Bistability of Atmospheric Oxygen and the Great Oxidation: Implications for Life Detection

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Abstract. Earth's atmospheric evolution was punctuated by a rapid and nonlinear transition in oxygen inventory 2.4 – 2.3 billion years ago, from $< 2 \times 10^{-6}$ atm to $> 10^{-3}$ atm, known as the Great Oxidation. The cause of the Great Oxidation has been a major problem in understanding the evolution of the Earth system. In particular, oxygenic photosynthesis is thought to have evolved by 2.7 billion years ago, at least 300 million years before the Great Oxidation. We have shown that the origin of oxygenic photosynthesis gave rise to two simultaneously stable steady states for atmospheric oxygen. The existence of a low oxygen steady state explains how a reducing atmosphere persisted long after the onset of oxygenic photosynthesis. The Great Oxidation can be understood as a switch to the high oxygen steady state. The bistability arises because ultraviolet shielding of the troposphere by ozone becomes effective once oxygen exceeds 2×10^{-6} atm, causing a nonlinear increase in the lifetime of atmospheric oxygen. Identification of oxygen or ozone in an extrasolar planetary atmosphere has been proposed as an indicator of life, but the existence of a low oxygen stable steady state introduces an important false negative case of planets with stable low (undetectable) oxygen but thriving oxygenic photosynthesis. An oxygen rich atmosphere, detectable remotely and capable of supporting complex life, is likely to occur only on planets of similar size to Earth; too small and bulk atmospheric loss occurs, too large and energetic limitation of hydrogen escape prevents atmospheric oxidation.

1. Introduction

The evolution of the redox state of the atmosphere during the Precambrian (< 0.542 billion years ago (Ga)) can be characterised as reducing conditions until 2.4 – 2.3 Ga, then a rapid transition to oxidising conditions (Fig. 1). The strongest indicator of anoxia is evidence of mass independent fractionation (MIF) of sulphur isotopes in rocks 2.4 Ga and older (Farquhar *et al.* 2000, 2007; Papineau *et al.* 2007), but absent since 2.32 Ga (Bekker *et al.* 2004). Evidence of MIF has generally been taken to indicate $fO_2 < 2 \times 10^{-6}$ atm, but Zahnle *et al.* (2006) show that sufficient methane levels and volcanic sulphur input are equally important in causing a MIF signal. The transition to an oxic atmosphere is termed the "Great Oxidation". This was probably the largest chemical transition in Earth history, causing reorganisations of the major geochemical cycles,
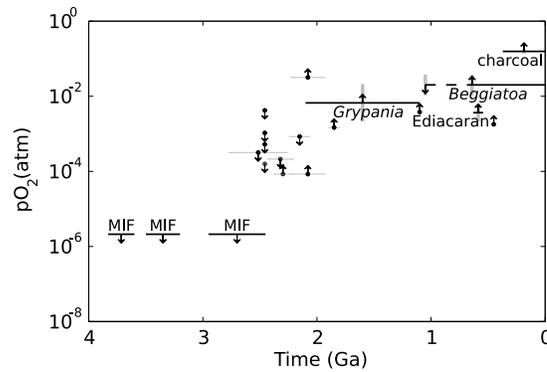
Figure 1.   Compilation of oxygen constraints (Goldblatt *et al.* 2006), plus additional MIF data (Farquhar *et al.* 2007; Papineau *et al.* 2007). Upward arrow indicates lower bounds and downward arrows indicate upper bounds. Solid black lines are duration of the constraint. Circles represent palaeosols. Ediacaran, Grypania and Beggiatoa are biological constraints. Charcoal requires sufficient oxygen for combustion.

changing the dominant modes of microbial respiration and revolutionising atmospheric chemistry. The Great Oxidation would be most easily understood as the immediate consequence of the origin of oxygenic photosynthesis (Kopp *et al.* 2005), but evidence from biomarkers (Brocks *et al.* 1999, 2003; Summons *et al.* 1999), suggests this innovation had occurred at least 300 million years (My) earlier, by 2.7 Ga. This time lag has been a major puzzle in understanding the evolution of the Earth system. In section 2 we develop the solution offered by Goldblatt *et al.* (2006) to this problem. Whilst an alternate view suggesting high oxygen throughout Earth history exists (e.g. Ohmoto 1997; Ohmoto *et al.* 2006) this is a minority view (e.g. Holland 1999; Farquhar *et al.* 2007).

