_{N:P}=R_O=R_{NF}$, which was R_{ORG} in TT's notation). N_2-fixers are given a lower maximum growth rate on P because of the energy demands of N_2-fixation. For the default parameter settings including a fixed weathering flux of P to the ocean, deep ocean $PO_4=1.75\,\mu mol\,kg^{-1}$ and the deep ocean N:P ratio:

$$\frac{NO_3}{PO_4} = \frac{(r_{N:P}\times1.475)+2}{1.75} \quad (37)$$

Hence in both models, if it is assumed that the N:P ratio of the phytoplankton ($r_{N:P}$) determines the N:P threshold that triggers N_2-fixation ($r_{N:P,Fix}=r_{N:P}$ in LW), then the deep ocean N:P ratio will track changes in $r_{N:P}$, dropping further below it the more $r_{N:P}$ is increased (Fig. 5). This
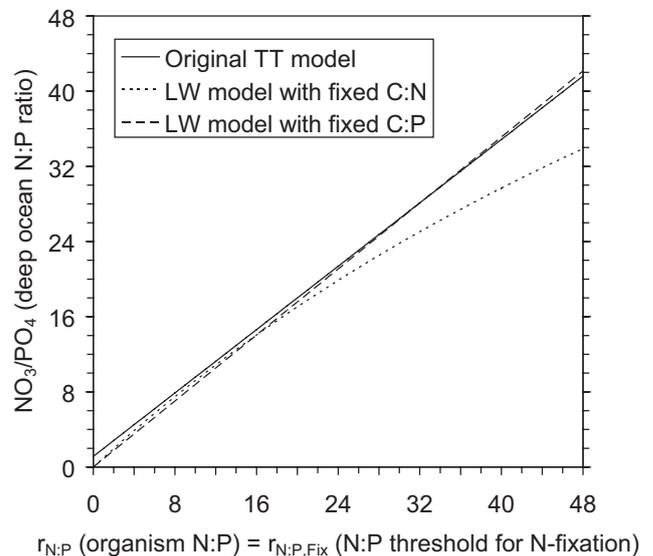
Fig. 5. Analytic solutions for the dependence of the steady state deep ocean N:P ratio on the N:P Redfield ratio of the phytoplankton, when assuming that it determines the N:P threshold that triggers N_2-fixation ($r_{N:P}=r_{N:P,Fix}$ in the LW model). This assumption is implicit in the TT model for the default parameter settings. Results for the original TT model (solid line), and the LW model when assuming either fixed C:N Redfield ratio ($r_{C:N}=117/16=7.3125$, dotted line) or fixed C:P Redfield ratio ($r_{C:P}=117$, dashed line).
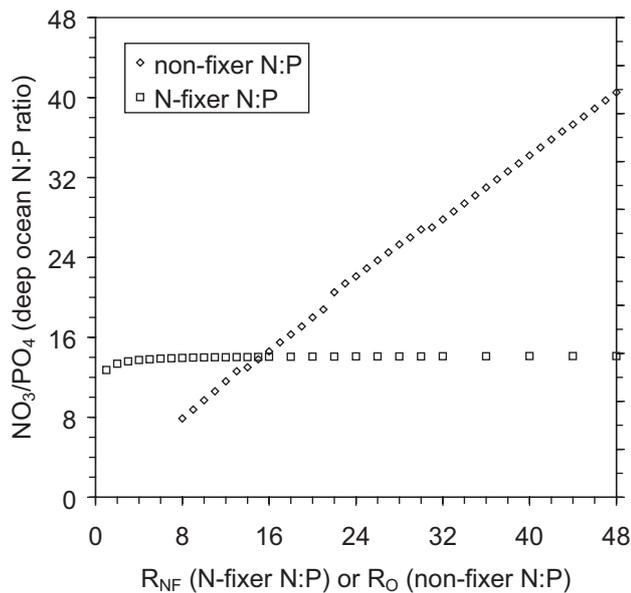
Fig. 6. Numerical solutions for the dependence of the deep ocean N:P ratio on the N:P Redfield ratio of either N_2-fixing organisms, R_{NF} (squares) or other non-fixers, R_O (diamonds), in the extended TT model. When varying one Redfield ratio the other is held constant at 16. A stable steady state could not be found for R_O=7 or less.

