

# 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 O<sub>2</sub> 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 CO<sub>2</sub>, 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.

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## 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 O<sub>2</sub> and it has long been suggested that a rise in atmospheric O<sub>2</sub> 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 O<sub>2</sub> > 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 O<sub>2</sub> > 0.1 PAL [Rhoads and Morse, 1971].

[3] Free oxygen reached 0.0012 < O<sub>2</sub> < 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 O<sub>2</sub> exceeded the 0.05 PAL required by the sulphide oxidizer *Beggiatoa* 1.05–0.64 Ga [Canfield and Teske, 1996]. Neoproterozoic

δ<sup>13</sup>C 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 <sup>87</sup>Sr/<sup>86</sup>Sr ratio of carbonates increased markedly through the late Neoproterozoic, consistent with an increase in overall weathering rate [Walter *et al.*, 2000]. Together, δ<sup>13</sup>C and <sup>87</sup>Sr/<sup>86</sup>Sr 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 O<sub>2</sub> 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) 99

[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  $\varepsilon$  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  $\varepsilon$  may be increased by the emerging land biota as they evolve to more efficiently

weather rock and extract P. If  $\varepsilon$  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).

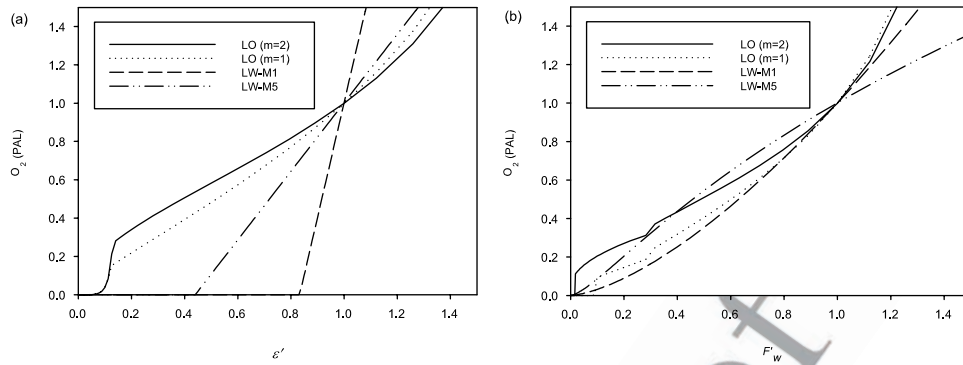
[12] LW define an ‘‘anoxic fraction’’  $A$  that represents the fraction of the ocean where low  $O_2$  concentrations exist in the water column:

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

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 ( $\varepsilon'$ ) 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  $\epsilon'$ , 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.

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

$$O_2 = F_w^{1.5}(6\epsilon' - 5). \quad (6)$$

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

$$O_2 = F_w^{1.5}(6\epsilon' - 2.65)(1 + 2.35F_w')^{-1}. \quad (7)$$

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

223 [13] LO use a well-known box model of ocean circulation  
224 [Sarmiento and Toggweiler, 1984] that yields for oxygen  
225 concentration in the deep ocean:

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

227 Here the subscripts  $d$  and  $h$  refer to concentrations in deep  
228 water and high-latitude surface water respectively, and  $r_{O_2/P}$   
229 ( $= 172 \text{ molO}_2/\text{molP}$ ) is a Redfield ratio of  $O_2$  consumption  
230 to P production. The equations developed by LO assume  
231 implicitly that oceanic P is constant at today's values. We  
232 add a simple P cycle by expanding equation (2) for total  
233 phosphate concentration  $[P]$  in the ocean to:

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

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

organic matter from the surface ocean (new production). 240  
The P burial flux is written as a power law of this sinking 241  
flux and hence  $[P]$ . Thus increases in  $[P]$  generate larger 242  
sediment fluxes and lead to greater loss of P (i.e.,  $m > 0$ ). 243  
The value of  $m$  is however uncertain, and might alter with 244  
time. Steady-state of equation (9) then requires: 245

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

In the LO model, the organic carbon burial flux is assumed 247  
to depend linearly on the P weathering flux,  $F'_w\epsilon'$  in our 248  
treatment. LO assume dependencies also on continental area 249  
and atmospheric  $CO_2$ , which we hold constant. Organic 250  
carbon burial also depends on sedimentation rate, which LO 251  
assume proportional to soil erosion rate. We substitute 252  
overall weathering flux  $F'_w$  for soil erosion rate in the LO 253  
model. The  $O_2$  equation is then (1) with, including constants 254  
from LO Table 1: 255

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

$$F_{s,O_2} = 7.5 \times 10^{12} F_w' O_2^{0.5} (0.162 F_w' + 0.8380 O_2^{0.5}) \quad (12)$$

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

In expression (11) for  $F_{c,org}$ , under oxic conditions ( $[O_2]_d > 261$   
15  $\mu\text{M}$ ) ( $M = \text{mol/l}$ ): 262

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

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

We assume that  $[P]_h$  as well as  $[P]_d$  scales with total  $[P]$  and 266  
hence equation (8) becomes: 267

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

268 Under near-anoxic conditions ( $o_d < 15 \mu\text{M}$ ):

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

271 The steady state of the  $\text{O}_2$  equation (1) and P equation (10)  
272 were solved numerically for  $\text{O}_2$  as a function of  $\epsilon'$  or  $F'_w$  with  
273 constant  $m = 1$  or  $2$ .

