

Biotic enhancement of weathering, atmospheric oxygen and carbon dioxide in the Neoproterozoic

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[1] It has been suggested that biological colonization of the land surface began in the Neoproterozoic 1000–544 million years ago (Ma). We hypothesize that this colonization involved selective weathering of P from rocks, as well as an amplification of overall weathering rates. We show that two recent models, despite differences in the feedback mechanisms represented, predict that an increase in the weathering flux of P to the ocean would have caused a rise in atmospheric O₂ in the Neoproterozoic. This in turn may have provided a necessary condition for the evolution of animals with hard skeletons seen in the ‘Cambrian explosion’. Increased weathering of silicate rocks would also have caused a decline in atmospheric CO₂, which could have been a causal factor in the Neoproterozoic glaciations. *INDEX TERMS*: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0330 Atmospheric Composition and Structure: Geochemical cycles; 1886 Hydrology: Weathering (1625); 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 9619 Information Related to Geologic Time: Precambrian. *Citation*: Lenton, T. M., and A. J. Watson (2004), Biotic enhancement of weathering, atmospheric oxygen and carbon dioxide in the Neoproterozoic, *Geophys. Res. Lett.*, 31, L05202, doi:10.1029/2003GL018802.

1. Introduction

[2] The Neoproterozoic was a time of severe glaciations and a major transition from microscopic to macroscopic life forms. The evolution of large metazoans depended on sufficient atmospheric O₂ and it has long been suggested that a rise in atmospheric O₂ triggered their evolution [Nursall, 1959]. The first fossils of large metazoan life are the soft-bodied Ediacara, appearing at ~570 Ma, some of which required an estimated O₂ > 0.01–0.03 PAL (Present Atmospheric Level) [Runnegar, 1991]. The animals of the Cambrian explosion beginning ~544 Ma had hard skeletons and a consequently higher requirement for O₂ > 0.1 PAL [Rhoads and Morse, 1971].

[3] Free oxygen reached 0.0012 < O₂ < 0.043 PAL in the great oxidation 2250 Ma [Yang and Holland, 2003] and has been > 0.01 PAL since then [Rye and Holland, 1998]. A secondary oxidation is thought to have occurred in the Neoproterozoic, in which atmospheric O₂ exceeded the 0.05 PAL required by the sulphide oxidizer *Beggiatoa* 1.05–0.64 Ga [Canfield and Teske, 1996]. Neoproterozoic

δ¹³C values of carbonates fluctuate with a huge range (~20‰) but are generally strongly positive in non-glacial periods, indicating a high ratio of organic carbon to carbonate burial [Walter *et al.*, 2000]. Sulfur isotope ratios also indicate a tendency towards a greater reducing flux into the sediments during the early Neoproterozoic [Canfield and Teske, 1996]. The ⁸⁷Sr/⁸⁶Sr ratio of carbonates increased markedly through the late Neoproterozoic, consistent with an increase in overall weathering rate [Walter *et al.*, 2000]. Together, δ¹³C and ⁸⁷Sr/⁸⁶Sr records suggest that the organic carbon burial flux peaked in the late Neoproterozoic [Derry *et al.*, 1992].

[4] Here we develop the hypothesis [Heckman *et al.*, 2001] that a Neoproterozoic rise in atmospheric O₂ was driven by the biological colonization of the land surface. Although there is no unequivocal fossil evidence of photosynthetic land life in the Precambrian, there are possible microfossils and indications from carbon isotopes of highly productive, photosynthesizing microbial communities on land after 1200 Ma [Horodyski and Knauth, 1994]. Protein sequence analyses suggest that green algae and the major lineages of fungi had diverged by ~1000 Ma and this allows for the possibility that lichens (from fungal symbiosis with either cyanobacteria or green algae) could have evolved thereafter [Heckman *et al.*, 2001].

