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## *Waiting for O<sub>2</sub>*

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### ABSTRACT

**Oxygenic photosynthesis appears to be necessary for an oxygen-rich atmosphere like Earth's. However, available geological and geochemical evidence suggests that at least 200 m.y., and possibly as many as 700 m.y., elapsed between the advent of oxygenic photosynthesis and the establishment of an oxygen atmosphere. The interregnum implies that at least one other necessary condition for O<sub>2</sub> needed to be met. Here, we argue that the second condition was the oxidation of the surface and crust to the point where free O<sub>2</sub> became more stable than competing reduced gases such as CH<sub>4</sub>, and that the cause of Earth's surface oxidation was the same cause as it is for other planets with oxidized surfaces: hydrogen escape to space. The duration of the interregnum was determined by the rate of hydrogen escape and by the size of the reduced reservoir that needed to be oxidized before O<sub>2</sub> became favored. We speculate that hydrogen escape determined the history of continental growth, and we are confident that hydrogen escape provided a progressive bias to biological evolution.**

### INTRODUCTION

This volume addresses Earth from its beginnings in the Hadean ca. 4.4 Ga to the rise of oxygen in the Paleoproterozoic a mere 2.2 b.y. ago. Two very interesting things happened on Earth during the first half of its history: (1) life began, and (2) later, and perhaps a bit less important, the atmosphere began to fill up with oxygen. From the perspective of its inhabitants, these may be the two most important events in Earth's history. Neither is well understood.

Oxygen raises two issues that are usefully separated. One is the matter of abundant O<sub>2</sub>, which is the distinctive feature of Earth's atmosphere. The other is the oxidation of the surface and

atmosphere, a state that is more widespread in the solar system. Oxygen and oxidation are different things and reflect different processes acting on different time scales, although it is plausible that one is prerequisite to the other. It could be that it was free oxygen in the atmosphere that oxidized the surface, or it could be that oxidation of the surface allowed free oxygen to endure. Here, we presume that surface oxidation is a prerequisite to O<sub>2</sub>. It has long been considered probable from hints in the geological record that oxygenic photosynthesis appeared much earlier than widespread crustal oxidation (Holland, 1962; Buick, 2008), and thus that surface oxidation played a role in the rise of oxygen (Berkner and Marshall, 1965). Where we go beyond Berkner and Marshall is that we give a reason: Oxygenation is caused by the

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steady loss of hydrogen to space. In our story, the apparent delay between the origin of oxygenic photosynthesis and the establishment of an oxygenated atmosphere is explained by how long it took to oxidize the surface through the steady loss of hydrogen to space (Catling et al., 2001; Claire et al., 2006).

This chapter is not intended to give an even-handed overview of the history of oxygen, if such were possible. The intent of the October 2011 Pardee symposium on which this volume is based was for the speakers to take clear and opposing points of view. This essay holds to the original intent. Our point of view is as stated earlier, but it harms nothing to state it again more forcefully: We think that oxygenation of Earth was caused by hydrogen escape. Hydrogen escape stepped Earth through a series of titratable reservoirs and provided the bias that drove biological evolution to develop the O<sub>2</sub> atmosphere. Readers seeking a modern, broadly encompassing review of oxygen that is relatively free of overt biases would be well served to read Farquhar and Johnston (2008).

## OXIDATION

More than 60 years ago, Harold C. Urey (1952, p. 352) wrote that the “highly oxidized condition is rare in the cosmos and exists in the surface regions of the Earth and probably only in the surface regions of Venus and Mars. Beyond these we know of no highly oxidized regions at all, although undoubtedly other localized regions of this kind exist.” His underlying interest in the matter was in the conditions pertinent to the spontaneous origin of life. Urey was greatly influenced by Oparin’s arguments in favor of an anaerobic origin of life. Oparin regarded a prebiotic source of organic molecules as essential to the phenomenon, and therefore concluded that Earth’s first atmosphere was strongly reducing (Urey, 1952). Urey argued that, because hydrogen is the most abundant element in the cosmos, a reduced atmosphere is to be expected at early times relevant to the origin of life, while the “highly oxidized condition of planetary surfaces” is an evolutionary result of hydrogen escape. In addition, Urey regarded the tension between the reduced interior and the oxidized surface as contributing to life’s subsequent evolution. This too is an important insight into the boundary conditions imposed by a planet on life and its evolution.