## 274 5. Results and Discussion

275 [14] Results for the LW and LO models are shown in  
276 Figure 1. Whereas LO conclude from their model that  
277 atmospheric  $\text{O}_2$  has probably been above 0.6 PAL since  
278 the Archean, we find that this extreme stability is in part  
279 a result of their assumption of an unchanging P supply  
280 and P concentration. The revised model with a simple P  
281 balance admits much lower  $\text{O}_2$  concentrations. High  
282  $C_{\text{organic}}/P_{\text{reactive}}$  burial ratios are predicted under near-  
283 anoxic conditions, e.g., 1944 for varying  $\epsilon$  with  $m = 1$   
284 or  $2$ , due to LO's assumption of a 7-fold increase in the  
285 organic carbon burial flux from present to near-anoxic  
286 conditions. Whilst  $(C/P)_{\text{organic}}$  burial ratios up to 4500  
287 have been observed,  $C_{\text{organic}}/P_{\text{reactive}}$  only reaches 400  
288 [Anderson et al., 2001].

289 [15] Both models predict that  $\text{O}_2$  declines if  $\epsilon'$  or  $F'_w$  are  
290 reduced, and  $\text{O}_2$  goes to zero if  $\epsilon'$  or  $F'_w$  are sufficiently low.  
291 The models agree therefore that the evolution of more  
292 selective weathering for P in the Neoproterozoic, and/or a  
293 substantial increase in overall weathering rate should result  
294 in a marked rise in  $\text{O}_2$ . However, the shape of the curves  
295 depends on the models, and in particular how much nega-  
296 tive feedback is assumed, so that for example a decrease of  
297 a factor of two in  $\epsilon$  from the modern value gives results that  
298 range from  $\sim 40\%$  decrease in  $\text{O}_2$  to complete disappearance  
299 of  $\text{O}_2$ . An increase in overall weathering rate ( $F_w$ ) could not  
300 be sustained indefinitely, because over periods of  $10^8$  yr the  
301 supply of rock is limited by tectonic uplift. However, a  
302 change in P weathering efficiency ( $\epsilon$ ) is not subject to such a  
303 limit.

304 [16] A biologically driven increase in overall weathering  
305 rate would have had a second major effect on the atmo-  
306 sphere. More intense silicate weathering would lead to a fall  
307 in atmospheric  $\text{CO}_2$  concentration, and may have contrib-  
308 uted to the glacial climates of the Neoproterozoic. As  $\text{CO}_2$   
309 and temperature declined, this would have suppressed  
310 silicate-weathering rate until a new steady state was  
311 achieved. Declining temperature would have tended to  
312 suppress the P weathering flux [Guidry and Mackenzie,  
313 2000], thus counteracting the effect of biologically-driven  
314 increases in overall weathering rate ( $F_w$ ) and reducing or  
315 eliminating their impact on atmospheric  $\text{O}_2$ . However, a  
316 change in P weathering efficiency ( $\epsilon$ ) is not subject to such  
317 limitation.

## 318 6. Analogy with Later Events

319 [17] The evolution of vascular plants is thought to have  
320 enhanced silicate weathering and organic carbon burial,  
321 leading to lower  $\text{CO}_2$  and higher  $\text{O}_2$  concentrations, peaking  
322 in the Permo-Carboniferous [Bernier, 1994; Bernier et al.,  
323 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 signifi-  
cant land colonization occurred in the Neoproterozoic has  
the attraction that the predicted changes in  $\text{CO}_2$  and  $\text{O}_2$  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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## References