Fig. 7. Dependence of the deep ocean N:P ratio on the fraction of the surface ocean occupied by N_2-fixers (f_A) in the extended TT model, assuming an N:P Redfield ratio of 16 for both N_2-fixers and other phytoplankton. Square symbols indicate a stable solution, diamond symbols a limit cycle (oscillating solution). The oscillations are small, with a maximum amplitude of ∼0.75% (e.g. 13.3–13.5 for f_A=0.3), and the diamonds are plotted at the mid point of the oscillations. The transition from a stable steady state to a limit cycle occurs in the range f_A=0.329–0.330.

is consistent with the direct dependence of deep ocean N:P on decoupled changes in the N:P threshold that triggers N_2-fixation (Fig. 3) and may be contrasted with the insensitivity of deep ocean N:P to de-coupled changes in phytoplankton N:P (Fig. 4). In the TT model, fixing the weathering flux of P to the ocean gives a constant deep ocean PO_4 at steady state, which is equivalent to fixing the C:P Redfield ratio ($r_{C:P}$) in the LW model. In both cases (Fig. 5), deep ocean N:P linearly tracks the phytoplankton N:P ratio entirely through changes in NO_3. The only difference between the models is in the default gradient (0.84 in TT, 0.88 in LW) and offset (1.14 in TT, 0 in LW) of the relationship.
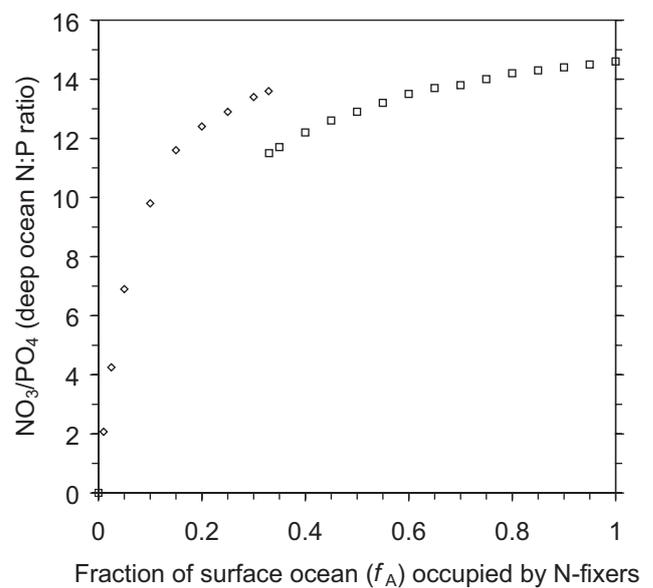
If the C:N Redfield ratio is fixed in the LW model, then NO_3 is fixed and deep ocean N:P tracks phytoplankton N:P entirely through changes in PO_4. In this case, it is instructive to re-write Eq. (36) in the form:

$$\frac{NO_3}{PO_4} = \frac{r_{N:P}}{1 + r_{N:P} r_{C:N} k_P / C_0} \qquad (38)$$

Now, the larger the N:P ratio of the phytoplankton, the further the deep ocean N:P ratio drops below it (Fig. 5). However, as $r_{C:N} k_P / C_0$ is small, the offset is modest.