2. Selective Weathering of Phosphorus

[5] We hypothesize that the colonizers of the land surface evolved to amplify weathering of essential elements from continental rocks, and in particular to selectively weather P minerals relative to bulk silicate minerals. Selection would have been strongest for elements where demand most outstripped supply. P is an extreme example given its high requirement in biochemistry, low concentration in rain or aerosol particles and the lack of an atmospheric gaseous source. Even now, the P cycling ratio (the ratio of the flux through photosynthesis to the input flux from weathering) in terrestrial ecosystems is ~50, indicating that the source from weathering is far from meeting photosynthetic requirements [Volk, 1998].

[6] Sedimentary and igneous calcium phosphate minerals (e.g., apatite) are the largest P source [Guidry and Mackenzie, 2000] and being alkaline they dissolve more readily in acid and wet conditions. Selective weathering of P is observed in a range of organisms that may have appeared in the Neoproterozoic. Micro-organisms selectively colonise and weather P mineral inclusions in feldspars (silicate rocks)

[Rogers *et al.*, 1998]. Microbial communities dominated by cyanobacteria that live at a depth of 0.5–3.0mm inside limestone enrich this endolith zone in P [Ferris and Lawson, 1997]. Soil bacteria and lichenous fungi secrete a range of organic acids, which dissolve rock phosphate [Landeweert *et al.*, 2001].

3. Phosphate and Oxygen Budgets

[7] Selective weathering of P would have led to increased biological availability of P and P weathering flux to the ocean. We explore the possible effects in terms of the budgets for the oceanic phosphate concentration $[P]$ (mol/l) and the atmospheric oxygen reservoir O_2 (mol). For steady state, when averaged over times $>10^7$ yr:

$$dO_2/dt = F_{c,org} - F_{s,O_2} - F_{v,O_2} \approx 0. \quad (1)$$

Where $F_{c,org}$ (molC/yr) is the small fraction of biologically derived reduced carbon that escapes oxidation and is buried in sediments (assuming a 1:1 relationship between C buried and O_2 liberated), F_{s,O_2} and F_{v,O_2} (mol O_2 /yr) are the oxygen demands to oxidize reduced components of rock weathered on the continents, and volcanic gases respectively. The volcanic term today is $\sim 25\%$ of the weathering term [Lasaga and Ohmoto, 2002]. Oxidation and reduction of sulfur compounds also make $\sim 10\%$, contributions to the oxygen balance, ignored here. A similar balance applies to phosphate concentration in the ocean, when averaged over $\sim 10^5$ yr:

$$V d[P]/dt = P_{priver} - F_{psed} \approx 0. \quad (2)$$

Where V is ocean volume (l), F_{priver} (molP/yr) is the flux of biogeochemically available P derived from rock weathering and supplied by rivers and F_{psed} (molP/yr) is the total biogeochemically available P flux to sediments. If the flux due to weathering increases, the P concentration in the ocean will increase and, since P is an important limiting nutrient, this would be expected to lead to greater ocean productivity and biological flux to sediments. This in turn results in greater burial fluxes of P and organic C, restoring the P balance, while also driving up O_2 .

[8] The P flux due to weathering can be written $F_{priver} = F_w r_p \varepsilon$, where F_w (mol/yr) is an overall rate of weathering of rock, r_p (molP/mol) the mole fraction of P in the rock and ε the fraction of this which is made biogeochemically available. It is estimated that, pre-agriculture, between 25 and 60% of the total flux of P to the oceans was biogeochemically available [Howarth *et al.*, 1996]. We hypothesize that before the evolution of selective weathering for P, this proportion was substantially lower. The oxygen used in weathering rock can be written $F_w r_{ox}$, where r_{ox} (mol O_2 /mol) is the oxygen demand per mole of weathered rock. If we introduce $r_{c/p}$ (molC/molP) as the ratio of the organic carbon burial to biogeochemically active P burial flux ($=F_{c,org}/F_{psed}$), and apply $F_{priver} = F_{psed}$, then:

$$dO_2/dt = F_w r_p \varepsilon r_{c/p} - F_w r_{ox} - F_{v,O_2} \approx 0. \quad (3)$$