It turns out that oxidation of planetary surfaces is not rare in the solar system. In all cases apart from Earth, the oxidation is clearly caused by hydrogen escape. For example, several icy satellites (Ganymede, Europa, Rhea) have extremely thin O<sub>2</sub> atmospheres derived from splitting water molecules in ice by ultraviolet (UV) photons or energetic particle bombardment (Cruikshank, 2010). Hydrogen escapes easily, but oxygen, which is much heavier, does not. As a consequence, over time, the surface ice and any contaminants in the ice become highly oxidized.

Mars provides a more Earth-like example. Mars is red because much of the iron at its surface is oxidized. On Earth, red surfaces like these first appear in the geological record during the Huronian glaciation ca. 2.32 Ga and are one of the classic

indicators of the first appearance of an oxic atmosphere (Holland, 1999; Kump, 2008; Guo et al., 2009; Bekker and Holland, 2012). Mars’s surface is locally characterized by the presence of strong oxidants such as peroxides (seen by *Viking*; Hunten, 1979) and perchlorates (seen by *Phoenix*; Hecht et al., 2009), and on a global scale, there are extensive and locally thick sulfate deposits (encountered by the Mars exploration rovers on the ground and mapped by satellites from above). Hydrogen escape is fast enough on Mars to generate its modest atmospheric reservoir of O<sub>2</sub> in just 10<sup>5</sup> yr (Nair et al., 1994; Zahnle et al., 2008). On Mars, the oxidation appears to be quite shallow, with no evidence that oxidation extends to the mantle or even to the deeper crust. If so, planetary oxidation would have been quick (Hartman and McKay, 1995).

In contrast to the other worlds of the solar system, most accounts of the rise of oxygen on Earth either marginalize or ignore the role of hydrogen escape in oxidizing the surface. Rather, oxidation of the surface is usually ascribed to a shrinking influence of reduced volcanic gases from a reduced mantle compared to the accumulation of reduced carbon (from CO<sub>2</sub>) in continents, or to an enhanced role of continents versus the mantle in weathering, or both, although how the mechanism(s) might work is debated (Holland, 1962; Kasting et al., 1993; Kump et al., 2001; Holland, 2002, 2009; Kump and Barley, 2007; Gaillard et al., 2011). A variant that is easier to understand posits the preferential subduction of reduced matter by the mantle (Hayes and Waldbauer, 2006). The variant is easier to understand because, like H escape, it actually oxidizes the surface.

What these theories have in common is the primacy they assign to secular cooling in Earth’s evolution. Secular cooling is undeniable and has been viewed as a major driver of planetary evolution since the nineteenth century, if not before. For example, Lowell (1908) provides a good general overview of the hypothesis. Secular cooling is obviously a major factor setting the direction and pace of planetary evolution. Its consequences are easy to see throughout the solar system. However, secular cooling does not by itself change the surface’s oxidation state. Hence, theories of oxygenation that start with secular cooling depend on second-order effects to produce oxidation. These are usually effects that decrease the influence of the mantle on the surface over time, either through changes in the rate or style of plate tectonics or in the quantity or quality of volcanic gases, or more indirectly through the consequences of continental growth (which, if a fact, might have something to do with cooling).

On the face of it, the idea that the mantle oxidizes the surface is rather puzzling. The gases that come from the mantle are reducing and have always been reducing, because the mantle is reduced. That they might have been more or less reducing in the past does not make them oxidizing. The reasonable expectation is that the surface would be reduced by these gases. Why the sum of second-order effects should favor oxidizing the surface is a fair question. Net oxidation of the surface by the mantle can occur only if the surface exports more reductant to the mantle (via subduction) than the mantle exhales in volcanic gases. In

other words, convention makes the rather awkward argument that an oxidized surface oxidizes itself by further reducing an already reduced mantle. The Hayes and Walbauer mechanism is not immune from this criticism. By contrast, hydrogen escape acts directly on the redox state of the surface and is categorically oxidizing.