- Anderson, L. D., et al. (2001), Carbon to phosphorus ratios in sediments:  
Implications for nutrient cycling, *Global Biogeochem. Cycles*, *15*, 65–  
79.
- Berner, R. A. (1994), Geocarb II: A revised model of atmospheric  $\text{CO}_2$  over  
Phanerozoic time, *Am. J. Sci.*, *294*, 56–91.
- Berner, R. A., et al. (2000), Isotope fractionation and atmospheric oxygen:  
Implications for Phanerozoic  $\text{O}_2$  evolution, *Science*, *287*, 1630–  
1633.
- Canfield, D. E., and A. Teske (1996), Late Proterozoic rise in atmospheric  
oxygen concentration inferred from phylogenetic and sulphur-isotope  
studies, *Nature*, *382*, 127–132.
- Colman, A. S., and H. D. Holland (2000), The global diagenetic flux of  
phosphorus from marine sediments to the oceans: Redox sensitivity and  
the control of atmospheric oxygen levels, in *Marine Authigenesis: From  
Global to Microbial*, edited by C. R. Glenn, J. Lucas, and L. Prévôt-  
Lucas, pp. 53–75, Soc. for Sediment. Geol., Tulsa, Okla.
- Dery, L. A., et al. (1992), Sedimentary cycling and environmental change  
in the Late Proterozoic: Evidence from stable and radiogenic isotopes,  
*Geochim. Cosmochim. Acta*, *56*, 1317–1329.
- Edwards, D., et al. (1995), Hepatic characters in the earliest land plants,  
*Nature*, *374*, 635–636.
- Ferris, F. G., and E. A. Lawson (1997), Ultrastructure and geochemistry of  
endolithic microorganisms in limestone of the Niagara escarpment, *Can.  
J. Microbiol.*, *43*, 211–219.
- Guidry, M. W., and F. T. Mackenzie (2000), Apatite weathering and the  
Phanerozoic phosphorus cycle, *Geology*, *28*, 631–634.
- Heckman, D. S., et al. (2001), Molecular evidence for the early colonization  
of land by fungi and plants, *Science*, *293*, 1129–1133.
- Horodyski, R. J., and L. P. Knauth (1994), Life on land in the Precambrian,  
*Science*, *263*, 494–498.
- Howarth, R. W., et al. (1996), Transport to, and processing of, P in near-  
shore and oceanic waters, in *SCOPE-54: Phosphorus in the Global  
Environment—Transfers, Cycles and Management*, edited by H. Tiessen,  
pp. 323–346, John Wiley, Hoboken, N. J.
- Landeweert, R., et al. (2001), Linking plants to rocks: Ectomycorrhizal  
fungi mobilize nutrients from minerals, *Trends Ecol. Evol.*, *16*, 248–  
254.
- Lasaga, A. C., and H. Ohmoto (2002), The oxygen geochemical  
cycle: Dynamics and stability, *Geochim. Cosmochim. Acta*, *66*,  
361–381.
- Lenton, T. M., and A. J. Watson (2000a), Redfield revisited: 1. Regulation  
of nitrate, phosphate, and oxygen in the ocean, *Global Biogeochem.  
Cycles*, *14*, 225–248.
- Lenton, T. M., and A. J. Watson (2000b), Redfield revisited: 2. What  
regulates the oxygen content of the atmosphere?, *Global Biogeochem.  
Cycles*, *14*, 249–268.
- Nursall, J. R. (1959), Oxygen as a prerequisite to the origin of the Metazoa,  
*Nature*, *183*, 1170–1172.
- Rhoads, D. C., and J. W. Morse (1971), Evolutionary and ecological sig-  
nificance of oxygen-deficient marine faunas, *Lethaia*, *4*, 413–428.
- Rogers, J. R., et al. (1998), Feldspars as a source of nutrients for micro-  
organisms, *Am. Mineral.*, *83*, 1532–1540.
- Runnegar, B. (1991), Precambrian oxygen levels estimated from the bio-  
chemistry and physiology of early eukaryotes, *Global Planet. Change*,  
*97*, 97–111.
- Rye, R., and H. D. Holland (1998), Paleosols and the evolution of atmo-  
spheric oxygen: A critical review, *Am. J. Sci.*, *298*, 621–672.
- Sarmiento, J. L., and J. R. Toggweiler (1984), A new model for the role  
of the oceans in determining atmospheric  $\text{PCO}_2$ , *Nature*, *308*, 621–  
624.

- 397 Van Cappellen, P., and E. D. Ingall (1996), Redox stabilization of the  
398 atmosphere and oceans by phosphorus-limited marine productivity,  
399 *Science*, 271, 493–496.
- 400 Volk, T. (1998), *Gaid's Body—Toward a Physiology of the Earth*, Coperni-  
401 cus, New York.
- 402 Walter, M. R., et al. (2000), Dating the 840–544 Ma Neoproterozoic inter-  
403 val by isotopes of strontium, carbon, and sulfur in seawater, and some  
404 interpretative models, *Precambrian Res.*, 100, 371–433.
- Yang, W. B., and H. D. Holland (2003), The Hekpoort paleosol profile in 405  
strata 1 at Gaborone, Botswana: Soil formation during the great oxidation 406  
event, *Am. J. Sci.*, 303, 187–220. 407
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