[9] Potentially both F_w and ε may be increased by the emerging land biota as they evolve to more efficiently

weather rock and extract P. If ε increases with other variables constant, O_2 will clearly increase, and balance must be restored by negative feedbacks. The feedbacks stabilizing atmospheric O_2 have been the subject of many studies. Most recent authors favour mechanisms that result in more C burial per mole of P (an increase in $r_{c/p}$) when O_2 concentrations decline. These include increased P availability due to recycling from iron-sorbed P or organic P in anoxic sediments [Colman and Holland, 2000; Van Cappellen and Ingall, 1996].

[10] In such mechanisms, deep-ocean O_2 concentration is a controlling variable, and this is a function not only of atmospheric O_2 but also the amount of biological production that sinks into the deep sea. Increasing the flux of P to the oceans will tend to increase production. This will tend to decrease bottom water oxygen concentrations and increase $r_{c/p}$, enhancing the initial imbalance in the O_2 source and sink, and requiring a larger final increase in atmospheric O_2 to restore steady state. For this reason, increases in overall weathering rate F_w are expected to have a greater effect on the O_2 source than the O_2 sink and thus force higher O_2 at steady state.

4. Model Analyses

[11] To be more quantitative, we solve equations based on two recent models, representing substantially different views of the oxygen cycle, [Lenton and Watson, 2000b] (hereinafter LW), and [Lasaga and Ohmoto, 2002] (hereinafter LO).

[12] LW define an ‘‘anoxic fraction’’ A that represents the fraction of the ocean where low O_2 concentrations exist in the water column:

$$A = 1 - k_a O_2' (N')^{-1}. \quad (4)$$

The primed notation is used throughout this paper to indicate a normalized variable, equal to unity under modern-day pre-industrial conditions. Here N is marine new (biological) production. LW include a nitrogen cycle and the more limiting nutrient out of NO_3 or PO_4 determines N . However, this choice does not affect the steady state solution for O_2 [Lenton and Watson, 2000a]. Hence we simplify here by assuming N is proportional to $[P]$. The constant $k_a (= 0.86)$ is specified using present-day observations. Organic, iron-sorbed and calcium-bound P fluxes to sediments are treated separately, with the organic and calcium-bound fractions varying as $[P]^2$ and the iron-sorbed flux proportional to $(1-A)$. Here we add the ability to vary P weathering efficiency, independently of other weathering, by modifying LW equation 8 to:

$$F_{priver} = k_5 F_w' \varepsilon'. \quad (5)$$

Where $k_5 (= 3.6 \times 10^{10}$ molP/yr) is a constant. We then solve analytically the steady states of LW equations 12 and 14 for O_2 as a function of normalized P weathering efficiency (ε') and normalized total weathering rate (F_w'). In the LW M1 model, in which the only feedback on O_2 is recycling of iron-sorbed P from anoxic sediments,