## OXYGENIC PHOTOSYNTHESIS

There is at present little doubt that oxygenic photosynthesis is required to create an oxygen-rich atmosphere like Earth's. Although it is possible to imagine atmospheres that might become oxygenated abiotically through some combination of vigorous hydrogen escape and high rates of stellar UV irradiation, to the best of our knowledge no one has yet succeeded in demonstrating this convincingly with an actual photochemical model. The fundamental reason for this is that thermo-dynamics of typical planetary materials favor O<sub>2</sub> only at very high temperatures. Photosynthesis on Earth makes O<sub>2</sub> from 5800 K sunlight. Even under Mars's favorable circumstances (weak gravity, an oxidized surface, extremely limited weathering owing to extremely low water activities and low surface temperatures, and minimal volcanism and crustal recycling), abiotic processes produce an O<sub>2</sub> partial pressure that is only  $4 \times 10^{-5}$  that of Earth. Detailed photochemical models show that for an Earth-like planet, the abiotic photochemical source of O<sub>2</sub> would be overwhelmed by Earth's volcanic gases, resulting in O<sub>2</sub> partial pressures at the surface on the order of  $10^{-12}$  bar (Kasting and Walker, 1981; Kasting, 1993; Haqq-Misra et al., 2011).

Oxygenic photosynthesis uses sunlight to split water molecules into hydrogen and oxygen. The O<sub>2</sub> is released to the atmosphere as a by-product. The hydrogen is used to reduce CO<sub>2</sub> to water and organic matter. Under an oxygenated atmosphere, most of the organic matter is aerobically respired, closing the cycle, but a fraction of the organic matter is further reduced to inedible carbon that is ultimately buried. Methane is also a product, but it is mostly eaten (using O<sub>2</sub>, sulfate, nitrate, or even ferric iron; Bekker et al., 2010) before it reaches the atmosphere. On long time scales, the net effect of oxygenic photosynthesis today is approximately CO<sub>2</sub> → C + O<sub>2</sub>. This is why C burial is often treated as the source of O<sub>2</sub> (Hayes et al., 1983). Many models focus on biological and geological controls on C burial to reconstruct Phanerozoic histories of O<sub>2</sub> (Bernier, 2001).

Under an anoxic atmosphere, aerobic respiration might still be possible locally where O<sub>2</sub> is made, but we would expect a bigger role for anaerobic pathways and a higher fraction of the organic matter to be reduced, and a much higher fraction of the organic matter made by oxygenic photosynthesis to reach the atmosphere as methane (Walker, 1987). Most of the CH<sub>4</sub> reaches the stratosphere, where it is oxidized with the help of solar UV. Most of the H in CH<sub>4</sub> is destined to escape to space. The net is therefore H<sub>2</sub>O = ½O<sub>2</sub> + H<sub>2</sub> (to space). When oxygenic photosynthesis leads to methane, H escape becomes a source of O<sub>2</sub> (Catling et al., 2001).

Methane is much less reactive than O<sub>2</sub>. If both are vented to the atmosphere by an oxygenic photosynthetic ecosystem, the O<sub>2</sub> and free radicals that are made from O<sub>2</sub> will react with rocks and such (Berkner and Marshall, 1965), while the CH<sub>4</sub> reacts only with free radicals generated from O<sub>2</sub>. As a result, one expects the atmosphere after the origin of oxygenic photosynthesis to be CH<sub>4</sub> rich rather than O<sub>2</sub> rich, and that this will remain the state of the atmosphere for as long as chemical sinks for O<sub>2</sub> remain easily accessed and plentiful. Methane itself leaves few geological traces, but it can polymerize to make aerosols, possibly nitrogenous or sulfurous (Pavlov et al., 2001; Domagal-Goldman et al., 2008; Trainer et al., 2006; Zerkle et al., 2012), which should be isotopically and structurally distinctive. A methane-rich atmosphere also welcomes other more fragile biogenic reduced gases, like sulfides, and thus may reveal itself indirectly by enabling a richer sulfur cycle (Zahnle et al., 2006; Kurzwil et al., 2013).