3.3 Relative effects of N_2-fixer and non-fixer N:P

Our extension of the TT model to include different N:P ratios for N_2-fixers and non-fixers, allows us to examine their relative effects on the deep ocean N:P ratio. N_2-fixers often

have a higher N:P ratio than non-fixers (Klausmeier et al., 2004) with reported N:P values for N_2-fixing *Trichodesmium* colonies ranging from 18.3 (Sañudo-Wilhelmy et al., 2001) to 125 (Karl et al., 1992). However, this should have little effect on the N:P of deep water, because the density of N_2-fixers is regulated by the N:P requirements of the non-fixers. Model results (Fig. 6) confirm this; for example, steady-state deep water N:P ratio is 14.6 when N_2-fixers have an N:P ratio of 16 and 14.7 when N_2-fixers have an N:P ratio of 125. In contrast, deep ocean N:P ratio varies linearly with the N:P ratio of non-fixers (Fig. 6). Thus, contrary to Redfield (1958) (as quoted in Sect. 1), it is the N:P ratio of non-fixers (rather than N_2-fixers) that sets the N:P threshold for N_2-fixation, which consequently determines the deep ocean N:P ratio.

3.4 What if N_2-fixation is restricted to a fraction of the surface ocean?

If N_2-fixation is restricted to a progressively smaller fraction (f_A) of the surface ocean, we find that deep ocean N:P is remarkably well regulated (Fig. 7). As f_A is reduced from 1 to 0.33, steady state deep ocean N:P declines from 14.6 to 11.5; for example, when only 50% of the ocean is available to N_2-fixers, deep N:P is 12.9. As f_A is reduced below 0.33, the system undergoes a Hopf bifurcation to an oscillating

Table 2. Limits on ocean composition predicted from theoretical limits on the N:P stoichiometry of phytoplankton (Klausmeier et al., 2004) using the TT and LW models, and assuming in the latter that phytoplankton N:P is the N:P threshold that triggers N_2-fixation.

Limit	Phytoplankton N:P	Predicted N:P of deep ocean		
		TT	LW with $r_{C:P}$=117	LW with $r_{C:N}$=7.3
Control	16	14.6	14.0	14.0
Exponential growth	8.2	8.1	7.2	7.7
Light limitation	35.8	31.3	31.4	27.3
N-limitation	37.4	32.7	32.8	28.2
P-limitation	45.0	39.1	39.5	32.3

Table 3. Expected ocean composition if dominated by various phyla of phytoplankton. Predicted from the Redfield ratios found by (Quigg et al., 2003) and the adapted LW model, assuming the N:P Redfield ratio is the threshold below which N_2-fixation occurs.

Phylum/superfamily (and age)	C:N:P ratio	NO_3 (μmol kg^{-1})	PO_4 (μmol kg^{-1})	NO_3:PO_4
Prasinophyceae (1200 Myr)	200:25:1	28	1.4	20
Chlorophyceae (1000 Myr)	200:33:1	38	1.4	27
Dinophyceae (440 Myr)	140:13:1	21	1.9	11
Prymnesiophyceae (210 Myr)	60:9:1	32	4.0	8.0
Diatoms (<200 Myr)	70:10:1	32	3.5	9.2

solution, and deep N:P actually increases, oscillating in the range 13.5–13.7 for f_A=0.329. As f_A is reduced further, deep N:P declines in a non-linear fashion; for example, when only 25% of the ocean is available to N_2-fixers, the deep N:P oscillates in the range 12.8–13.0, whereas when N_2-fixers are restricted to 15% of the surface ocean, deep N:P is still 11.5–11.7. As f_A tends to zero, deep ocean N:P also tends to zero, and in the absence of N_2-fixers, the oscillations disappear.

Such homeostatic control over the deep ocean N:P ratio is maintained in the model because N_2-fixers reach higher densities when restricted to smaller fractions of the ocean's surface, compensating for their reduced distribution. Although the predicted values of deep N:P fall below those observed, this is sensitive to the choice of model parameters. If we assume that the N:P Redfield ratio of non-fixers (R_O) is somewhat greater than 16, this can compensate for restricting N_2-fixers to a fraction of the ocean's surface, for example, with f_A=0.5, R_O=18 recovers a deep ocean N:P=14.3.

3.5 What if the Redfield ratios change?

Theoretical limits on the N:P requirements of phytoplankton of 8.2–45.0 have been estimated (Klausmeier et al., 2004).

