What caused the rise of atmospheric O$_2$?

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ABSTRACT

Oxygenic photosynthesis appears to have evolved well before O$_2$ levels increased in the atmosphere, at around 2.4 Ga. This has led to numerous suggestions as to what may have kept O$_2$ suppressed and then eventually allowed it to rise. These suggestions include changes in the recycling of carbon and sulfur relative to water (or hydrogen), a switch from dominantly submarine to dominantly subaerial volcanism, gradual oxidation of the continents and a concomitant decrease in reduced metamorphic gases, a decline in deposition of banded iron-formations, a decline in nickel availability, and various proposals to increase the efficiency of photosynthesis. Several of these different mechanisms could have contributed to the rise of O$_2$, although not all of them are equally effective. To be considered successful, any proposed mechanism must make predictions that are consistent with the carbon isotope record in marine carbonates, which shows relatively little change with time, apart from transient (but occasionally spectacular) excursions. The reasons for this constancy are explored here, but are not fully resolved. In the process of making these comparisons, a self-consistent redox balance framework is developed which will hopefully prove useful to others who may work on this problem and to astronomers who may one day try to decipher spectral signatures of oxygen on Earth-like exoplanets.

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1. Introduction

It gives me great pleasure to contribute to a volume honoring Dick Holland. Dick was one of my greatest scientific mentors during my

career, along with Jim Walker and Jim Pollack. Jim Walker actually suggested to me some thirty years ago that I needed to meet Dick because we all three shared an interest in atmospheric evolution. Dick and I did meet at an AGU carbon cycle meeting in Tarpon Springs, Florida, back in 1984, and we remained in more or less constant scientific communication until shortly before his death. Our conversations, including several during Dick's last year, have been a continuing source of inspiration.

When Dick and I got together, talk invariably revolved around the topic of early atmospheric composition and, in recent years, the cause of the rise of atmospheric O_2. Dick, of course, devoted a large segment of his scientific career to this subject. He was a very good geochemist and had an encyclopedic knowledge of the geochemical literature surrounding this question. In the old days, prior to the revelations from the sulfur MIF record published by Farquhar et al. (2000), much of the debate was about when exactly atmospheric O_2 rose and how low it might have been prior to that time. Since Farquhar's paper, most workers agree that O_2 rose for the first time between 2.33 Ga and 2.45 Ga (Bekker et al., 2004), although transient increases may have occurred just before that time (Anbar et al., 2007). But the question of exactly *why* O_2 levels rose at this time continues to provoke debate. The question is complicated, because most researchers think that cyanobacteria were producing O_2 well before the so-called "Great Oxidation Event", or GOE, at 2.45 Ga. This argument is based on several different lines of geologic evidence, including organic biomarkers in sediments (*e.g.* Brocks et al., 1999; Summons et al., 1999), carbon isotope patterns (Hayes, 1983; Hayes, 1994), trace metal anomalies (Anbar et al., 2007), and stromatolite morphology (Bosak et al., 2009). I will not develop these arguments fully here, as they have been discussed in detail by various authors (*e.g.* Canfield, 2005; Claire et al., 2006; Holland, 2006; Farquhar et al., 2011). In truth, the evidence is not as solid as one might wish, and other authors continue to dispute this claim (Liang et al., 2006; Kirschvink and Kopp, 2008). But if even a few of the remaining arguments are correct, then the question of what caused the rise of atmospheric O_2 has been turned on its head. We now ask: What was it that *delayed* the rise of O_2? These questions are, of course, closely related, because once the reason for the delay went away, then O_2 was free to rise.

Dick himself proposed a detailed hypothesis to address this question (Holland, 2002, 2009). His mechanism involves changes in the amount of carbon and sulfur relative to hydrogen in volcanic gases caused by increased recycling as the Earth matured. I will discuss this hypothesis in some detail because it does indeed appear to be an important part of the answer, although my interpretation of how it works is slightly different than Dick's. Others have offered a variety of different hypotheses to explain the rise of O_2. Hunten and Donahue (1976) pointed out that escape of hydrogen to space should leave behind oxygen that might have oxidized iron in Earth's crust, eventually leading to O_2 accumulation. I myself believed for many years that the upper mantle became progressively more oxidized as a result of loss of hydrogen to space, causing volcanic gases to also become more oxidized with time (Kasting et al., 1993). But this hypothesis was dealt a severe blow by measurements of Cr and V in ancient basalts, which showed that the redox state of the upper mantle has remained approximately constant since 3.5 Ga, or even earlier (Canil, 1997; Delano, 2001; Canil, 2002; Li and Lee, 2004; Trail et al., 2011). So, I will not discuss that hypothesis further here. Since then, the number of different hypothesis for triggering the GOE has proliferated. Catling et al. (2001) and Claire et al. (2006) suggested that hydrogen escape to space caused oxidation of the *continents*, not the mantle, and this resulted in a gradual decrease over time in reduced metamorphic gases. Kump and Barley (2007), and later Gaillard et al. (2011), proposed that the rise of O_2 was caused by a gradual switch from submarine to subaerial outgassing, which caused volcanic gases to become more oxidized with time. Isley and Abbott (1999) suggested that the GOE was linked to a decrease in deposition of banded iron-formations, which may itself

have been linked to the end of a period of enhanced mantle plume activity (Barley et al., 2005). Konhauser et al. (2009) suggested that a decrease in Ni availability in the Late Archean led to a decrease in methanogenesis, which in turn led to the rise in O_2. Don Canfield and I have proposed a mechanism that involves changes in the rate of serpentinization of continents and seafloor, along with possible biological innovations, specifically, the evolution of nitrogenase protection mechanisms in cyanobacteria (Kasting and Canfield, 2012) (see also Anbar and Knoll (2002) and Grula (2005)). A related proposal involves productivity increased caused by changes in the availability of Mo and V (Zerkle et al., 2006; Scott et al., 2008, 2011). Each of these hypotheses is discussed in some detail in the sections that follow.

Several of the proposals mentioned above do not explicitly involve biology. That may seem surprising, because the rise of atmospheric O_2 is universally attributed to the invention of oxygenic photosynthesis by *cyanobacteria* (see, *e.g.*, Cloud, 1972; Walker, 1977). Cyanobacteria are single-celled true Bacteria that are widely believed to have been the first oxygenic photosynthesizers on the planet. The evidence for this is indisputable: the chloroplasts of algae and higher plants contain DNA that, when sequenced, puts them together with cyanobacteria on a single branch of the "universal" (ribosomal RNA) tree of life (Margulis, 1982). As already mentioned, though, oxygenic photosynthesis appears to have originated several hundred million years prior to the GOE, so that event cannot by itself be credited with causing the O_2 rise. Furthermore, from a geochemists' standpoint, the global redox budget had to be balanced both before and after the GOE, regardless of when oxygenic photosynthesis was invented. Trying to explain that is what the remainder of this paper is about.

2. The global redox budget

2.1. Defining the budget

Based on the perception that cyanobacteria appeared well before the GOE, various authors have proposed that the rise of O_2 was delayed by some geochemical mechanism: the sinks for O_2 outweighed its sources. To analyze this problem quantitatively, let us start by defining the *global redox budget* as the redox budget of the combined atmosphere–ocean system. Hayes and Waldbauer (2006) carried out a similar exercise for Earth's redox budget, but they included the crust, as well. That would not be appropriate for the problem being considered here, as the time scale for oxidizing the crust is hundreds of millions to billions of years, whereas the lifetime of O_2 in the atmosphere–ocean system today is only ~2 million years (Holland, 1984). The lifetime of H_2 in the Archean atmosphere–ocean system was even shorter, only ~30,000 years. (This is easily demonstrated by dividing the column mass of H_2 in a 1-bar atmosphere by the diffusion-limited escape rate of hydrogen to space, given by Eq. (7) below.) Hence, the redox state of the atmosphere–ocean system should remain in quasi-steady state on geological time scales, whereas the redox state of the crust continues to evolve with time.

Today, the atmosphere and the ocean freely exchange O_2, and so the global redox budget is typically described in terms of O_2 sources and sinks (see, e.g., Holland, 2002). On the early Earth, O_2 was scarce (Kasting, 1993) and the atmosphere and ocean would have freely exchanged reduced gases such as H_2 and CH_4. We are interested in the early Earth here, so I will keep track of the global redox budget in terms of H_2 equivalents. These are related to O_2 equivalents by the reaction:

$$2\,H_2 + O_2 \leftrightarrow 2\,H_2O \qquad (1)$$

Thus, 2 mol of H_2 consume 1 mol of O_2, and vice versa. If you prefer to keep track of redox in terms of O_2, just divide all my numbers by 2.