It is sometimes argued that the advent of oxygenic photosynthesis was not just a necessary, but also a sufficient condition to create an O<sub>2</sub> atmosphere (e.g., Kopp et al., 2005). The appeal here is to brute force kinetics: Photosynthesis using H<sub>2</sub>O is presumed to be so much more biologically productive than photosynthesis reliant on other hydrogen donors that it ought to take over the world on a biological time scale. This is not an irrefutable notion: It is not obvious a priori that the hydrogen source was much more limiting than all other nutrients, such that by removing this limit, biology would pour forth like a flood after a dam burst (Sleep and Bird, 2008). A second presumption is that the flux of biogenic O<sub>2</sub> into the atmosphere would be great enough to utterly overwhelm the capacity of weathering reactions or hungry mouths to consume it; this, too, is at least debatable, albeit there is some evidence in favor of an oxygen overshoot ca. 2.1 Ga (Bekker and Holland, 2012). A more serious problem with this hypothesis is that it has not proved possible to identify when exactly in the geological record the one true revolution took place (Des Marais, 2000; Buick, 2008; Guo et al., 2009). One extreme solution to this paradox is to argue that Earth's atmosphere has always been oxygenated and that the origin of oxygenic photosynthesis predates the geological record (Ohmoto, 1999). However, the overwhelming consensus recognizes several substantial changes in redox conditions at Earth's surface between 3.5 Ga and 2.1 Ga (to say nothing of the evolution of multicellular animals ca. 0.6 Ga, an innovation best explained as heralding the advent of breathable levels of O<sub>2</sub>; Knoll, 2004). The stepwise ratcheting up of oxygenation is inconsistent with its origin in a single event.

## WHERE DOES OXYGEN COME FROM?

The atmosphere, ocean, and crust are oxidized. There are  $0.37 \times 10^{20}$  moles of O<sub>2</sub> in the atmosphere. The current rate of C burial is estimated to be on the order of  $1 \times 10^{13}$  moles/yr (Holland, 2002). At this rate, it would take only 4 m.y. to build up the O<sub>2</sub> in the modern atmosphere. The equivalent to another  $5 \times 10^{20}$  moles of O<sub>2</sub> is stored on the continents as sulfates and sedimentary ferric iron (e.g., iron formations); these are obvious

products of oxic weathering. It would take only 50 m.y. at current rates to build up these inventories.

The buried reservoir of reduced carbon is bigger than the sedimentary reservoirs of oxidized iron and sulfur. A net accumulation of reduced materials in the crust is to be expected if the surface chemistry is dominated by input of reduced gases from the mantle and hydrogen escape is negligible. This is the relationship to be expected if reduced (organic) carbon burial is the reason the surface is oxidized. The  $12 \times 10^{20}$  moles of reduced carbon in the continents (Claire et al., 2006) correspond to 120 m.y. of accumulation. Evidently, oxic weathering of old continental reduced carbon back to  $\text{CO}_2$  must be a major part of the modern oxygen cycle. The final victory of  $\text{O}_2$  has sometimes been identified with a pronounced excursion of  $^{13}\text{C}$  in carbonates to high positive values ca. 2.22–2.06 Ga, called the Lomagundi event (Karhu and Holland, 1996; Bekker et al., 2006; Melezhik et al., 2007; Bekker and Holland, 2012). The isotopic excursion suggests a simultaneous massive burial of reduced carbon. The 120 m.y. time scale for reduced carbon to accumulate in continents corresponds to the duration of the Lomagundi event.

