



Regulation of atmospheric oxygen during the Proterozoic



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ABSTRACT

Many studies suggest that oxygen has remained near modern levels throughout the Phanerozoic, but was much less abundant from the “Great Oxygenation Event” around 2.4 Ga until the late Neoproterozoic around 600 Ma (Kump, 2008). Using a simple model, we show that the maintenance of atmospheric pO_2 at $\sim 1\%$ of present atmospheric levels (PAL) is inconsistent with modern biogeochemical cycling of carbon, sulfur and iron unless new feedbacks are included. Low oxygen conditions are stable in our model if the flux of phosphorus to the oceans was greatly reduced during the Proterozoic. We propose a mechanism to reduce this flux through the scavenging of phosphate ions with an “iron trap” driven by greater surface mobility of ferrous iron in a low pO_2 world. Incorporating this feedback leads to two stable equilibria for atmospheric oxygen, the first quantitative hypothesis to explain both Proterozoic and Phanerozoic O_2 concentrations.

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1. Introduction

Atmospheric oxygen has passed through three broad plateaus in earth history (Kump, 2008). Mass-independent sulfur isotopes show that it was negligibly low during the Archean, rising abruptly around 2.4 Ga (Pavlov and Kasting, 2000). Paleosols (Rye and Holland, 1998), pyrite and uraninite grains (Holland, 1984), sulfur isotopes (Canfield and Teske, 1996), and widespread ferrous and euxinic basins (Poulton and Canfield, 2011) point to a moderately oxygenated Proterozoic, likely 1–10% PAL (Kump, 2008). Though pO_2 may have varied between these bounds through the Proterozoic, the appearance of large multicellular animals and large colonial algae supports a second rise in O_2 near the end of the Neoproterozoic (Anbar and Knoll, 2002), and the charcoal record requires at least 60% PAL since the Silurian (Scott and Glasspool, 2006). The two major oxidation events may have been complex oscillations in pO_2 (e.g. Anbar et al., 2007; Dahl et al., 2010), but the associated changes in the proxy record are abrupt compared to the length of the intervening periods. At hundreds of millions of years, this stability time scale is much greater than the residence times of redox-sensitive species, so the oxygen system must have been in several different steady states over geological history.

Much research has been devoted to the “Great Oxidation Event” of 2.4 Ga and the second oxidation in the terminal Proterozoic. These events have been attributed to any number of drivers. For the late Archean, these include abrupt overturning of a redox-stratified mantle (Kump et al., 2001), rapid hydrogen escape (Catling et al., 2001), or a change from more reducing submarine

volcanism to more oxidized subaerial outgassing (Kump and Barley, 2007); for the late Proterozoic, the evolution of biological ballast (Logan et al., 1995), more active clay formation (Kennedy et al., 2006), or a perturbation related to the Snowball glaciation (Hoffman and Schrag, 2002).

Unfortunately, it is difficult to evaluate these hypotheses given our incomplete understanding of redox dynamics. The result of a perturbation or a change in geochemical cycling is only meaningful in the context of a dynamical system, which dictates the steady state values of pO_2 and the feedbacks that maintain them. To understand the oxygenation events and any transient oscillations, it is therefore necessary to understand the mechanisms underlying the long periods of stability in the Archean, Proterozoic and Phanerozoic. Goldblatt et al. (2006), for example, have suggested a model for bistability around the Great Oxidation Event, based on Archean photochemistry. In this study we use a simple model of ocean-atmosphere electron cycling to explore the feedbacks that can produce a two-state redox system corresponding to the Proterozoic and Phanerozoic.

Previous work on redox dynamics has mostly focused on the stability of the Phanerozoic atmosphere. Some models for past O_2 levels avoid the need for explicit feedbacks by using constraints from carbon isotope variations in marine carbonate, assumed to represent fluctuations in the burial of organic carbon relative to calcium carbonate (Bernier, 2006). Other studies have explored the dynamical stability of the Phanerozoic using different negative feedbacks, particularly an oxygen-dependent weathering rate for reduced minerals (Kump and Garrels, 1986; Bernier and Canfield, 1989; Lasaga and Ohmoto, 2002; Bergman et al., 2004). Oxygen-dependent burial efficiencies for organic carbon and sulfide have also been proposed (Kump and Garrels, 1986;

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Berner and Canfield, 1989; Lasaga and Ohmoto, 2002). One study has investigated the stability of low-oxygen Proterozoic conditions (Fennel et al., 2005), but their model explicitly excluded the negative feedbacks known from the Phanerozoic work.

The series of feedbacks referenced above, when taken together, make it impossible to maintain very low pO_2 , as low O_2 leads to higher organic carbon burial and the inevitable build-up of oxygen. Stabilizing O_2 at both high Phanerozoic levels and low Proterozoic levels requires either a slowly evolving external forcing, or a new feedback, previously undescribed. Rather than proposing a particular hypothesis, we build a model tuned to present-day conditions, and explore the sensitivity of its stable pO_2 level to different changes in the model parameters. By identifying those changes that can produce stable, Proterozoic-like conditions, we aim to narrow the list of geochemical processes that might host the forcing or feedbacks that allow for a two-state system.

2. Model

Our model couples the carbon, iron and sulfur cycles through first-order chemical reactions in a two-layer, phosphorus-limited (Tyrrell, 1999) ocean. The time-dependent equations are given Table 1, and the flux parameterizations discussed below are summarized in Table 2. The values of the model constants and the integration procedure are given in the Supplementary Material. The Phanerozoic equilibrium model is shown in Figure S1. This state was tuned to reproduce major electron fluxes, resulting in equilibrium pO_2 at 1.1 PAL.