To facilitate the analysis it is convenient to define reference, or "neutral", oxidation states for compounds containing hydrogen, carbon, nitrogen, iron, and sulfur. I take these to be, respectively, H_2O, CO_2, N_2,

FeO, and SO_2. The choice of the first four of these compounds is straightforward. The first three are dominant components of the atmosphere and hydrosphere and are relatively stable, both thermodynamically and kinetically, at Earth's surface. By defining these as neutral, one can avoid keeping track of their inputs and outputs from the combined atmosphere–ocean system. Ferrous iron, represented here as FeO, is the dominant form of iron in the mantle and the probable initial state of most iron in the crust, as well, so this is also an obvious choice for a reference state. The choice of SO_2 as the neutral sulfur species is more negotiable. SO_2 is the dominant sulfur gas emitted from subaerial volcanoes today, and this was probably true in the distant past, as well; hence, SO_2 has routinely been taken as redox neutral in past analyses of the Archean atmospheric redox budget (e.g., Kasting, 1990; Zahnle et al., 2006). Today, however, volcanic SO_2 is nearly all oxidized to sulfate, which for redox purposes we can represent as sulfuric acid, H_2SO_4. Thus, most geochemists (e.g., Holland, 2002) have used sulfate as the sulfur reference state for analyzing the modern global redox budget. But there are advantages to doing this differently and remaining consistent with the atmospheric modelers. Today, sulfur leaves the ocean either as oxidized minerals, mostly gypsum ($CaSO_4 \cdot 2H_2O$) in evaporites, or as the reduced mineral pyrite (FeS_2) in sediments. By choosing SO_2 as the neutral sulfur species, the burial fluxes of gypsum and pyrite appear explicitly in the global redox budget. This turns out to be useful, because gypsum does form today but it did not do so during the Archean (Huston and Logan, 2004). Some barite, $BaSO_4$, did form prior to 3.2 Ga (ibid.) from reaction of Ba with sulfate that may have been produced photochemically (Pavlov and Kasting, 2002); however, I assume here that this process was quantitatively unimportant in the redox budget.

The next step in calculating the global redox budget is to define the total flux of reduced volcanic (and metamorphic) gases, $\Phi_{out}(Red)$, as

$$\Phi_{out}(Red) = \Phi_{out}(H_2) + \Phi_{out}(CO) + 4\Phi_{out}(CH_4) + 3\Phi_{out}(H_2S) \\ + 4\Phi_{out}(S_2) + \ldots \qquad (2)$$

The stoichiometric coefficients preceding each outgassing term come from converting these species to the neutral species defined above, using H_2O as the oxidant and counting the H_2's released, e.g.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3)$$

$$H_2S + 2H_2O \rightarrow SO_2 + 3H_2 \qquad (4)$$
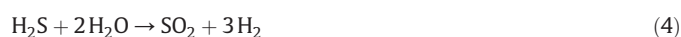
Volcanic outgassing is only one source of hydrogen on the early Earth. Hydrogen should also have been produced by reactions that oxidized ferrous iron (Fe^{+2}) to ferric iron (Fe^{+3}) anaerobically, i.e., without using O_2 or sulfate. Examples of such reactions are serpentinization of ultramafic rocks on the continents and seafloor and deposition of banded iron-formations, or BIFs, many of which may have been formed by anaerobic, iron oxidizing bacteria (see, e.g., Konhauser et al., 2002). Some BIFs may have been precipitated by reaction with free O_2 following the evolution of cyanobacteria, but this distinction should not matter in analyzing their effect on the global redox budget. In both cases the dominant iron-bearing oxide mineral produced is magnetite, Fe_3O_4. (The iron in BIFs is thought to have precipitated initially as ferric oxyhydroxides; however, most of it was subsequently converted to magnetite during diagenesis or metamorphism.) Magnetite can be thought of as consisting of two parts ferric iron and one part ferrous. Thus, its effect on the redox budget can be written as

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \qquad (5)$$

The production of hydrogen is thus equal to the rate of deposition of magnetite, or to 1/3rd the rate of deposition of iron as magnetite. Some oxide BIFs include hematite, Fe_2O_3, as well, the formation of

which would yield slightly more hydrogen (1/2 mol of H_2 per mole of Fe), but I'll neglect this in the analysis that follows.

On the modern Earth, hydrogen is also produced when outgassed SO_2 is oxidized and buried as gypsum. We can represent this schematically in the redox budget by using sulfuric acid as a surrogate for gypsum (because sulfur has the same oxidation state in both compounds).

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2 \qquad (6)$$

Thus, burial of 1 mol of gypsum releases 1 mol of H_2. Most analyses of the modern oxygen budget (e.g., Holland, 2002) take sulfate as the reference oxidation state for sulfur; hence, burial of gypsum does not explicitly appear. But then SO_2 must be treated as a reduced volcanic gas. That's misleading, in my view, because even though it is initially oxidized, most SO_2 is eventually reduced and buried as pyrite. This is also true for the Archean, as pointed out previously.

An additional, very large, source for hydrogen (or sink for oxygen) in the modern global redox budget comes from oxidation of the continents and seafloor. I shall represent this term as Φ_{OW}, where the subscript 'OW' stands for 'oxidative weathering'. On the continents, this process involves oxidation of organic carbon, ferrous iron, and sulfide during weathering, and the oxidant is generally O_2 (Holland, 1978, 2002). On the seafloor, the relevant reaction is oxidation of ferrous iron, and the primary oxidant is sulfate (Sleep, 2005). Both processes serve as sinks for O_2, and therefore as sources for H_2 in the redox budget. Bear in mind, though, that while this oxygen sink is very large today, it should have been essentially absent on the Archean Earth. The preservation of reduced detrital minerals such as pyrite and uraninite shows that oxidative weathering was not occurring on the continents (Cloud, 1972), while sulfur isotopic data indicate that dissolved sulfate levels in the ocean were exceedingly low (Canfield et al., 2000).

Let's turn now to sinks for hydrogen. The first, and most obvious, is escape of hydrogen to space, $\Phi_{esc}(H_2)$. I assume, following others (Hunten, 1973; Walker, 1977; Kasting and Brown, 1998) that hydrogen escapes to space at the diffusion-limited rate:

$$\Phi_{esc}(H_2) \cong 2.5 \times 10^{13} f_T(H_2)/0.00374 = 6.7 \times 10^{15} f_T(H_2) \text{ mol/yr} \qquad (7)$$

The factor of 0.00374 converts from photochemists' units (molecules $cm^{-2} s^{-1}$) to geochemists' units (mol/yr). Here, $f_T(H_2)$ is the total mixing ratio of hydrogen in the stratosphere expressed in terms of H_2 equivalents:

$$f_T(H_2) = 0.5f_H + f_{H_2} + f_{H_2O} + 2f_{CH_4} + \ldots \qquad (8)$$

I will not deal much with this equation in this paper, as this has been done many times elsewhere (e.g., Kasting, 1993; Kasting and Brown, 1998; Kharecha et al., 2005; Kasting and Canfield, 2012). But this equation allows one to estimate H_2 concentrations in the Archean atmosphere, given an H_2 outgassing rate, and from that to calculate vertical profiles for O_2 and other minor atmospheric constituents.

Hydrogen is also lost when carbon is buried as organic matter. If that organic matter is produced by oxygenic photosynthesis, the relevant reaction is

$$CO_2 + H_2O \rightarrow CH_2O + O_2 \qquad (9)$$

The O_2, however, eventually reacts with reductants, consuming hydrogen according to reaction (1). Thus, the net reaction is just the sum of reactions (1) and (9)

$$CO_2 + 2H_2 \rightarrow CH_2O + H_2O \qquad (10)$$

Conveniently, reaction (10) also represents H_2-based anoxygenic photosynthesis, which may well have been widespread during the Archean (Kharecha et al., 2005). Other forms of anoxygenic photosynthesis use Fe^{+2} or $S^=$ as the reductant. They are accounted for

by reaction (5) above and reaction (11) below. As mentioned previously, iron-based photosynthesis actually produces $Fe(OH)_3$ or other ferric oxy-hydroxides; however, based on observations of BIFs, most of this ferric iron was reduced to magnetite, Fe_3O_4, either before or shortly after it was buried.

Finally, burial of pyrite in sediments is also a sink for hydrogen, according to

$$4\,SO_2 + 10\,H_2 + 2'FeO' \rightarrow 2\,FeS_2 + 10\,H_2O \qquad (11)$$

Here, 'FeO' represents ferrous iron which, during the Archean, would have been supplied as dissolved Fe^{+2} in seawater. According to this equation, 5 mol of H_2 is consumed for each mole of pyrite that is buried.

Putting all of these processes together yields the following equation for the global redox budget:

$$\begin{aligned}\Phi_{out}(Red) &+ \Phi_{OW} + \Phi_{burial}(CaSO_4) + \Phi_{burial}(Fe_3O_4) \\ &= \Phi_{esc}(H_2) + 2\,\Phi_{burial}(CH_2O) + 5\,\Phi_{burial}(FeS_2)\end{aligned} \qquad (12)$$

Here, $\Phi(i)$ is the flux of species i into or out of the atmosphere–ocean system. The terms on the left are hydrogen sources; the terms on the right are hydrogen sinks. The coefficients preceding each term convert to units of H_2 equivalents. The individual terms are:

$\Phi_{out}(Red)$ = Total outgassing flux of reduced volcanic and metamorphic gases
Φ_{OW} = Rate of oxidative weathering of the continents and seafloor
$\Phi_{burial}(CaSO_4)$ = Burial flux of gypsum and anhydrite
$\Phi_{burial}(Fe_3O_4)$ = Rate of anaerobic iron oxidation (from BIFs and serpentinization)
$\Phi_{esc}(H_2)$ = Rate of hydrogen escape to space
$\Phi_{burial}(CH_2O)$ = Burial rate of organic carbon in sediments
$\Phi_{burial}(FeS_2)$ = Burial rate of pyrite in sediments.

This equation should be valid for both the modern and early Earth, although the relative importance of the various terms are quite different for these two cases.

2.2. Comparison with Claire et al. redox budget formulation

A similar flux-based analysis of the global redox budget was presented not long ago by Catling and Claire (2005) and Claire et al. (2006). I repeat it here in order to highlight the similarities and the differences from Eq. (12) above and to take advantage of other aspects of their terminology, which turn out to be quite useful.