The early Earth is used as an analogue for possible inhabited extrasolar planets. The only practical method for assessing whether an extrasolar planet is inhabited is by remote analysis of its atmospheric content for signs of life (Lovelock 1965; Hitchcock and Lovelock 1967; Des Marais *et al.* 2002); understanding the evolution of Earth's atmosphere is thus a prerequisite for interpreting data from extrasolar planets. In section 3 of this paper, we discuss the implications of our new understanding of the dynamics of oxygen evolution for the search for extrasolar life.

2.   Biogeochemical Modelling

2.1.   Model Description

A three box model of the global redox system is briefly described here, following Goldblatt *et al.* (2006), to which the reader should refer for a full description. The model comprises a box for the atmosphere and surface ocean containing O_2 ($\mathbb{O}$) and CH_4 ($\mathbb{M}$) and a box of organic carbon in the crust ($\mathbb{C}$). Reservoir sizes are in moles.

A key driver of the model is the marine biosphere; this is driven mainly by a net primary productivity from oxygenic photosynthesis ($CO_2 + H_2O + hv \longrightarrow CH_2O + O_2$), N, which is set as a boundary condition. Decomposition of organic matter is by aerobic respiration (reverse of oxygenic photosynthesis) if there is sufficient ambient oxygen and by fermentation and acetotrophic methanogenisis otherwise. If there is sufficient oxygen, methane oxidising bacteria (methanotrophs) will utilise the methane produced ($CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$). When oxygen availability is limited, the net effect of the biosphere is to deliver oxygen and methane to the atmosphere in a 2:1 stochiometric ratio ($CO_2 + H_2O + hv \longrightarrow \frac{1}{2}CH_4 + \frac{1}{2}CO_2 + O_2$), thus promoting the strong chemical disequilibrium in the atmosphere which is a characteristic of life (Lovelock 1965; Hitchcock and Lovelock 1967). Ω is the fraction of N which has this fate.

The major process in restoring equilibrium is atmospheric methane oxidation. This takes place as a series of reactions, some of which are photochemically mediated, but can be represented as an effective bimolecular reaction ($CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$). We empirically parameterise this flux as a function of methane and oxygen abundances, fitting it to the results of detailed photochemical models (Pavlov *et al.* 2001; Pavlov and Kasting 2002; Pavlov *et al.* 2003), obtaining oxidation rate $\Psi\mathbb{M}^{0.7}$, where Ψ is a polynomial function of oxygen concentration. An important property of the atmospheric chemistry embodied in Ψ is that, once oxygen has increased to a certain level, an ozone layer forms shielding the troposphere from UV radiation. This dramatically decreases the rate of photolysis of water vapour in the troposphere, reducing hydroxyl radical availability, thus suppressing the rate of methane oxidation (Kasting and Donahue 1980; Pavlov and Kasting 2002).

Hydrogen loss to space is the source of long-term global oxidation (Hunten and Donahue 1976). For the Earth, H loss is diffusion limited, so depends on total H mixing ratio at the homopause (Hunten 1973). With methane as the only H bearing species in our model atmosphere, the loss rate can be represented $s\mathbb{M}$, where s is a constant. The stochiometry of methane derived H loss can be represented as $CH_4 + hv \longrightarrow 4H + C$ followed by $C + O_2 \longrightarrow CO_2$, net $CH_4 + O_2 + hv \longrightarrow 4H + CO_2$ (Catling *et al.* 2001).

Geologic forcing is set as a boundary condition with net input of reduced material, r, to the atmosphere–ocean system, from the solid Earth. The crustal organic carbon cycle is represented by burying a fraction, β, of the net primary productivity, N. It is assumed that the weathering rate of organic carbon is controlled by uplift and exposure, so is proportional to $\mathbb{C}$ with constant w.