2.1. Primary production and export

Primary production (NPP) and all subsequent organic cycling occurs at a fixed C:P Redfield ratio (r) of 106:1. Production proceeds to quantitative uptake (Sarmiento and Gruber, 2006) of phosphorus in the upper ocean layer during each time step. Production remaining after respiration, adsorption, and burial in shallow water sediments is exported to deep waters (EP).

2.2. Water-column remineralization

Remineralization in the water column is modeled as oxic respiration (R_{wc}) in the presence of oxygen, and sulfate reduction (S_{wc}) otherwise. Sulfate reduction rates are observed to follow Michaelis–Menten kinetics (e.g. Ingvorsen et al., 1984); our model uses a linear approximation. This results in a mineralization rate that is somewhat over-sensitive to sulfate levels above the Michaelis constant of $\sim 200 \mu M SO_4^{2-}$ (Ingvorsen et al., 1984), though linearized behavior is a good approximation far from this value. We repeated our analysis using a Michaelis–Menten parameterization, and the basic results are not affected. Both modes of respiration are therefore modeled as linear in the concentration of the appropriate electron acceptor, $[O_2]$ or $[SO_4^{2-}]$, and in $[C_{org}]$.

2.3. Organic carbon deposition

Organic carbon is deposited on the seafloor by two processes: ballasting (Armstrong et al., 2002) and unassisted sinking. The ballasted flux (B_a) is proportional to bulk sediment delivery (W_a) assuming a monolayer organic coat (Hedges and Keil, 1995), and to the availability of fresh organic material, represented by NPP. Organic ballast may be inappropriate for modeling the Proterozoic (Logan et al., 1995); sensitivity to this term is explored in Section 4.3.1. Unballasted sinking (B_c) is proportional to the unadsorbed, unrespired organic carbon concentration. This burial also scales with riverine nutrient inputs, such that when river delivery

accounts for a larger fraction of new production, deposition under shallow waters increases at the expense of export. Details are given in Tables 2 and Table S1.

2.4. Sedimentary remineralization

Remineralization of organic carbon in the sediment includes oxic respiration (R_{sd}) and sulfate reduction (S_{sd}). Both processes are modeled as first order with oxidant concentration in the overlying water. The existence of such an “oxygen effect” has been controversial (Cowie et al., 1995; Hedges et al., 1999); detailed analysis of this parameterization is presented in Section 4.4.1.

The rate constant for sulfate reduction is modulated by a factor β , which scales linearly with the “lability” of carbon reaching the sulfate reduction zone, defined here as $(R_{sd} + R_{wc} + S_{wc})/NPP$. This increases the reduction rate when sulfate reducers have access to less degraded organic matter (Westrich and Berner, 1984).

2.5. Remineralization by other electron acceptors

Other electron acceptors are not included in the model as they are quantitatively much less important than oxygen and sulfur. Denitrification today is only a few percent of O_2 consumption (Canfield, 1993; DeVries, 2012). Iron and manganese are the dominant electron acceptors in some sedimentary environments, but in these cases the flux of metals to the sediment is an order of magnitude smaller than the reduction of those metals, requiring continuous reoxidation by more abundant species such as oxygen and sulfate (e.g. Wang and Van Cappellen, 1996). Globally, the modern fluxes of sulfate and highly reactive iron to the oceans are $\sim 4 Tmol yr^{-1}$ (Elderfield and Schultz, 1996; Poulton and Raiswell, 2002), meaning sulfate can potentially oxidize eight times more organic carbon than iron. Even total titration of sulfur as FeS_2 in an anoxic ocean (Poulton and Canfield, 2011) requires only one electron out of every fifteen to be donated to iron.

Methanogenesis remineralizes about ten times less carbon globally than does sulfate reduction (Canfield, 1993). Some have argued methanogenesis is more important in the absence of other electron acceptors (Wang and Van Cappellen, 1996), an idea that has been invoked to model the Archean with burial efficiencies identical to today (Habicht et al., 2002). However, in Black Sea sediment cores only 0.3% of NPP is degraded via methanogenesis, compared to 4% via sulfate reduction (Jorgensen et al., 2001; Arthur et al., 1994), a ratio typical of oxic marine sediments despite burial efficiencies far above the global average (Arthur et al., 1994; Muller-Karger, 2005). In the sulfate-limited sediments of Cape Lookout Bight, methanogenesis accounts for a larger portion of anaerobic metabolism (Capone and Kiene, 1988), but still degrades less than ten percent of organic carbon reaching the sediment (Martens and Klump, 1984). At these scales, methanogenesis is negligible: our results are not affected if we include methane formation at a constant $1.3 Tmol C yr^{-1}$, 10% of modern sulfate reduction.

Recently Crowe et al. (2011) reported that $\sim 85\%$ of primary production in ferruginous Lake Matano is degraded via methanogenesis, based on a methane flux through the pycnocline calculated from an assumed value for a diffusion coefficient. If exported organic matter is consumed primarily by methanogens, the CO_2 produced at depth should be enriched in ^{13}C to balance the production of methane. However, Crowe et al. report deep water $\sum CO_2 \delta^{13}C$ that is 1‰ depleted relative to surface waters, implying that methane production account for a much smaller fraction of organic matter degradation.

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