Exponential growth favours greater allocation to P-rich assembly machinery and hence a lower N:P ratio. Competitive equilibrium favours greater allocation to P-poor resource-acquisition machinery and hence a higher N:P ratio. Whether light, N or P is limiting has a second-order effect, with P-limitation favouring the least allocation to assembly and the highest N:P ratio. We take the estimated limits from Klausmeier et al. (2004) as plausible bounds on the composition of the phytoplankton.

Corresponding limits on deep ocean N:P can be derived for the TT model and for the LW model assuming $r_{N:P,Fix}$=$r_{N:P}$ with either fixed $r_{C:P}$ or fixed $r_{C:N}$ (Table 2 and Fig. 5). All three model variants give similar results. Fixed $r_{C:N}$ in the LW model is the most defendable, because existing data indicate that phytoplankton C:N is less variable than N:P and C:P (Geider and La Roche, 2002; Quigg et al., 2003). This model variant suggests that deep ocean N:P has a maximum range of 7.7–32.3 (i.e. about a factor of 2 either side of deep ocean values in the modern ocean).

We can also use the LW model to consider the effect on ocean composition of systematic changes in the phytoplankton C:N:P over evolutionary time (Quigg et al., 2003), assuming that changes in phytoplankton N:P drove
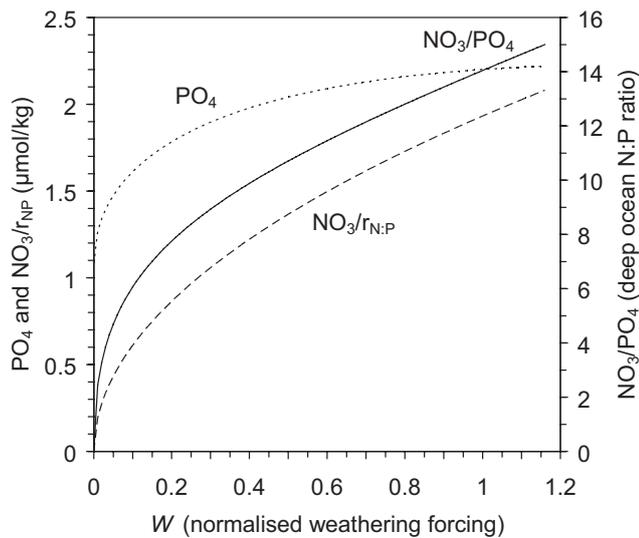
Fig. 8. Analytic solutions for the dependence of steady state PO_4 (dotted line), $NO_3/r_{N:P}$ (dashed line), and deep ocean N:P ratio (solid line) on weathering forcing (W) in the LW model. Note that steady state is only achieved for $W \leq 1.163$.

corresponding changes in the N:P threshold triggering N_2-fixation ($r_{N:P,Fix} = r_{N:P}$). Table 3 shows the ocean composition predicted (from Eq. 36) if it were dominated by each of a series of phyla/super-families of decreasing antiquity. This suggests that a general decrease in N:P ratios of marine phytoplankton over the past ~1000 Myr would have tended to decrease deep ocean N:P. This is predicted to have occurred via increasing ocean PO_4, due to the general decrease in phytoplankton C:P, whereas the relative constancy of the phytoplankton C:N ratio would not have forced NO_3.

3.6 What if phosphorus weathering changes?

Thus far we have assumed weathering forcing (W) is fixed, which has not been the case (Bergman et al., 2004; Lenton and Watson, 2004). The biological colonisation of the land surface has tended to accelerate weathering, in particular of phosphorus. This in turn has tended to increase atmospheric O_2. Retaining the dependence on weathering forcing in the LW model but assuming $r_{N:P,Fix} = r_{N:P}$ gives:

$$\frac{NO_3}{PO_4} = r_{N:P} \left(1 + \frac{r_{C:P} k_P}{C_0 W^{\frac{1}{2}}} (4.025 - 3.025W) \right)^{-1} \quad (39)$$

A general increase in weathering forcing (W) toward the present, due to biotic colonisation of the land surface would have tended to increase deep ocean N:P (Fig. 8), bringing it closer to the N:P of the phytoplankton. The increase in deep ocean N:P occurs through a proportionally greater increase in NO_3 than PO_4. The reason that NO_3 drops more under decreased W than PO_4 is that O_2 drops and anoxia increases

(Eqs. 16–17), and this both increases denitrification, lowering NO_3, and encourages Fe-P recycling from sediments, counteracting the decline in P input to the ocean.