In steady state, redox balance in the Claire et al. (2006) model is expressed by the equation:

$$F_E + F_B = F_V + F_M + F_W \qquad (13)$$

The left-hand side of the equation contains hydrogen sinks (oxygen sources), while the right-hand side contains hydrogen sources (oxygen sinks). Specifically, F_E is the hydrogen escape flux, F_B represents burial of organic carbon, F_V is the volcanic reduced gas flux, F_M is the reduced gas flux from metamorphic processes on the continents, and F_W represents oxidative weathering. In terms of the variables used in Eq. (12), $F_E = \Phi_{esc}(H_2)$, $F_B = 2\,\Phi_{burial}(CH_2O)$, $F_V + F_M = \Phi_{out}(Red)$, and $F_W = \Phi_{OW}$. Besides the fact that the hydrogen sinks are on the left in Eq. (13) and on the right in Eq. (12) and that Claire et al. do their budgeting in terms of O_2 rather than H_2, the differences between the equations are the following: i) F_V and F_M are broken out separately in Eq. (13), whereas they are combined in Eq. (12); ii) Eq. (12) contains an additional hydrogen sink term from burial of pyrite (Claire et al. did not include sulfur in their model), iii) Eq. (12) contains an additional hydrogen source term, $\Phi_{burial}(Fe_3O_4)$, that does not appear in Eq. (13);

iv) Eq. (12) contains an additional hydrogen source from burial of sulfate that is absent in Eq. (13). The terminology in my Eq. (12) is also written with the mineralogy expressed explicitly to indicate the appropriate redox stoichiometry.

The difference in redox budget formulations between the Claire et al. model and the model presented here reflect the authors' different perceptions of the importance of various terms. Claire et al. argued that the metamorphic reduced gas flux, F_M, is the key to understanding the rise of O_2; I think that other terms, including anaerobic iron-oxidation, $\Phi_{burial}(Fe_3O_4)$, are probably more important. I will examine the numbers more closely in the following section.

Claire et al. also define a parameter, K_{OXY}, which represents the ratio of oxygen sources to oxygen sinks, *not including oxidative weathering or hydrogen escape*. In their model,

$$K_{OXY} = \frac{F_B}{F_V + F_M} \qquad (14)$$

When $K_{OXY} < 1$, oxygen sinks outweigh oxygen sources; thus, excess hydrogen builds up in the atmosphere and escapes to space. When $K_{OXY} > 1$, oxygen sources outweigh oxygen sinks; hence, O_2 builds up in the atmosphere and is consumed by oxidative weathering. According to the authors, $K_{OXY} \cong 6$ today, indicating that the redox balance is shifted well over to the oxidized side. Thus, one needs to either boost the oxygen source or reduce the oxygen sinks by a considerable amount in order to switch over to a reduced atmosphere back in the Archean. That is the essence of the problem outlined in the Introduction.

The Claire et al. approach seems useful, so I will define a similar parameter based on the terms in Eq. (12). Formation of $CaSO_4$ requires an excess of oxygen, so it is left out of K_{OXY}, along with oxidative weathering and hydrogen escape. (This is an advantage of choosing SO_2, rather than sulfate, as the reference redox state for sulfur.) In my nomenclature, one gets:

$$K_{OXY} = \frac{2\,\Phi_{burial}(CH_2O) + 5\,\Phi_{burial}(FeS_2)}{\Phi_{out}(Red) + \Phi_{burial}(Fe_3O_4)} \qquad (15)$$

The difference between this equation and Eq. (14) is the addition of the pyrite burial flux in the numerator and the anaerobic iron-oxidation term in the denominator. To be fair, Catling and Claire (2005) mentioned Fe^{+2} as an additional O_2 sink, but they did not bring it up again in Claire et al. (2006). Recall that this term represents processes, such as serpentinization or BIF deposition, that oxidize iron without the need for oxidants such as O_2 or sulfate. As before, values of $K_{OXY} < 1$ lead to a reduced atmosphere; $K_{OXY} > 1$ leads to an oxidized atmosphere.

2.3. The modern global redox budget

Let us now try to estimate the magnitude of these redox budget terms on the modern Earth. Most of the numbers below are drawn from Holland (2002) and Sleep (2005). I have changed things in two ways, though, from the budgeting done in Holland (2002). First, I present numbers in terms of H_2 equivalents rather than O_2 equivalents. Second, I have defined SO_2 as the 'neutral' sulfur species, rather than sulfate. This causes Holland's pyrite weathering and deposition terms to be multiplied by 5/7 (because the sulfur valence shift is 5 going from SO_2 to FeS_2, compared to 7 going from H_2SO_4 to FeS_2). Terms in the modern redox budget are given in Table 1.

A few comments should be made concerning Table 1. First, I have not worked hard to achieve equality between H_2 sources and sinks, even though these numbers should, in fact, balance. The numbers agree to within the (very large) error bars on the estimates. Second, Canfield et al. (2006) estimate much lower numbers for H_2 outgassing, $(0.18-0.5) \times 10^{12}$ mol/yr (included in $\Phi_{out}(Red)$ in Table 1). Their numbers, though, reflect only subaerial outgassing of H_2. The value

Table 1
The modern global redox budget.

H$_2$ sources	Rate (10^{12} mol/yr)	Reference
$\Phi_{out}(Red)$	4.8 ± 3.6	Holland (2002)
Φ_{OW} (continents)[*]	30 ± 8	Holland (2002)
Φ_{OW} (seafloor)	2 ± 1	Sleep (2005)
$\Phi_{burial}(CaSO_4)$	1.0	Lasaga et al. (1985)
$\Phi_{burial}(Fe_3O_4)$	0.4 ± 0.2	Sleep (2005)
Total	38.2 ± 8.8	
H$_2$ sinks		
$\Phi_{esc}(H_2)$	0.04 ± 0.01	Walker (1977)
$2\,\Phi_{burial}(CH_2O)$	20 ± 6.6	Holland (2002)
$5\,\Phi_{burial}(FeS_2)$[*]	10 ± 5	Holland (2002)
Total	30.1 ± 8.3	

[*] Calculated using SO_2 as the neutral sulfur species.

listed in Table 1 includes submarine outgassing of H$_2$S, as well, which provides at least 1×10^{12} mol H$_2$ equivalent/yr (Holland, 2002). The Canfield et al. (2006) numbers are based on observed H$_2$/SO$_2$ ratios in subaerial volcanic gases, along with satellite measurements of the SO$_2$ flux. These latter measurements capture only explosive volcanism and may underestimate the total SO$_2$ release rate, which is better derived by ratioing to H$_2$O and CO$_2$ in sampled volcanic gases (H. D. Holland, priv. comm.). Sleep and Bird (2007) also argued for a relatively small hydrogen outgassing flux, and Holland (2009) replied, arguing that they were underestimating some terms and neglecting submarine outgassing of H$_2$S. I side with Holland in both cases and have used his higher H$_2$ outgassing fluxes throughout. If the total hydrogen outgassing rate today is lower than he assumed, the problem of producing a reduced atmosphere during the Archean becomes that much more difficult.

As an immediate application of these numbers, let us use them to calculate K_{OXY} from Eq. (15). Neglecting the uncertainties, and plugging in numbers from Table 1 in units of 10^{12} mol/yr, yields

$$K_{OXY} = \frac{20 + 10}{4.8 + 0.4} = \frac{30}{5.2} = 5.8 \qquad (16)$$

This is essentially the same as the value of 6 estimated by Claire et al. (2006). So, we both see the modern redox budget in the same way, probably because we both rely largely on numbers generated by Norm Sleep and Dick Holland.

2.4. Application to the early Earth: constraints from carbon isotopes

Now, consider how these numbers should have changed on the early Earth. First, and most importantly, oxidative weathering of the continents and seafloor, Φ_{OW}, would have been negligible, based on the short lifetime of O$_2$ in the atmosphere (Pavlov et al., 2001) and the low O$_2$ and sulfate concentrations in seawater (Canfield et al., 2000). This diminishes the list of H$_2$ sources to only about 5.2×10^{12} mol/yr (the $\Phi_{out}(Red) + \Phi_{burial}(Fe_3O_4)$ terms on the left-hand side of Eq. (12), given modern degassing rates. (The remaining H$_2$ sources constitute the denominator in Eq. (16).) Degassing rates could, of course, have been significantly higher on the Archean Earth, given a hotter upper mantle and likely a higher geothermal heat flux. Sleep and Zahnle (2001) estimated that the heat flux was 2–3 times higher in the mid-Archean and that outgassing rates scale as heat flux squared; thus, the volcanic H$_2$ source could conceivably have been larger by a factor of 4–9. Jun Korenaga, however, suggests that geothermal heat flow was no higher in the Archean than at present because thick crustal plates would have slowed everything down (Korenaga, 2006, 2007, 2008a,b). If he is correct, then Archean outgassing rates may have been no higher than today. As there is no generally accepted theory of how plate tectonics changed over time, one cannot be certain who is right in this argument. If one assumes

that a certain percentage of outgassed CO$_2$ is buried as organic carbon, as some authors have done (see below), then increased outgassing rates would not have changed the redox balance much, because the increased release rate of reduced volcanic gases would have been offset by increased burial of organic carbon. If one relaxes this assumption, however, then higher outgassing rates during the Archean should have increased the net flux of hydrogen into the atmosphere–ocean system, thereby promoting a more reduced atmosphere.