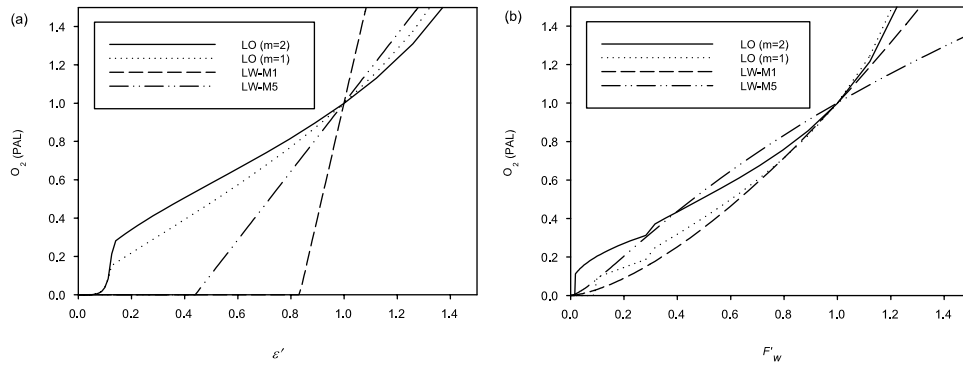


Figure 1. Steady state solutions for the dependence of the atmospheric oxygen (O_2) reservoir on rock weathering parameters, for different models: (a) O_2 versus ϵ' , the efficiency with which P in rocks is made available to the biota, normalized for the pre-industrial modern day. (b) O_2 versus F'_w , the normalized overall weathering rate. Results are shown for two variants of the LW model [Lenton and Watson, 2000b]: (M1) O_2 is stabilized only by anoxic recycling of iron-sorbed P, (M5) O_2 is stabilized by anoxic recycling of both organic P and iron-sorbed P. Results are also shown for the LO model [Lasaga and Ohmoto, 2002], modified as described in the text, for two different powers of sediment P flux dependence on phosphate concentration. Discontinuities in the slope of the LO solutions at low O_2 are due to the change-over from their oxygenated to anoxic equations.

inserting values for constants given in Table 3 of LW, we obtain:

$$O'_2 = F_w'^{1.5}(6\epsilon' - 5). \quad (6)$$

For the LW M5 model, in which organic P is also recycled more efficiently under anoxic conditions, we obtain:

$$O'_2 = F_w'^{1.5}(6\epsilon' - 2.65)(1 + 2.35F_w')^{-1}. \quad (7)$$

Both LW models have relatively weak feedback on declining O_2 . In contrast, LO argue for a strong inverse dependence of organic carbon burial (the O_2 source) on dissolved oxygen concentration, $[O_2]$ (mol/l). LO also assume that the oxygen demand for oxidative weathering (r_{ox}) is not constant but increases with rising atmospheric O_2 , providing further negative feedback on O_2 .

[13] LO use a well-known box model of ocean circulation [Sarmiento and Toggweiler, 1984] that yields for oxygen concentration in the deep ocean:

$$[O_2]_d = [O_2]_h - r_{O_2/P}([P]_d - [P]_h). \quad (8)$$

Here the subscripts d and h refer to concentrations in deep water and high-latitude surface water respectively, and $r_{O_2/P}$ ($= 172 \text{ molO}_2/\text{molP}$) is a Redfield ratio of O_2 consumption to P production. The equations developed by LO assume implicitly that oceanic P is constant at today's values. We add a simple P cycle by expanding equation (2) for total phosphate concentration $[P]$ in the ocean to:

$$V d[P]/dt = k_{priver}[F_w'\epsilon' - ([P]')^m]. \quad (9)$$

Where k_{priver} is a constant. Marine new production is assumed to be proportional to $[P]$ as with the LW model. Relating this to the Sarmiento and Toggweiler [1984] model, we assume $[P]_d$ scales with total $[P]$, because the upwelling flux of $[P]_d$ determines the sinking flux of

organic matter from the surface ocean (new production). The P burial flux is written as a power law of this sinking flux and hence $[P]$. Thus increases in $[P]$ generate larger sediment fluxes and lead to greater loss of P (i.e., $m > 0$). The value of m is however uncertain, and might alter with time. Steady-state of equation (9) then requires:

$$[P]' = (F_w'\epsilon')^{1/m}. \quad (10)$$

In the LO model, the organic carbon burial flux is assumed to depend linearly on the P weathering flux, $F_w'\epsilon'$ in our treatment. LO assume dependencies also on continental area and atmospheric CO_2 , which we hold constant. Organic carbon burial also depends on sedimentation rate, which LO assume proportional to soil erosion rate. We substitute overall weathering flux F_w' for soil erosion rate in the LO model. The O_2 equation is then (1) with, including constants from LO Table 1:

$$F_{c,org} = 1 \times 10^{13} F_w'\epsilon' \xi (0.003)^{-1} F_w'^m \quad (11)$$

$$F_{s,O_2} = 7.5 \times 10^{12} F_w' O_2^{0.5} (0.162 F_w' + 0.838 O_2^{0.5})^{-1} \quad (12)$$