The model is written as a set of ordinary differential equations:

$$\frac{d\mathbb{M}}{dt} = \frac{1}{2}\Omega(N + r) - s\mathbb{M} - \frac{1}{2}\Psi\mathbb{M}^{0.7} - \frac{1}{2}\Omega(\beta(N + r) - w\mathbb{C}) \tag{1}$$

$$\frac{d\mathbb{O}}{dt} = \Omega N - (1 - \Omega)r - s\mathbb{M} - \Psi\mathbb{M}^{0.7} + (1 - \Omega)(\beta(N + r) - w\mathbb{C}) \tag{2}$$

$$\frac{d\mathbb{C}}{dt} = \beta(N + r) - w\mathbb{C} \tag{3}$$

2.2. Steady State Solutions

Goldblatt *et al.* (2006) solved Eqs. $1 - 3$ for steady state. However, the crustal organic carbon cycle has a timescale $\sim 500\,\text{Myr}$, so it is more appropriate to
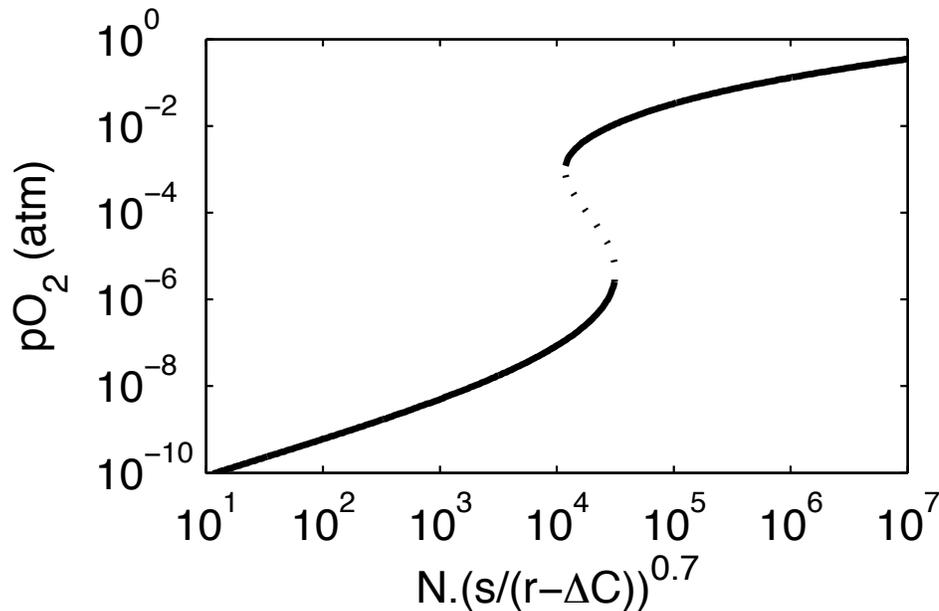
Figure 2.   Steady state solutions for oxygen against composite forcing. Solid line indicates stable steady state and dotted line unstable steady state.

consider steady state for the atmosphere (Eqs. 1 and 2) with respect to some given $\frac{d\mathbb{C}}{dt} = \Delta\mathbb{C}$. Directly we find

$$\mathbb{M} = \frac{r - \Delta\mathbb{C}}{s} \tag{4}$$

and with the simplifying assumptions $N \gg r$ and $N \gg |\Delta\mathbb{C}|$ we find

$$\frac{\Psi}{\Omega} = N\left(\frac{s}{r - \Delta\mathbb{C}}\right)^{0.7} \tag{5}$$

where Ψ/Ω incorporates all oxygen dependency. Eq. 5 is solved numerically (Fig 2). There are two sets of stable steady state solutions for oxygen in the presence of oxygenic photosynthesis; a low oxygen solution, consistent with the MIF constraint, and a high oxygen, consistent with oxygen constraints after the Great Oxidation. The cause of the bistability is a strong nonlinear positive feedback on oxygen levels. Once oxygen exceeds 2×10^{-6} atm an ozone layer starts to form, decreasing the rate of methane oxidation. This reduced oxygen sink causes oxygen levels to increase, promoting the formation of the ozone layer. Oxygen continues to rise until the photochemical loss again balances the biospheric source. Inclusion of oxygen dependency in the biosphere (methanotrophy and aerobic respiration) is essential to obtain realistic oxygen levels on the high oxygen solution.