3.7 Combined effects

We have predicted that over the past ~1000 Myr, a decline in the N:P Redfield ratio and an increase in weathering forcing would have had counteracting effects on the deep ocean N:P ratio, the former tending to decrease it, the latter to increase it. However, their effects are mediated by different nutrients. A declining N:P Redfield ratio with relatively constant C:N tends primarily to increase PO_4, whereas an increase in weathering tends primarily to increase NO_3. The combined effect (given by Eq. 39) is rather complex, so let us consider an illustrative case: ~1000 Myr ago, we suggest $W=0.5$, and estimate C:N:P=200:29:1 from averaging the values for Prasinophyceae and Chlorophyceae in Table 3 (Quigg et al., 2003). The predicted ocean composition is $NO_3 = 23.2 \, \mu\text{mol kg}^{-1}$, $PO_4 = 1.47 \, \mu\text{mol kg}^{-1}$, and deep ocean N:P=15.7. The lower NO_3 relative to the present day is due entirely to the lower weathering rates and the lower PO_4 is due primarily to the estimated higher C:P of the phytoplankton (compare the result with the top entries in Table 3).

4 Discussion

As Redfield recognised, phytoplankton C:N:P=106:16:1 simply represents an average of the present phytoplankton community, there is as yet no evidence that it is optimal, and C:N:P is now known to vary with growth conditions, among species, and (probably) over evolutionary time. We find that the N:P ratio that triggers N_2-fixation sets the N:P ratio of the deep ocean (referring here to the average concentrations of N and P, not the proportions in which they are remineralised). Hence deep ocean N:P would be insensitive to changes in the N:P Redfield ratio of sinking material if there were no corresponding changes in the N:P threshold that triggers N_2-fixation. However, in reality all three N:P ratios are coupled: The N:P requirement of non-fixing phytoplankton determines the N:P threshold for N_2-fixation, and this in turn influences deep ocean N:P. Furthermore, N_2-fixation can be limited by Fe, temperature, light or other factors, such that N_2-fixers are restricted to a modest fraction of the surface ocean, but they can still maintain deep ocean N:P relatively close to the N:P of non-fixing phytoplankton.

An additional mechanism not modelled herein is that phosphorite formation and consequent P removal from the ocean can be associated with fixed N removal due to denitrification (Piper and Codispoti, 1975; Schulz and Schulz, 2005). Qualitatively this acts in the right direction to further stabilise the deep ocean N:P ratio, although its effect will clearly depend on the (as yet unknown) proportions in which N and P are

removed. However, it may not be quantitatively important because phosphorite formation in upwelling zones is a small part of the global sink for P, and the associated denitrification is probably only a small part of the global sink for N.

Our conclusions regarding deep ocean N:P are robust to uncertainties in the nutrient uptake parameters P_H and P_N (Cullen, 1999). Our simple approach of restricting N_2-fixers to a decreasing fraction of the surface ocean may be reasonable for both temperature and light controls which vary inversely with latitude. However, it is not necessarily a good model for Fe-limitation and it would be interesting instead to limit the total biomass of N_2-fixers, or to include an Fe cycle in the model. Our results with the extended TT model may also be sensitive to the formulation of competitive dynamics, in particular, allowing the competitive disadvantage for N_2-fixers to be set by a lower maximum growth rate on P. In the real ocean, competition between N_2-fixers and non-fixers occurs under low nutrient conditions, for which the optimal N:P ratio may be very high (Klausmeier et al., 2004). Under such conditions, N_2-fixers, with an essentially unlimited N supply, may be able to synthesize more nutrient acquisition proteins and hence gain a competitive advantage (C. M. Moore, personal communication).