$$F_{v,O_2} = 2.5 \times 10^{12} \quad (13)$$

In expression (11) for $F_{c,org}$, under oxic conditions ($[O_2]_d > 15 \mu\text{M}$) ($M = \text{mol/l}$):

$$\zeta = (0.003)^{f/f^0}, n = 1.26, \quad (14)$$

$$f = [O_2]_d ([O_2]_d + 20)^{-1}, f^0 = 0.894. \quad (15)$$

We assume that $[P]_h$ as well as $[P]_d$ scales with total $[P]$ and hence equation (8) becomes:

$$[O_2]_d = 340O'_2 - 172[P]'\mu\text{M}. \quad (16)$$

Under near-anoxic conditions ($[O_2]_d < 15 \mu\text{M}$):

$$\zeta = 0.021, \quad n = 0.3 \quad (17)$$

The steady state of the O_2 equation (1) and P equation (10) were solved numerically for O_2 as a function of ϵ' or F'_w with constant $m = 1$ or 2.

5. Results and Discussion

[14] Results for the LW and LO models are shown in Figure 1. Whereas LO conclude from their model that atmospheric O_2 has probably been above 0.6 PAL since the Archean, we find that this extreme stability is in part a result of their assumption of an unchanging P supply and P concentration. The revised model with a simple P balance admits much lower O_2 concentrations. High $C_{\text{organic}}/P_{\text{reactive}}$ burial ratios are predicted under near-anoxic conditions, e.g., 1944 for varying ϵ with $m = 1$ or 2, due to LO's assumption of a 7-fold increase in the organic carbon burial flux from present to near-anoxic conditions. Whilst $(C/P)_{\text{organic}}$ burial ratios up to 4500 have been observed, $C_{\text{organic}}/P_{\text{reactive}}$ only reaches 400 [Anderson et al., 2001].

[15] Both models predict that O_2 declines if ϵ' or F'_w are reduced, and O_2 goes to zero if ϵ' or F'_w are sufficiently low. The models agree therefore that the evolution of more selective weathering for P in the Neoproterozoic, and/or a substantial increase in overall weathering rate should result in a marked rise in O_2 . However, the shape of the curves depends on the models, and in particular how much negative feedback is assumed, so that for example a decrease of a factor of two in ϵ from the modern value gives results that range from $\sim 40\%$ decrease in O_2 to complete disappearance of O_2 . An increase in overall weathering rate (F_w) could not be sustained indefinitely, because over periods of 10^8 yr the supply of rock is limited by tectonic uplift. However, a change in P weathering efficiency (ϵ) is not subject to such a limit.

[16] A biologically driven increase in overall weathering rate would have had a second major effect on the atmosphere. More intense silicate weathering would lead to a fall in atmospheric CO_2 concentration, and may have contributed to the glacial climates of the Neoproterozoic. As CO_2 and temperature declined, this would have suppressed silicate-weathering rate until a new steady state was achieved. Declining temperature would have tended to suppress the P weathering flux [Guidry and Mackenzie, 2000], thus counteracting the effect of biologically-driven increases in overall weathering rate (F_w) and reducing or eliminating their impact on atmospheric O_2 . However, a change in P weathering efficiency (ϵ) is not subject to such limitation.

6. Analogy with Later Events

[17] The evolution of vascular plants is thought to have enhanced silicate weathering and organic carbon burial, leading to lower CO_2 and higher O_2 concentrations, peaking in the Permo-Carboniferous [Bernier, 1994; Bernier et al., 2000]. It seems unlikely however that this was the first

period when continental weathering was influenced by the land biota, since we know that the land was colonized much earlier [Edwards et al., 1995]. The hypothesis that significant land colonization occurred in the Neoproterozoic has the attraction that the predicted changes in CO_2 and O_2 can help explain the cold climate of the time and provide a necessary condition for the explosive diversification of fossil forms in the Cambrian.

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