Two bigger reservoirs of oxidized material in the crust are often neglected. Iron in aging continental basalts is generally more oxidized than the iron in freshly erupted basalts. The difference suggests that  $20 \times 10^{20}$  moles of  $\text{O}_2$  have gone into oxidizing continental basalts (Lecuyer and Ricard, 1999). Another way to see this is to compare the mantle, which has an  $\text{Fe}_2\text{O}_3$  content of only 0.1–0.4 wt% (Canil et al., 1994), to average continents, which have 3 wt%  $\text{Fe}_2\text{O}_3$  (Lecuyer and Ricard, 1999). The oxygen reservoir linked to continental ferric iron is bigger than the reduced carbon reservoir, which means that the continental crust as well as the surface are oxidized. This is the relationship to be expected if H escape is the reason the surface is oxidized. The mechanism may be abiotic (e.g.,  $3\text{FeO} + \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + \text{H}_2$ ), but the result would be a net source of  $\text{H}_2$  to the atmosphere and biosphere while the continents accumulated. If this  $\text{H}_2$  passed directly to space without passing through life, it might be possible to keep continental oxidation separated from carbon burial (which would leave the hypothesis that  $\text{O}_2$  originates by burying carbon liberated from  $\text{CO}_2$  intact), but in reality, the  $\text{H}_2$  would be utilized biologically (Kharecha et al., 2005), thus entangling continental oxidation with the carbon cycle.

The biggest oxidized crustal reservoir is  $\text{CO}_2$  in carbonates. Although  $\text{CO}_2$  ice can be abundant in comets, most carbon in asteroids, comets, and meteorites is reduced. Earth probably accreted most of its carbon in a reduced form. Substantial amounts of reduced carbon in a reduced early mantle cannot be ruled out (Hirschmann and Dasgupta, 2009). The  $50 \times 10^{20}$  moles of  $\text{CO}_2$  at Earth's surface (and another  $>100 \times 10^{20}$  moles of  $\text{CO}_2$  in the mantle) were probably (but not certainly) oxidized during accretion or early in the Hadean, and they may have been oxidized by processes taking place inside the mantle (McCammon, 2005), and if so would not count toward the oxidized inventories, but they do represent a significant reservoir that became oxidized on Earth. It is worth recalling that there is little evidence that

much of the  $50 \times 10^{20}$  moles of  $\text{CO}_2$  now in the continents was present in the Archean (Holland, 2009).

The crustal reservoirs are small compared to what could be lost to the mantle, and it is possible that too much has been made of them. Evidence that the upper mantle has not changed its oxidation state since 3.8 Ga (Canil, 2002; Delano, 2001; Trail et al., 2011) tells us little about the lower mantle. The effect of export to the mantle could go either way. Oxidation of the surface could have been accomplished by net export of reduced carbon (Hayes and Waldbauer, 2006) and sulfur rather than by H escape. On the other hand, oxidized iron could have been exported to the mantle.

The excess oxygen in the crust and atmosphere must derive ultimately from splitting  $\text{H}_2\text{O}$  followed by hydrogen escape to space or from splitting  $\text{CO}_2$  and subsequent burial of reduced carbon in the mantle. In other words, what is needed is to separate the oxygen from the reductant and then to keep them separated, forever. Hydrogen escape is clearly irreversible, while carbon burial just as clearly is not. Both are possible on a planet with oxygenic photosynthesis. In practice most discussions of the history of oxygen on Earth have focused on  $\text{CO}_2$  and carbon burial, because hydrogen escape today is negligible.

## WHEN DID OXYGEN FIRST APPEAR?

The geological record of the anoxic-oxic transition between ca. 2.5 Ga and 2.1 Ga is often referred to as the Great Oxidation Event (GOE). Authorities differ on what the GOE means, on how broadly it should be defined, or on what geologic indicators should take precedence. Figure 1 provides a cartoon summary of some key events. The classical evidence is concisely summarized by Holland (1999). Changes that mark the GOE include the near disappearance of reduced detrital minerals such as sulfides, siderite, and uraninite from fluvial deposits (Rasmussen and Buick, 1999; Hofmann et al., 2009); changes in the weathering rates of redox-sensitive elements (Anbar et al., 2007; Frei et al., 2009; Reinhard et al., 2009); the appearance of oxidized sediments (red beds) in the place of comparable unoxidized sediments (gray beds; Holland, 1999); the first appearance of massive sulfate deposits (Melezhik et al., 2005); the changing redox state of soils revealed by redox-sensitive elements such as cerium and iron; the evolution and eventual disappearance of massive banded iron formations (this was drawn out well into the Proterozoic; Canfield, 2005; Bekker et al., 2010); fluctuations in iron isotopes that speak of biological meddling (Rouxel et al., 2005; Bekker et al., 2010); and looming above all, the end at 2.45 Ga of huge mass-independent fractionations of sedimentary sulfur isotopes (MIF-S), a signal for which the only plausible source is photochemistry in an anoxic atmosphere (Farquhar et al., 2000; Farquhar and Wing, 2003; Farquhar and Johnston, 2008). In Figure 1, we have put this event at 2.45 Ga. A more conservative assessment of the sparse temporal record brackets the event between 2.32 and 2.45 Ga (Bekker et al., 2004).