The discovery of this bistability led Goldblatt *et al.* (2006) to hypothesise that (1) the Great Oxidation can be understood as a switch between the two
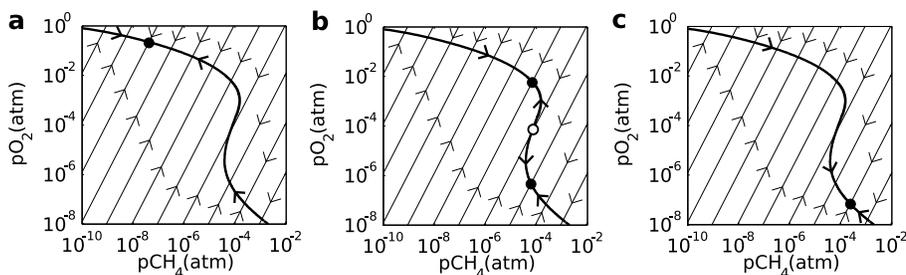
Figure 3.   Methane–Oxygen phase space portraits. Filled circles indicate asymptotically stable improper nodes and the open circle an unstable saddle node. **a** Monostable high oxygen, $N(\frac{s}{r-\Delta\mathbb{C}})^{0.7} = 3.7 \times 10^6$. **b** Bistable region, $N(\frac{s}{r-\Delta\mathbb{C}})^{0.7} = 1.2 \times 10^4$. **c** Monostable low oxygen, $N(\frac{s}{r-\Delta\mathbb{C}})^{0.7} = 8.3 \times 10^3$.

stable states (2) the time lag between the origin of oxygenic photosynthesis and the Great Oxidation can be explained as the atmosphere residing in the low oxygen stable steady state (3) there was an earlier transition from prebiotic oxygen levels ($< 2 \times 10^{-13}$ atm, Kasting *et al.* 1979) to the low oxygen steady state when oxygenic photosynthesis evolved. Hypothesis (2) is supported by new geochemical data: trace metal (Anbar *et al.* 2007; Wille *et al.* 2007) and sulphur isotope (Kaufman *et al.* 2007) evidence indicates the existence of trace quantities of oxygen at 2.5 Ga, before the Great Oxidation, as predicted by our model.

We emphasise that the Great Oxidation was a rapid event defined by a strong nonlinearity in the atmospheric chemistry: formation of the ozone layer. It is not necessary to invoke major contemporaneous changes in boundary conditions to explain the transition.

2.3.   Phase Portraits

The time dependent behaviour of the system can be illustrated with sample phase space portraits (Fig. 3). Note that, during the transition from the low to high oxygen stable steady states, the path through the phase space is sinuous. Whilst oxygen increases monotonically, methane will first decrease, then increase as UV shielding becomes effective and finally decrease once the high oxygen stable steady state has been reached. Explicit time dependent runs are described in Goldblatt *et al.* (2006) and Goldblatt (2008).

2.4.   Climatic Implications

It has previously been suggested a crash in methane concentrations associated with the Great Oxidation could have caused drastic global cooling, triggering the low latitude (possibly "Snowball Earth") glaciations in the Palaeoproterozoic (Pavlov *et al.* 2000; Kasting 2005). This hypothesis was based on three premises which now appear incorrect. (1) Climate model results suggested that methane could contribute up to 30°C warming (Pavlov *et al.* 2000), but this is now known to have been a very large overestimate (Goldblatt 2008; Haqq-Misra *et al.* 2008). (2) The assumption that the Great Oxidation was accompanied by a methane

decrease. Our results suggest otherwise. Ozone, which becomes abundant at the Great Oxidation is a greenhouse gas and the UV shielding it provides will have increased the photochemical lifetimes of methane and nitrous oxide. After the Great Oxidation, a sulphidic ocean may have provided a large biogenic source of nitrous oxide (Buick 2007). Thus, we suggest that the Great Oxidation caused significant warming due to increased ozone, methane and nitrous oxide levels. (3) The notion that glaciation followed the Great Oxidation. New MIF data (Papineau *et al.* 2007) show that the atmosphere remained reducing *after* the first Palaeoproterozoic glaciation.