Next, consider the sinks for hydrogen. On the modern Earth, these come predominantly from burial of organic carbon and pyrite. What can we say about these burial fluxes in the past? For carbon, we can get some guidance from the carbon isotope record. Because carbon isotopes are fractionated during photosynthesis, organic carbon is generally depleted in ^{13}C relative to ^{12}C by about 30‰. Label this fractionation as Δ_B. At 2.7 Ga, some organic carbon is depleted in ^{13}C by as much as 60‰, suggesting some kind of double isotopic fractionation (Hayes, 1983, 1994). (This is part of the evidence for the early evolution of oxygenic photosynthesis that I mentioned briefly in the Introduction.) As Fig. 1 demonstrates, however, most of the time organic carbon in rocks is depleted by ~30‰ compared to carbonate rocks of the same age.

Given the carbon isotope record, mass balance arguments can be used to calculate the fraction of CO$_2$ entering the atmosphere–ocean system that is buried as organic carbon, f_{org}, (see, *e.g.*, Kump et al., 2010, p. 226). Carbon emanating from the mantle has a δ^{13}C value, δ_{in}, close to -6‰, and this is roughly true for bicarbonate produced by continental weathering, as well (because it includes a contribution from oxidative weathering of organic carbon). Equating input and output of the two carbon isotopes yields

$$f_{org} = \frac{\delta_{carb} - \delta_{in}}{\Delta_B} = \frac{\delta_{carb} + 6}{30} \qquad (17)$$

Here, δ_{carb} represents the δ^{13}C value of marine carbonates, and I have used the Phanerozoic value for Δ_B. Except for brief, but occasionally spectacular, excursions, δ_{carb} has remained remarkably close to 0‰ throughout much of Earth history (Fig. 1). This has led many authors (*e.g.*, Kump et al., 2001; Holland, 2002) to conclude that f_{org} has remained close to 0.2 during most of this time. That said, DesMarais et al. (1992), Bjerrum and Canfield (2004), and Canfield (2005) have all argued that the carbon isotope data are not that constant and that the average value of f_{org} may have increased with time. But these arguments are themselves disputed (Claire et al., 2006). In particular, the Bjerrum and Canfield (2004) model assumes a biologically pumped gradient in δ^{13}C between the surface ocean and seafloor, but measurements of 3.46 Ga carbonates associated with seafloor basalts show no such gradient (Nakamura and Kato, 2004). The most recent analysis (Hayes and Waldbauer, 2006) suggests that f_{org} was ~0.15 during most of the Archean and that it did not reach a value of 0.2 until just the last few hundred million years (see Fig. 2). The lower value of f_{org} comes mostly from a higher estimated value for Δ_B (36‰) during the Archean.

This hydrogen budget analysis leads directly to a problem that has confronted many different authors. During the Archean, the rate of H$_2$ input was of the order of 5×10^{12} mol/yr, or possibly higher if outgassing rates were higher. But, based on the carbon isotope data, the rate of H$_2$ loss via organic carbon burial appears to have been at least 20×10^{12} mol/yr (the modern value), and higher yet if it scales with the outgassing rate. Indeed, the estimated source of oxygen from organic carbon burial alone exceeds the estimated sinks for oxygen by a substantial amount. Burial of pyrite and loss of hydrogen to space simply compound the problem by providing additional sources for O$_2$. Or, to put this another way, it is hard to see how the value of K_{OXY} could have been less than 1 during the Archean. Where did all of the required excess hydrogen come from? Or, alternatively, what
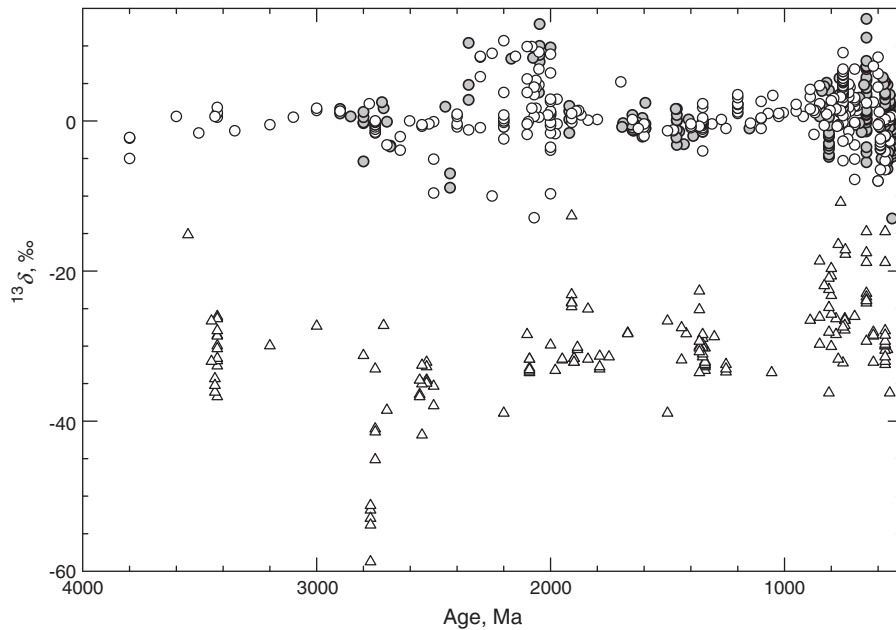
Fig. 1. The carbon isotopic record of carbonates (circles) and organic carbon (triangles). Filled symbols represent samples from geologic units that are well dated. [From Hayes and Waldbauer (2006); data originally from Shields and Veizer (2002).]

assumptions have we made in carrying out this analysis that might possibly be wrong?

3. Published hypotheses for the cause of the GOE

3.1. Holland's tectonic evolution model and variations thereof

Holland (2002, 2009) solved the redox budget problem by postulating that the relative amounts of H_2O, CO_2, and SO_2 coming out of volcanoes change with time. In particular, he assumed that increased

Fig. 2. Top panel: calculated values of the organic carbon burial fraction, f_{org}, based on the isotopic data shown in Figure 6.2. The broken lines represent values obtained from carbon isotope excursions during the Lomagundi event. Bottom panel: integrated organic carbon burial, based on these same data. [From Hayes and Waldbauer, 2006.]

subduction rates of carbon- and sulfur-rich sediments over time led to more CO_2 and SO_2, as compared to H_2O, in volcanic gases. The H_2O is accompanied by H_2 at a ratio which is set by the oxygen fugacity of the QFM (quartz-fayalite-magnetite) synthetic buffer—a proxy for upper mantle redox state. Thus, early in Earth history, according to this model, larger amounts of H_2O and H_2 were coming out of volcanoes, providing a bigger oxygen sink. Later in Earth history, larger amounts of CO_2 and SO_2 were emitted. Precisely 20% of the outgassed CO_2 was reduced to organic carbon in this model, and some fraction, f, of the outgassed SO_2 was reduced to pyrite. If $f < 1$, then not enough hydrogen is available to reduce all the SO_2 and oxygen begins to accumulate. If one picks the right parameters, the crossover between an O_2-poor and O_2-rich atmosphere occurs around 2.5 Ga, the observed time of the GOE.

Holland's model is attractive for several reasons, the most important one being that it *works*, at least conceptually. If the Earth system changed in the manner postulated, then O_2 should have increased at the time when it did. In addition, some of Holland's suppositions are widely accepted. In particular, the idea that sulfur was less mobile, and therefore less available, in the Archean has been emphasized by many different authors (*e.g.*, Walker and Brimblecombe, 1985; Ono et al., 2003; Canfield et al., 2006). This, by itself, should have a substantial effect on the oxidation parameter K_{OXY} in Eqs. (15) and (16) because it should lead to a substantial decrease in pyrite burial at that time. If none of the pyrite in continental rocks was mobilized during weathering, then the flux of sulfur entering the atmosphere–ocean system would have been just the volcanic sulfur flux, which is mostly SO_2. As mentioned above, the modern rate of SO_2 outgassing has been underestimated in some models because they only consider explosive volcanism. A reasonable value, based on measured SO_2:CO_2 ratios in volcanic gases (Holland, 2002) and estimated CO_2 outgassing rates (Catling and Kasting, in preparation) is about 2×10^{12} mol SO_2/yr. If all of this SO_2 was eventually buried as pyrite, the pyrite flux would be one-half this value, and the equivalent H_2 sink (O_2 source) would be 5 $\Phi_{burial}(FeS_2) \cong 5 \times 10^{12}$ mol H_2/yr. By comparison, the modern pyrite burial flux (Table 1) is twice this value. Thus, Eq. (16) becomes (in units of 10^{12} mol/yr)

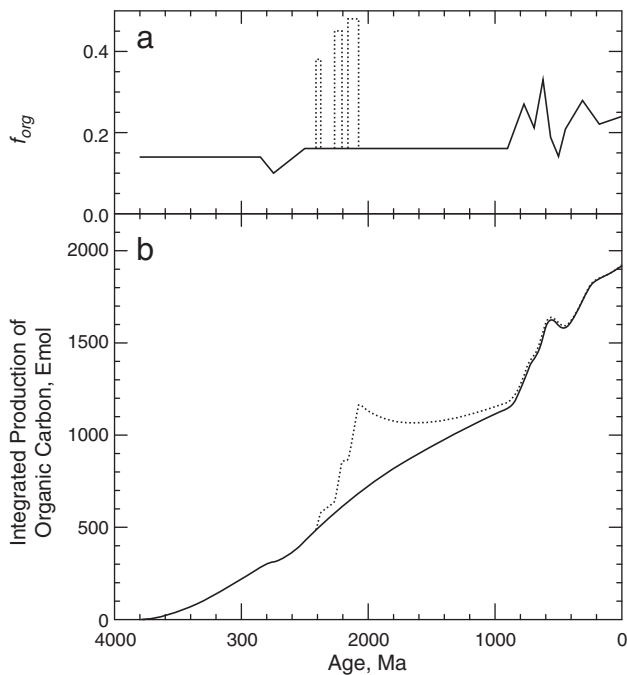$$K_{OXY} = \frac{20 + 5}{4.8 + 0.4} = \frac{25}{5.2} \cong 4.8 \qquad (18)$$