The models we use assume a tight coupling between the supply and assimilation of N and P, which is not observed on annual timescales in some areas of the world ocean, notably High Nutrient Low Chlorophyll (HNLC) regions. However, if iron and/or light are the alternative limiting factors of primary productivity in such regions (e.g. the Southern Ocean) then they are unlikely to support N_2-fixers anyway, and the model experiment is like the ones we show where N_2-fixers are restricted to a fraction of the surface ocean.

We have restricted our analysis to times when the deep ocean was well oxygenated. In the anoxic world of the Archean, prior to $\sim$2400 Ma, iron would have been more abundant, removing one limiting factor on N_2-fixation, and N would have been in the form of ammonium (Falkowski, 1997). With the rise of atmospheric O_2 in the Great Oxidation Event $\sim$2400 Ma, nitrification and subsequent denitrification would have removed fixed N from the ocean, and a period with very low deep ocean N:P has been predicted (Fennel et al., 2005). Once the ocean became fully oxygenated, nitrate would have built up and deep ocean N:P is predicted to have risen to values consistent with the present study (Fennel et al., 2005). However, the deep ocean may have remained anoxic and become sulphidic for much of the Proterozoic (Canfield, 1998). Under these conditions, trace metals including Fe and Mo would have been scarcer than they were in the Archean, potentially limiting both N_2-fixation and denitrification (Anbar and Knoll, 2002). The full oxygenation of the deep ocean may not have occurred until a second significant rise in atmospheric O_2 during the Neoproterozoic (Canfield, 1998; Lenton and Watson, 2004).

4.1 Changes in deep ocean N:P since the Neoproterozoic

The weathering flux of phosphorus to the ocean is thought to have increased with the biological colonisation of the land surface over the past 1000 Myr (Lenton and Watson, 2004). Although this would have had some effect on ocean PO_4, its dominant effect is predicted to have been an increase in ocean NO_3, caused by increasing atmospheric O_2 and consequently suppressing denitrification. Thus, a reduction in phosphorus weathering alone $\sim$1000 Ma would have tended to reduce the deep ocean N:P ratio (Fig. 8).

Our model of the effects of changes in weathering is quite simplistic. The scavenging of P by iron oxides in an oxygenated ocean may be more effective than modelled. Also, the organic C/P burial ratio may increase with anoxia (Van Cappellen and Ingall, 1996; Lenton and Watson, 2000). Both processes provide negative feedback on changes in atmospheric O_2. Including the latter process in the LW model tends to maintain higher O_2 and lower PO_4 under reductions in weathering, but does not alter the NO_3 prediction (Lenton and Watson, 2000). Consequently, the deep ocean N:P ratio tends to drop less under a reduction in weathering, but it still drops.

In contrast, members of phytoplankton groups that were present $\sim$1000 Ma have higher N:P and C:P than today's average Redfield ratios (Quigg et al., 2003). Hence they do not have the composition expected if they had simply adapted to the ocean conditions predicted for the time they evolved. Instead, they are predicted to have altered those conditions: The higher N:P and C:P Redfield ratios $\sim$1000 Ma would have tended to decrease PO_4 and hence increase the deep ocean N:P ratio (Table 3).

Thus estimated changes in weathering and in phytoplankton composition over the past $\sim$1000 Myr are predicted to have had counteracting effects on the deep ocean N:P ratio. These effects could fortuitously have cancelled at times, thus maintaining a similar deep ocean N:P ratio to today (Sect. 3.7), but perfect or sustained cancelation are inherently improbable.