We suggest two alternate hypotheses for the glaciations: (1) The Archean greenhouse may have been from a carbon dioxide, methane, ethane mixture (Haqq-Misra *et al.* 2008). A decrease in r earlier than the Great Oxidation, caused by changing patterns of volcanism (Kump and Barley 2007) or crustal oxidation (Claire *et al.* 2006), may have caused a step decrease in methane and ethane concentrations, triggering glaciation whilst oxygen remained low. Continued decrease in r may then have caused the switch to high oxygen at around 2.3 Ga, after the final glaciation, when the first geologic evidence of high oxygen is found. (2) Changes in the carbonate–silicate cycle might have caused glaciation: Rino *et al.* (2004) find a gap in the age distribution of detrital zircons between 2.5 and 2.3 Ga, implying low rates of crustal formation so low volcanic carbon dioxide emissions. In either case, the Great Oxidation probably assisted recovery from glaciation rather than causing glaciation.

3.   Implications for Life Detection

Life detection by atmospheric analysis was initially proposed by Lovelock (1965) and Hitchcock and Lovelock (1967) as a search for disequilibrium in atmospheric chemistry generated by life. This was successfully demonstrated for the Earth with Galileo data by Sagan *et al.* (1993), but the necessary resolution would make this rigorous approach difficult for extrasolar planets (Kasting 1996). Hence recent discussion has focused on "biosignature" gases (e.g. Des Marais *et al.* 2002). Oxygen or ozone are seen as the most important as they are taken to indicate extant oxygenic photosynthesis. Also, Catling *et al.* (2005) argue that abundant oxygen is necessarily required by complex life (metazoa). Several possible false positives have been identified; abiotic production of O_2 in high H_2O or CO_2 atmospheres, or a frozen surface preventing oxidation of reduced rocks, but these can generally be excluded by other planetary properties (Des Marais *et al.* 2002) or by taking co-identification of O_3, CO_2 and H_2O as the indicator of life (Selsis *et al.* 2002). Also, O_3 may not be detectable in some O_2 rich atmospheres (Selsis *et al.* 2002).

Concentrations of oxygen or ozone detectable by proposed Terrestrial Planet Finder and Darwin missions correspond to those found after the Great Oxidation (Kaltenegger *et al.* 2007). Thus our identification of a low oxygen stable steady state introduces an important potential false negative. Undetectable levels of O_2 and O_3 are an *expected* property of some planets with extant oxygenic photo-synthesis. Depending on planetary conditions, this could persist for any length of time, possibly longer than the > 300 My for Earth. Observable biogenic oxygen would require not only oxygenic photosynthesis, but the right combination

of geochemical conditions to have caused a Great Oxidation on the planet in question.

The early Earth is a useful analogue for the properties of yet unexplored extrasolar worlds, but it is important to consider how different physical characteristics of such planets would affect both their habitability and the chances of detecting life. Consider a planet smaller than Earth, for example Mars. Most of Mars's atmosphere was lost early due to a combination of impact erosion, hydrodynamic loss and stripping by the solar wind (Catling 2009). These processes operated effectively because of Mars's small mass and corresponding low escape velocity, so bulk atmospheric loss should be expected for a small planet. A thin atmosphere would be unlikely to support abundant life (or contain sufficient atmospheric oxygen for aerobic metazoa) and would be a poor candidate for a positive detection of life by atmospheric analysis.

Conversely, the problem for a larger planet would relate to weaker loss to space. Hydrogen escape, the source of long term oxidation, is diffusion limited on Earth. This can be considered a buoyancy flux, so increases with planetary mass as g increases. However, at some mass greater than Earth's there will be a regime transition to energetic limitation of hydrogen escape (Watson *et al.* 1981). In this regime, the escape flux decreases with increasing mass as the gravitational binding energy which must be overcome is higher. Thus a "super-Earth" planet would be unlikely to oxidise sufficiently to form an oxygen rich atmosphere due to weak hydrogen escape, regardless of whether oxygenic photosynthesis exists.

In looking for an extrasolar planet with detectable oxygen (or, arguably, complex life), we must follow a 'Goldilocks' principle of neither too big nor too small. Conversely, a lack of observable oxygen or ozone does not indicate the absence of oxygenic photosynthesis.

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