This change in the sulfur cycle, which must have occurred, goes part of the way towards producing an O_2-poor Archean atmosphere, but not nearly far enough. Recall that K_{OXY} must be <1 during the Archean to keep the atmosphere reduced. Inspection of Eq. (18) suggests that the main problem is the large burial rate of organic carbon, which is responsible for the value of 20 in the numerator. In Holland's model, the organic carbon burial rate was smaller in the past because less carbon was getting recycled by subduction, and hence less CO_2 was emitted from volcanoes. This could indeed have been true, but it is difficult to prove it because we have no record of past subduction rates. However, there is another way to think about this problem that leads to a similar conclusion, using slightly different reasoning. I outline this argument below.

Today, most of the carbon entering the combined atmosphere–ocean system comes from weathering of carbonates and organic matter on the continents. According to Lasaga et al. (1985), weathering of carbonates yields about 24×10^{12} mol HCO_3^- yr^{-1}. These same authors list an input of 4×10^{12} mol/yr of CO_2 from oxidative weathering of organic matter on the continents. Holland (2002) gives (7.5 ± 2.5) mol/yr for this same oxidative weathering rate. I will use Holland's higher value, as I have used his numbers elsewhere in this paper, and it is best to be self-consistent. The third modern input of CO_2 to the atmosphere–ocean system is outgassing from volcanoes and from continental metamorphism, which total to about $(7.5 \pm 2.5) \times 10^{12}$ mol/yr (Jarrard, 2003; Catling and Kasting, in preparation). Berner (2004) lists a similar value, $(7 \pm 3) \times 10^{12}$ mol/yr. This outgassing is more or less evenly distributed between arc volcanism, hotspot volcanism, and midocean ridge volcanism, with a somewhat smaller contribution, $\sim 1 \times 10^{12}$ mol/yr, from metamorphism. The total input of CO_2 is thus some 39×10^{12} mol/yr, which, from an isotopic standpoint, is roughly consistent with Holland's organic carbon burial rate of 10×10^{12} mol/yr. Complete consistency with the carbon isotope record would require that 20% of the CO_2 input, or $\sim 8 \times 10^{12}$ mol/yr, leaves the system as organic carbon.

Now, consider what might have happened back in the Archean. To begin, the input of CO_2 from oxidative weathering of organic matter would likely have been absent, just as was true for input of sulfur from pyrite weathering. (See also Bekker and Holland (2012), who make this same assumption.) This would have reduced the total CO_2 input by ~20%. But, if the Archean continents were significantly smaller than today, then input of HCO_3^- from carbonate weathering would have been smaller, as well. The question of how fast the continents grew has been a long-term topic of debate. In a comprehensive analysis based on various geochemical indicators, Taylor and McLennan (1995) concluded that ~60% of the continental crust was emplaced by the Late Archean. This does not, however, guarantee that it was above sea level. Recently, Flament et al. (2008) calculated that only 10% of the present continental area was above sea level as late as 2.5 Ga, based on geophysical modeling. If this was true, then continental weathering rates could have been slow even though continental volume was significant. As an extreme example, assume for the moment that emergent continents were entirely absent. CO_2 input would then have been restricted to volcanic outgassing. Using present outgassing rates, the amount of CO_2 input would be reduced by ~80% compared to its present value. Thus, the organic carbon burial term in the redox budget would be reduced from 20×10^{12} mol/yr to 4×10^{12} mol/yr. If all other factors remained equal (which they probably do not—see below), the corresponding value of K_{OXY} would be

$$K_{OXY} = \frac{4+5}{4.8+0.4} = \frac{9}{5.2} \cong 1.7 \qquad (19)$$

We've not quite produced a reduced Archean atmosphere, but we're getting closer. Note that higher volcanic outgassing rates in the Archean would affect this ratio very little, because the increase in CO_2 outgassing (and associated organic carbon burial) would be compensated by an increase in outgassing of hydrogen and other reduced gases.

Is this then an acceptable hypothesis for explaining the rise of atmospheric O_2? The numbers don't quite work, under the assumptions made here, but that is not a serious issue, given the large uncertainties in all of these fluxes. More troubling is the fact that this mechanism is completely dependent on the assumption that 20% of the outgassed CO_2 is buried as organic carbon. Holland made that assumption, as have others, because it is crudely consistent with the carbon isotope record. But it is hard to think of a good physical reason why this must have been true. Indeed, I am aware of only two published explanations.

The first is that the organic carbon burial fraction is controlled by the C:P ratio in igneous rocks (Junge et al., 1975): only enough P is available to bury 20% of CO_2 as organic matter. But this explanation seems unsatisfactory, as P can leave the ocean in several different ways (as phosphorites, for example) and because one might expect to see a secular change in organic carbon burial when the deep oceans became oxygenated, because P is remineralized less efficiently in sediments overlain by oxic waters (Van Cappellen and Ingall, 1996). This latter issue is complex, as the faster recycling of P in modern anoxic basins is largely due to the presence of sulfide, which occupies sites on ferric hydroxides in sediments that might otherwise bind P (Bjerrum and Canfield, 2002). (The sulfide itself is present because the modern oceans are rich in sulfate, which gets reduced to sulfide in anoxic regions.) Hence, these latter authors argued that P was actually removed very rapidly in the sulfide-free Archean oceans. But this hypothesis has itself been challenged, because the high abundance of dissolved silica in Archean ocean water may have tied up those same sites, again leading to efficient P recycling (Konhauser et al., 2007). Planavsky et al. (2010) use this to argue that P may actually have been more abundant in the Precambrian oceans than in today's ocean. In any case, there is little evidence to support the hypothesis that organic carbon burial is tightly constrained by P availability. If P were the controlling factor, one would expect to see more variability in δ_{carb} over time than is actually observed, because the P budget has itself been variable.

The second explanation (Holland, 1973) is that the organic carbon burial fraction is controlled by redox balance: only enough hydrogen is available to reduce ~20% of outgassed CO_2 to organic carbon. This mechanism has problems, as well, as one might expect f_{org} to have increased following the GOE because less hydrogen should have been lost to space. But perhaps this change was compensated by changes in other parameters affecting the carbon cycle, as discussed above, or by continued high loss of hydrogen to space due to enhanced Proterozoic CH_4 concentrations (Catling et al., 2002; Pavlov et al., 2003). The looser the isotopic constraints on f_{org}, the more likely it seems that availability of reducing power was the factor that controlled it. If so, then invoking a constant 20% organic carbon burial fraction as a constraint on global redox balance involves circular reasoning, thus weakening the proposal made by Holland (2002, 2009). So, we should look for other factors to explain the timing of the GOE.

3.2. Submarine versus subaerial outgassing mechanisms

Other ways to change the ratio of hydrogen production to hydrogen consumption have been suggested. One mechanism that has received considerable attention is the hypothesis proposed by Kump and Barley (2007) and further elaborated, using a different methodology, by Gaillard et al. (2011). In both of these models, the rise of O_2 is suggested to have been triggered by a gradual switch from submarine to subaerial volcanism. Submarine volcanic gases tend to be more reduced, according to Holland's f-value analysis, whereas subaerial volcanic gases are more oxidized. (I have just criticized the f-value analysis, but bear with me, I'll move away from it below.) Kump and Barley estimated that $f = 0.48 \pm 0.14$ for modern subaerial outgassing, and

$f = 1.04 \pm 0.04$ for submarine outgassing. Hence, a shift from totally submarine outgassing to a mix of subaerial and submarine outgassing would (just barely) produce the desired shift in redox state. But Kump and Barley also pointed out that, in a sulfate-free Archean ocean, the fluids passing through the hydrothermal vents should have been more reduced. Using methods from Kump and Seyfried (2005), they estimated that $f \cong 1.5$ for Archean hydrothermal vents. According to Holland's analysis, this would be sufficient to produce a reduced Archean atmosphere.

The Kump and Barley mechanism could be part of the answer to this puzzle. Submarine fluids do appear to be more reduced than sub-aerial volcanic gases, based on analyses like the one just described, and the idea that the continents were growing during this time has been frequently postulated. However, this proposal has several problems, any one of which could cause it to fail. First, it does not explicitly satisfy redox balance, i.e., Eq. (12) above. In particular, the presence or absence of sulfate in water entering the vents should not be used to estimate the redox state of water coming out of the vents. Indeed, the flow of sulfate-rich seawater into modern vents should *increase* the net input of hydrogen into the atmosphere–ocean system because it leads to oxidation of ferrous iron in the seafloor (included in the Φ_{OW} term in Eq. (12)). If this effect were included, the Kump and Barley mechanism, as described, might actually go the wrong way. The second problem is that the main reason that hydrothermal vent fluids appear to be more reduced than subaerial volcanic gases is because they have a higher S:C ratio. This causes their f value to be higher, according to Holland's mode of analysis. But, as pointed out above, the f-value analysis is inherently circular because it *assumes* that 20% of outgassed CO_2 is buried as organic carbon. Third, subaerial volcanoes today are fed by subducted slabs containing ferric iron that was oxidized by sulfate- and O_2-rich seawater; hence, it is not surprising that they are more oxidized than submarine volcanoes in which the basalts are formed from melting of mantle material. This would not have been true during the Archean, however, so an increase in subaerial outgassing might have had little effect on volcanic gas redox states.