Our inferences here are necessarily speculative, because of a shortage of direct proxies for NO_3, PO_4 and hence the deep ocean N:P ratio. The lower PO_4 predicted $\sim$1000 Ma is consistent with much lower PO_4 in the early Proterozoic 1900 Ma, followed by a rise in PO_4 due to less removal on iron oxides (Bjerrum and Canfield, 2002). In response to the proposed increase in weathering over the past 1000 Myr, the LW model predicts proportional increases in total P and organic C burial. The P burial record only extends as far back as the oldest ocean floor ($\approx$160 Myr). However, changes in the $\delta^{13}C$ records of carbonates and organic carbon during the Neoproterozoic have been used to infer an increase in the fraction of total carbon burial that occurs in organic form (Lenton and Watson, 2004). During the Phanerozoic, from the Devonian onwards, there is a further inferred increase in organic C burial and atmospheric O_2, also supported by a

predominance of rock types that are rich in organic carbon, and associated with rooted vascular plants colonizing the land surface (Lenton, 2001). There is clearly scope for further work testing the predictions of our hypothesis against the paleo record, potentially using the COPSE model (Bergman et al., 2004), which embeds the LW model.

Since the Neoproterozoic, there have been a few intervals, termed Oceanic Anoxic Events (OAEs), in which widespread anoxia returned to the deep ocean. During OAEs, denitrification and anammox would be greatly increased, tending to lower NO_3 and the deep ocean N:P ratio, and provoke a counter-balancing flux of N_2-fixation (Kuypers et al., 2004). The LW model has been adapted to study OAEs (Handoh and Lenton, 2003) and the predicted decline in the deep ocean N:P ratio during them is modest ($\approx$20%), with the OAEs characterised by high levels of both PO_4 and NO_3 maintaining high productivity and hence anoxia. However, other causal scenarios for the OAEs are popular, particularly reduced ocean ventilation, and may have different consequences for deep ocean N:P. Also, a different model (without a full O_2 cycle) finds a dramatic decrease of the deep ocean N:P ratio with the onset of widespread anoxia (Wallmann, 2003). Hence our conclusions may not apply to OAEs.

4.2 Co-evolution?

We have extended Redfield's (1958) argument for the present ocean by adding an evolutionary time dimension, suggesting that over the last $\sim$1000 Myr, the composition of the marine environment has been altered by evolutionary changes in the composition of marine organisms, and by the biological colonisation of the land surface. This (and the modelling herein) describes a one-way interaction; biotic factors altering abiotic factors. However, phytoplankton composition may also adapt (within limits) to the composition of the ocean, which introduces the reverse interaction; abiotic factors shaping biotic factors. We have not modelled this here, but we acknowledge that it could qualitatively alter the results. Closing the loop between changes in biotic and abiotic factors would allow them to "co-evolve". One suggestion is that the predicted increase in NO_3 and PO_4 would result in more production being carried out under higher nutrient regimes, and therefore select for phytoplankton with lower N:P ratios (C. M. Moore, personal communication). This provides a potential mechanism for "closing the loop" and explaining the lower N:P ratio within more recently evolved phyla. To examine such co-evolution we suggest that a model of competing populations with differing stoichiometry could be nested within a model of ocean composition subject to external drivers. The populations themselves could exhibit phenotypic plasticity in their stoichiometry as their resource allocation varies in response to prevailing conditions (Klausmeier et al., 2004). This is a topic for future work.

5 Conclusion

Despite potential changes in phytoplankton stoichiometry, weathering supply of phosphorus to the ocean, and widespread Fe, temperature and/or light limitation of N_2-fixation, we find that Redfield's mechanism can still regulate deep ocean N:P somewhat below the proportions that trigger N_2-fixation in those areas of the ocean where N_2-fixers are P-limited and suppressed by N addition. Furthermore, deep ocean N:P is unlikely to have varied by more than a factor of two in either direction whilst the deep oceans have been well oxygenated (i.e. since the Neoproterozoic, with the possible exception of Oceanic Anoxic Events). We extend Redfield's mechanism to suggest that within these bounds, the evolution of phytoplankton composition and the biological colonisation of the land surface could have driven long-term changes in ocean composition. Biotic stoichiometric controls on ocean composition could have operated much faster than phosphorus weathering controls, because they do not involve changes in atmospheric O_2.

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