The recent paper by Gaillard et al. (2011) bypasses some of these problems and hence is easier to analyze quantitatively. In their model, the composition of outgassed volcanic gases is estimated by computing thermodynamic equilibrium with a melt, and is thus independent of the composition of the circulating vent fluids. Somewhat surprisingly, applying the f-value analysis to their model suggests that it doesn't work very well (Kasting et al., 2012): The f-values computed at 100 bar pressure are only marginally higher than those computed at 1 bar (see Table 2). The reason is that the proportion of CO_2 in the released gases drops by a factor of 3 as the pressure decreases from 100 bar to 1 bar. Because the f-value analysis assumes that 20% of the outgassed CO_2 is buried as organic matter, this results in a decreased O_2 source (increased H_2 sink) as subaerial volcanism becomes more important, which of course goes the wrong way to explain the GOE. If one relaxes this assumption, though, then the mechanism works much better. Applying Eq. (2) to the Gaillard et al. data, using mole fractions rather than outgassed fluxes, allows one to calculate the relative values of the total hydrogen outgassing rate, $\Phi_{out}(Red)$, for both subaerial and submarine volcanism (Table 2

again). These values change by roughly a factor of 2 for both Case S1 and S2 of Gaillard et al., indicating that the submarine volcanic gases are about twice as reduced as the subaerial ones. So, it appears that the earlier hypothesis of Kump and Barley (2007) has merit, despite the problems detailed above.

Is this change enough to cause the atmosphere to flip its oxidation state? The answer depends on what other assumptions are made. If we start from Eq. (18) (the K_{OXY} parameter calculated using today's organic carbon and pyrite burial fluxes), then doubling $\Phi_{out}(Red)$ during the Archean yields

$$K_{OXY} = \frac{20 + 5}{9.6 + 0.4} = \frac{25}{10} = 2.5 \qquad (20)$$

So, in this case, this mechanism by itself is not enough to produce a reducing atmosphere. But if one modifies the burial fluxes as described in the previous section, i.e., if one starts from Eq. (19), then we get

$$K_{OXY} = \frac{4 + 5}{9.6 + 0.4} = \frac{9}{10} = 0.9 \qquad (21)$$

In this case, $K_{OXY} < 1$, and so the mechanism predicts a reduced Archean atmosphere and an oxidized modern one, in agreement with observations. In other words, it works, but only in combination with other factors and only if one assumes a switch from completely submarine to completely subaerial outgassing. But a significant fraction of the modern reduced gas flux comes from H_2S emanating from submarine hydrothermal vents (Kasting and Canfield, 2012, Table 7.1), so this switch is by no means complete even today. The Gaillard et al. (2011) model also neglects the possibility that submarine volcanic gases may reequilibrate with the rocks surrounding the hydrothermal vents at lower temperatures than those at which they were released (an assumption that is implicit in the earlier Kump and Barley (2007) model). Analyzing this process quantitatively would require a more elaborate outgassing model. I conclude that, while this mechanism may have contributed to the rise of O_2, it is unlikely to have been the primary trigger for the GOE, and its quantitative importance remains poorly determined.

3.3. Continental oxidation and hydrogen escape

Still other ways of modifying the Archean redox budget have been suggested. As mentioned earlier, Catling et al. (2001) (see also Catling and Claire, 2005; Claire et al., 2006) hypothesized that hydrogen escape to space oxidized the continents, and this change led to a decrease in reduced gases emanating from metamorphic processes such as mountain building. Metamorphism differs from volcanism in that the rocks that are involved heat up but do not melt. This proposal starts from an observation that is indisputably correct: escape of hydrogen to space oxidizes the planet. The reason this is true is that most of Earth's hydrogen is thought to have been brought in originally as H_2O, either as water ice or as water of hydration in silicate minerals. If hydrogen escapes too slowly to carry off oxygen, as was likely the case during most of Earth's history, then oxygen must be left behind by this process.

Some of the numbers also look good for this mechanism. Catling et al. (2001) argue convincingly that much of the ferric iron now present in ancient continental crust was created prior to the GOE. (This ferric iron is in continental basalts that have been oxidized metamorphically or hydrothermally, according to their Table 2, not in shales, which remained reduced during that time (Bekker and Holland, 2012).) Today, the Fe^{+3}/Fe^{+2} ratio in such rocks is of order unity. But in midocean ridge basalts, from which the continental crust was ultimately derived, the Fe^{+3}/Fe^{+2} ratio is <0.1; hence, a large amount of iron, equivalent to some 2×10^{21} mol O_2, must have been oxidized over time (Lecuyer and Ricard, 1999; Catling et al., 2001). The amount of buried organic

Table 2
Oxidation parameters for two Gaillard et al. (2011) models.

Pressure (bar)	Model S1		Model S2	
	f[a]	Relative $\Phi_{out}(Red)$[b]	f[a]	Relative $\Phi_{out}(Red)$[b]
1	0.60	0.22	0.73	0.16
100	0.62	0.40	0.88	0.33

[a] Holland f values computed by Kasting et al. (2012).
[b] Relative (dimensionless) fluxes computed by weighting the predicted mole fractions of the various volcanic gases by their stoichiometric weights from Eq. (2). To convert to dimensional units, one would need to normalize by the modern total reductant flux.

carbon tied up in crustal rocks is $<1.3 \times 10^{21}$ mol (Claire et al., 2006); thus, unless organic carbon was subducted more efficiently than ferric iron, which seems unlikely, much of the required oxygen must have come from hydrogen escape. A recent estimate of integrated hydrogen escape, based on the D/H ratio of hydrated minerals in 3.8-billion-year-old rocks from Isua, West Greenland, supports this notion (Pope et al., 2012). These authors estimate that ~1/4th of an ocean of water was lost subsequent to this time. The modern ocean contains 1.4×10^{21} kg of water, or ~2×10^{20} mol H_2O. Based on the stoichiometry of Eq. (1), this corresponds to an O_2 source of half that amount, or 1×10^{20} mol, which is just the amount needed to oxidize the continental crust.

Where did the escaping hydrogen come from, though, and how exactly did it oxidize the crust? Claire et al. (2006) point out at least half of outgassed hydrogen today comes from metamorphism, specifically the release of CH_4 from continental hydrothermal systems and mud volcanoes. They estimate that the current flux of metamorphic CH_4 is 1.5×10^{12} mol/yr in terms of O_2 equivalents, or 3×10^{12} mol/yr in H_2 units. By comparison, the total H_2 outgassing flux from Table 1 is 4.8×10^{12} mol/yr. Claire et al. suggest that this metamorphic CH_4 flux could have been up to 20 times higher in the Archean. If that were true, then the value of K_{OXY} in Eq. (14) or (16) would be well below 1, easily accounting for a reduced Archean atmosphere.

If one looks in more detail at this mechanism, however, problems appear. First, the continents were probably smaller back during the Archean, as pointed out earlier (Section 3.1). This, by itself, should have led to a lower flux of metamorphic gases. Second, most of the CH_4 coming from the continents today is *thermogenic* in origin: it comes from the breakdown of stored organic matter, some of which was produced by land plants and some of which is marine in origin (Etiope et al., 2009). This source of CH_4 could have been much smaller on the Archean Earth. The flux of CH_4 from strictly abiotic metamorphic process is several times less, ~0.3×10^{12} mol CH_4/yr, or 0.6×10^{12} O_2 equivalents/yr (Fiebig et al., 2007), about 2.5 times smaller than the value assumed by Claire et al. That would not be a problem, if indeed this flux was 20 times higher during the Archean. But would that actually have been true? The reason it scales up in the Claire et al. model is because they assume that the redox state of metamorphic gases is controlled by thermodynamic equilibrium with the rocks from which they are released. Archean continental rocks, by presumption, had lower Fe^{+3}/Fe^{+2} ratios; hence, they had lower oxygen fugacities and released more reduced metamorphic gases. Metamorphism occurs at relatively low temperatures, however, so the assumption of thermodynamic equilibrium is suspect. Furthermore, this model requires a kinetic mechanism by which to oxidize iron at modest temperatures, without using O_2. Such a mechanism is available: we know that water can oxidize certain types of ferrous iron-bearing rocks through the process of serpentinization, which I represented earlier by reaction (5). This reaction, though, is limited to ultramafic rocks; it does not happen spontaneously with normal basalts. Fortunately, the Archean continents may have been rich in ultramafic rocks. One of the defining petrologic features of that time period is the widespread occurrence of greenstone belts containing ultramafic rocks termed 'komatiites' (Arndt and Nisbet, 1982). Thus, it is likely that the Claire et al. mechanism did operate at some level. But the important factor that contributed to the GOE was that the abundance of greenstone belts decreased with time, leading to a reduced rate of H_2 production from serpentinization.

3.4. Serpentinization of seafloor

The real problem with the Claire et al. (2006) hypothesis is that it overlooks a related process that may have been even more important. If the Archean continents contained a lot of ultramafic rock that was prone to serpentinization, then should not the seafloor have followed suit? We asked this question in Kasting and Canfield (2012). The evidence for this process is less apparent than for continental oxidation,

as most of the seafloor has been subducted and lost; however, that is no reason to ignore it. Although we do not know for sure how plate tectonics has changed with time, all authors agree that upper mantle temperatures were higher than today. In many models (Burke et al., 1976; Sleep and Windley, 1982; Bickle, 1986; Moores, 1986, 1993; Davies, 2002; Moores, 2002; Sleep, 2007) these higher mantle temperatures should have led to an increased depth of partial melting at the ridges and, hence, to increased oceanic crustal thickness. Increased partial melting should also have tended to make this oceanic crust more mafic, because the greater the degree of melting, the more the igneous product should have resembled its mantle source. Because of the uncertainty about how plate tectonics operated in the past, it is difficult to quantify just how big the source of H_2 from seafloor serpentinization might have been. The modern value listed in Table 1 is only 0.4×10^{12} mol/yr. But if this process was 10 times more extensive during the Archean, it would have competed with volcanic outgassing as a source for H_2. As the mantle cooled and the seafloor became less ultramafic, the associated H_2 source would have decreased, facilitating the rise of atmospheric O_2. So, if changes in the composition of continental rocks contributed to the GOE, as argued in the previous section, then changes in seafloor composition with time should have been equally, or even more, important.

3.5. Banded iron-formations as the trigger for the GOE

A fifth category of mechanisms for triggering the GOE is based on the occurrence of banded iron-formations (BIFs) prior to 2.4 Ga and their relative disappearance afterwards (Isley and Abbott, 1999; Barley et al., 2005; Goldblatt et al., 2006; Bekker et al., 2010). Isley and Abbot compiled age dates of known BIFs and showed that their occurrence rate peaked just before 2.4 Ga and then dropped off considerably for several hundred million years after that before one final large deposition episode around 1.8 Ga. The timing of the initial decrease in BIF deposition agrees nicely with that of the GOE. These authors, along with Barley et al. (2005), argued that peak episodes of BIF deposition also correlate with evidence from flood basalts and komatiites for large-scale mantle plumes.

The ferric iron in BIFs could have been produced by reaction of upwelled ferrous iron with photosynthetically produced O_2. That was likely the dominant process in the early Proterozoic and perhaps in the Late Archean, as well, following the origin of cyanobacteria. Before that, iron may have been oxidized without the involvement of free O_2 by anaerobic photosynthetic bacteria (Ehrenreich and Widdel, 1994; Konhauser et al., 2002; Kappler and Newman, 2004). These organisms use ferrous iron to reduce CO_2 to organic carbon. The product is generally ferric oxy-hydroxides such as goethite, $Fe(OH)_3$; however, most of this ferric iron was converted to magnetite during either diagenesis or metamorphism, so the overall stoichiometry is similar to that shown by Eq. (5). (I'll ignore the time delay between these last two processes, although it implies that even more H_2 may have been released during the initial deposition of BIFs.) As noted earlier, iron oxidation is not likely to have occurred spontaneously within normal (silicic or mafic) crustal rocks. However, it is readily catalyzed by these bacteria, which use the energy of sunlight to make the reaction go. Indeed, sunlight itself—UV wavelengths shorter than ~300 nm—can oxidize ferrous iron to ferric in water solution with accompanying release of hydrogen (Braterman et al., 1983). From a redox balance standpoint, it doesn't really matter how the iron was oxidized or whether free O_2 was involved. As long as the dominant mineral phase in the oxide BIFs was magnetite, the rate of hydrogen production would have been determined by the stoichiometry of reaction (5).

Holland (2006) considered this process and concluded that BIF deposition was a minor, but non-negligible, sink for O_2. The minimum sink for O_2, or source for hydrogen, during the Late Archean can be estimated from the rate of iron deposition in the Hamersley BIF. That rate, according to Holland, was about 0.5×10^{12} mol Fe/yr, equivalent to

an H_2 source of one-third that value, or ~0.2×10^{12} mol/yr. This estimate assumes that the microbands are annual—an assumption that will be retained throughout this discussion (but see Isley (1995) and Krapez et al. (2003) for alternative views). That value is small, a few percent, compared to other terms in the global redox budget (*e.g.*, Eq. (19)). Holland's upper limit for iron deposition is 3×10^{12} mol Fe/yr, corresponding to an H_2 source of 1×10^{12} mol/yr. That would increase the denominator of Eq. (19) by about 20%. If this iron was supplied from hydrothermal vent fluids, as seems likely, even that relatively low number requires a factor of 80 increase in the hydrothermal iron flux compared to that emanating from modern vents, a mere 0.04×10^{12} mol Fe/yr (Kump and Holland, 1992). But it may nevertheless be a mistake to ignore this process. Although it sounds large, such an enrichment could have been caused by shallower ocean ridges and a corresponding decrease in the pressure within hydrothermal vent systems (Kump and Seyfried, 2005), coupled with lower oceanic sulfate concentrations at that time. Seawater pH drops sharply as one nears the two-phase boundary, causing it to dissolve much more Fe^{+2} from the basalts. Shallower ridge crests, in turn, could be related to thicker oceanic crust and smaller continents during the Archean (see references in Section 3.1), which would have made the ocean as a whole shallower by spreading it out over a larger area. The oceans are 4 km deep today, on average, and the continents occupy 30% of the Earth's surface, so eliminating the continents entirely should reduce average ocean depth by 1 km, lowering average ridge crest pressure by ~100 bar. Still, the numbers just quoted suggest that Holland was probably right, and that BIF deposition played a relatively minor role in delaying the rise of atmospheric O_2.

That said, there are other ways to put these numbers together that lead to much higher estimates for hydrogen production from BIFs. (This discussion comes from Kharecha et al. (2005)). Fittingly, they also start from Holland's numbers. According to Holland (1984, p. 388), the Archean deep oceans probably contained ~3 ppm Fe^{+2} by weight, or 0.054 mol Fe^{+2}/m^3. Holland derived this number by assuming that the Archean ocean contained modern Ca^{++} concentrations and that it was saturated with respect to both calcite ($CaCO_3$) and siderite ($FeCO_3$). This ferrous iron concentration is also about what one would need to explain the rate of deposition of the Hamersley Iron Formation, given 1 mm-thick annual bands and an upwelling rate of 3000 m/yr, similar to values observed off the coast of Peru, northwest Africa, and Baja, California (Holland, 1984, p. 396). So, the Hamersley is being invoked here, as well, albeit in a different way.

To extrapolate to global BIF deposition rates, we need to estimate a global average upwelling rate. Today, the ocean is on average 4 km deep and overturns in ~1000 yr, so the average upwelling rate is 4 m/yr. Assume that the global upwelling rate was similar during the Archean. Multiplying by the dissolved Fe^{+2} concentration and by the surface area of the ocean, 3.5×10^{14} m^2 yields an upwelled Fe^{+2} flux of 76×10^{12} mol/yr. This number is some 25 times larger than the quoted upper limit on the BIF deposition rate from Holland (2006). So, if even a fraction of it made its way into BIFs, the corresponding hydrogen source could have been much larger than estimated above, perhaps as high as 25×10^{12} mol/yr (Eq. (5)), which is comparable to the H_2 sink from burial of organic carbon shown in Table 2. Catling et al. (2001) did this same calculation in their Note 10 and got a similar answer. If this number is correct, one could keep the Archean atmosphere/ocean system reduced even with today's high rate of organic carbon burial. This would require an enormous dissolved Fe^{+2} flux from ridges, though, over 2000 times the modern flux. Most likely, much of the ferric iron deposited in BIFs was remobilized to dissolved Fe^{+2} by iron-reducing bacteria, so that only a small fraction of it made its way permanently into sediments. In that case, the required iron supply from vents could have been much smaller. But we need to think carefully about how much iron could conceivably have been supplied, as the potential hydrogen source from BIFs is clearly quite large.

3.6. Biological/trace element hypotheses

Finally, various authors have proposed biological triggers for the GOE, some of which involve the availability of different trace elements. Konhauser et al. (2009) suggested that a decline in mantle temperatures led to decreased production of ultramafic seafloor and hence to a decreased flux of Ni to the oceans. This idea is thus superficially similar to the one discussed in Section 3.4, except that the authors focused on the availability of Ni. Ni is an important constituent of various cofactors used by methanogens, so a decrease in Ni supply near the end of the Archean could conceivably have led to a decrease in methanogenesis and perhaps to a corresponding increase in atmospheric O_2 (Zahnle et al., 2006). On closer inspection, however, this mechanism fails to produce the desired result; indeed, it goes in the wrong direction. What matters is *not* the direct reaction of methane with O_2; rather, it's the effect of this process on the global redox budget. If the methane that was being produced originated from atmospheric hydrogen via

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{21}$$

then a decrease in methanogenesis should have decreased atmospheric total hydrogen mixing ratio (Eq. (8)), thereby decreasing both hydrogen loss and O_2 production. If, on the other hand, the methane was coming from fermentation and methanogenesis within sediments, the net reaction would have been

$$2CH_2O \rightarrow CH_4 + CO_2 \tag{22}$$

Each mole of CH_4 that was produced should have led to 2 mol of escaping H_2, but the 2 mol of CH_2O that would have been buried had the methanogens not been there are equivalent to 4 mol of H_2 (Eq. (10)); thus, the effect of this change is once again to decrease H_2 loss, and thus decrease O_2 production. So, this mechanism cannot have contributed to the rise of atmospheric O_2.

A more promising biological innovation would have been an increase in primary productivity caused by an increase in the availability of fixed nitrogen. Mo and V are both key components of different *nitrogenase* enzymes that are used by modern cyanobacteria to break the N_2 triple bond, and both elements are insoluble under reduced conditions. Scott et al. (2008, 2011) suggested that increased availability of Mo near the end of the Archean could have fueled biological productivity, thereby increasing organic carbon burial and associated O_2 production. And there does appear to have been an influx of Mo at that time, based on analysis of ancient sediments (Anbar et al., 2007). This raises the question: Why did this influx occur? Oxygen released into an anoxic atmosphere from localized 'oxygen oases' in the surface ocean (Kasting et al., 1992) should have formed short-lived plumes that would have dissipated with minutes to hours (Pavlov et al., 2001). It seems unlikely that such plumes have been capable of causing oxidative weathering on nearby continents. Perhaps the entire atmosphere switched from reducing to oxidizing for short time periods to create the Mo pulse. But, if that were the case, then Mo was more important in stabilizing the O_2 rise than in triggering it initially. That doesn't discount its importance, but it means that one must look for additional triggering mechanisms.

Alternatively, early cyanobacteria might have entirely lacked the ability to fix nitrogen (Grula, 2005; Kasting and Canfield, 2012). It is usually assumed that they could do this, as N-fixation capability is widespread among prokaryotes. However, nitrogenase is poisoned by O_2; hence, modern cyanobacteria have developed elaborate mechanisms, *e.g.*, circadian rhythms (used by *Trichodesmium*) or heterocysts (used by *Nostoc*), to keep these compounds separate. If early cyanobacteria lacked these protective mechanisms, then their productivity might have been self-limiting, because the O_2 that they produced would have deprived them of the fixed nitrogen they needed

to grow. Unlike the Mo hypothesis, this mechanism does not require that oxidative weathering occurred prior to the GOE. If genomics could provide support for this hypothesis, it would give a convenient explanation for the delay in the rise of O_2.

4. What triggered the GOE?

This brings us back to the question asked at the outset: What triggered the Great Oxidation Event? Unfortunately, the answer is still not obvious. Multiple factors appear to be required. I list them below in order of their importance, as I perceive it.

4.1. Cyanobacteria needed to invent oxygenic photosynthesis

The reason is that this is probably the only way to produce a large organic carbon burial flux *and maintain it in the presence of high concentrations of O_2*. Anoxygenic photosynthesis can produce a substantial amount of organic carbon, and the burial flux could be large if the burial efficiency was high, but maintaining a high burial flux in the presence of high O_2 is not possible in such an ecosystem. Cyanobacteria needed to become efficient at producing O_2, as well, and this required the availability of V and Mo—both supplied mostly after the O_2 rise—along with the evolution of nitrogenase protection mechanisms.

We can quantify the importance of oxygenic photosynthesis by comparing modern biological productivity with productivity in an anoxic Archean biosphere. Modern marine net primary productivity (NPP) is ~45 GtC/yr, or 3.8×10^{15} mol/yr (Prentice et al., 2001). Archean NPP has been estimated recently by Kharecha et al. (2005) and by Canfield et al. (2006). The two analyses are broadly similar. Both groups considered three different types of anaerobic photosynthetic metabolisms: H_2-based photosynthesis, Fe-based photosynthesis, and S-based photosynthesis. The first two of these are dominant, unless SO_2 outgassing during the Archean was much faster than today. I'll use Kharecha's numbers here. Kharecha et al. (2005) estimated rates of $(2-9) \times 10^{13}$ mol/yr for H_2-based productivity and 2×10^{13} mol/yr for Fe-based productivity. I'll neglect the latter term, because little of the organic matter from this process appears to have been buried, as evidenced by the paucity of organic matter in BIFs. I take a median value of ~4×10^{13} mol/yr as a reasonable estimate of Archean H_2-based NPP. That is roughly 100 times smaller than the modern rate.

Now, consider how much organic carbon was buried in sediments during the Archean. Today, the burial rate of organic carbon is 1×10^{13} mol/yr (Table 1), so the burial *efficiency* (the ratio of organic carbon burial to NPP) is 1×10^{13} mol yr^{-1}/(3.8×10^{15} mol yr^{-1}) = 0.26 %. The modern burial efficiency is low because most marine sediments are overlain by oxic water containing relatively high concentrations (~28 mM) of sulfate. This allows aerobic heterotrophic (decay) bacteria and sulfate-reducers to efficiently remineralize most of organic carbon that falls into sediments. In a completely anoxic, low-sulfate basin, the burial efficiency should be much higher because remineralization would have to occur by fermentation and methanogenesis. The modern Black Sea, a euxinic basin, has a burial efficiency of ~0.7–2% (Calvert et al., 1991; Arthur et al., 1994). According to Calvert et al., this burial efficiency is *not* anomalously high compared to oxic sediments formed at similar depths and sedimentation rates. But the Black Sea retains substantial sulfate concentrations at depth, and so the burial efficiency in a sulfate-free ocean would presumably be higher. In the absence of sulfate or dissolved O_2, these higher burial efficiencies would presumably apply on a global basis. For the sake of argument, let's assume a global burial efficiency of 2% for the Archean, prior to the origin of oxygenic photosynthesis. If this is correct, then the organic carbon burial rate at this time would have been ~4×10^{13} mol/yr $\times 0.02 = 0.8 \times 10^{12}$ mol/yr, or some 12 times smaller than the modern burial rate. The corresponding H_2 sink is twice this value, or 1.6×10^{12} mol/yr. By comparison, the corresponding

H_2 sink assumed in Eq. (19), for an Archean Earth with no continents, was 4×10^{12} mol/yr, a value some 2.5 times larger than the one just calculated. The fact that we did not get precisely the same answer should not be viewed as alarming, as our estimated Archean NPP and burial efficiency are both uncertain by at least this amount. The important point is that the organic carbon burial rate prior to the origin of oxygenic photosynthesis could have been 5–10 times smaller than today. This can be reconciled with the carbon isotope record if the rate of CO_2 input into the atmosphere–ocean system was also smaller than today, as discussed above. When oxygenic photosynthesis was invented, NPP could have increased by up to a factor of 100, if sufficient fixed nitrogen was available, and the organic carbon burial rate should have increased, as well.

4.2. The continents continued to grow between 3.0 and 2.0 Ga

Continental growth would have affected the global redox budget in multiple ways, as discussed in the previous section. It may have increased the recycling of sulfur and carbon, thereby leading to a relative decrease in the ratio of H_2 to SO_2 and CO_2 in volcanic gases. This was probably the most important change, as Holland (2002, 2009) suggested, and it is the key to reconciling the rise of O_2 with the carbon isotope record. Continental growth should also have increased the ratio of subaerial to submarine outgassing, causing volcanic gases to become more oxidized. And, it could also have led to increases in ocean depth, increasing the pressure within hydrothermal vent systems and reducing their output of ferrous iron, thereby causing a decline in BIF deposition. The basic driver in all three cases was the Earth's gradual tectonic evolution.

4.3. Both the continents and the seafloor became less mafic with time

The upper mantle was hotter back in the Archean, and this led to higher degrees of partial melting. This affected both volcanic rocks erupted on land and seafloor generated at midocean ridges. Both would have been more mafic during the Archean, and thus both were more prone to serpentinization. So, Catling et al. (2001) were correct in saying that gradual oxidation of the continents was a factor in controlling the rise of atmospheric O_2. But the same mechanism applies to the seafloor, as well, and both processes were associated with Earth's gradual tectonic evolution. In that sense, mechanism (iii) is closely related to mechanism (ii).

5. Conclusion

This paper has grown to be longer than originally intended, but that is because the rise of atmospheric oxygen is a complex process that has been studied by many authors.

If anything is new here, it is my attempt to compare the various published models as quantitatively as possible using a self-consistent redox balance framework. I hope Dick Holland would have approved of this effort, as Dick devoted a significant part of his career to calculating global redox budgets and exploring their implications for controls on atmospheric oxygen.

The redox budget analysis described here has other potential applications, as well. For the past 17 years or more, astronomers have been finding planets around other stars using a variety of clever observational techniques. Within the next 20–30 years, they should be able to take spectra of rocky exoplanet atmospheres. If we were to see the signature of O_2 or O_3, the question would immediately arise as to whether that signature is evidence for life. So, when we get to the point of making these observations, we will need to have a thorough understanding of the processes that led to an O_2-rich atmosphere on Earth.

Finally, this last point raises an additional question that has not been addressed here, namely, is atmospheric O_2 bistable, and what is the associated implication for remote life detection? Both Catling

et al. (2004) and Goldblatt et al. (2006) predicted bistable solutions for O_2 using redox balance models similar to the one described here but with time dependence included. In both models, the GOE is triggered by a gradual decrease in the influx of reductants, which tips the global redox balance from reducing to oxidizing. But, in their models, the nonlinear rate of reaction between atmospheric O_2 and CH_4, caused by the development of the ozone layer as oxygen accumulates, results in measureable atmospheric O_2 concentrations (as much as 1% of present) at the same reductant fluxes that are also consistent with much lower O_2 levels. Both astronomers studying exoplanets and geochemists studying the GOE will need to think carefully about this additional complication.

Acknowledgments

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