Oxygenic photosynthesis appears to predate the GOE significantly, although the earliest evidence is highly circumstantial

(Eigenbrode and Freeman, 2006; Buick, 2008). Buick (2008) regarded thick and widespread black shales ca. 3.2 Ga as suggestive of aerobic photoautotrophy. The Pongola ice ages ca. 2.94 Ga (Young et al., 1998) could signal the disappearance of major greenhouse gases, probably CO<sub>2</sub> or CH<sub>4</sub>. Cold climates can be interpreted as weak circumstantial evidence for oxygen, the enemy of CH<sub>4</sub> (although not of CO<sub>2</sub>), or they could be explained by an anti-greenhouse organic haze (Domagal-Goldman et al., 2008) triggered by an increase of biogenic CH<sub>4</sub>. The massive Steep Rock carbonate reefs suggest a great leap forward in biological productivity, as if some limit had been breached (Wilks and Nisbet, 1988). They are older than 2.78 Ga and probably younger than 2.82 Ga (Fralick et al., 2008).

Evidence that water was used as the hydrogen source in photosynthesis is found in 2.72 Ga lacustrine stromatolites that are big, biogenic, and “evidently phototrophic” (Buick, 2008). There is no evidence of any electron donor for photosynthesis apart from water (Buick, 2008). Although stealthy anoxygenic photosynthesis based on H<sub>2</sub> cannot be ruled out (Kharecha et al., 2005), evidence of oxygen bubbles (Bosak et al., 2009) and structural features characteristic of cyanobacterial mats (Flannery and Walter, 2012) strengthen the case for oxygenic photosynthesis. Extremely low δ<sup>13</sup>C values suggest both methanogenesis and methanotrophy (Hayes, 1994), and the latter implies that O<sub>2</sub> was consumed metabolically. A similar but more widespread prevalence of low δ<sup>13</sup>C values in deep-water carbonates paired with modern photosynthetic δ<sup>13</sup>C values in shallow water suggest a more far-reaching impact of aerobic ecosystems between 2.7 and 2.45 Ga, perhaps achieving global reach by 2.45 Ga (Eigenbrode and Freeman, 2006).

Molecular fossils in ca. 2.72–2.56 Ga rocks are indicative of sterol synthesis (Brocks et al., 2003; Eigenbrode et al., 2008). Biological synthesis of the original molecules demands the pres-

ence of O<sub>2</sub> itself (Summons et al., 2006; Waldbauer et al., 2011), which would leave little room for quibbling, were there not significant doubts that the molecular fossils are as old as the rocks (Rasmussen et al., 2008).

Between 2.7 Ga and 2.45 Ga, there are several reports of elements such as molybdenum and rhenium (Anbar et al., 2007) and chromium (Frei et al., 2009) and minerals such as pyrite (Stüeken et al., 2012), which are insoluble unless oxidized, being weathered from continents and washed into the sea. These occurrences have been given the memorable name “whiffs of oxygen” (Anbar et al., 2007). However, the reported signals, both elemental abundances and isotopic anomalies, are small compared to more modern undoubted products of weathering under an O<sub>2</sub>-rich atmosphere (Scott et al., 2008). Oxidation of Cr to the Cr<sup>+6</sup> of soluble chromate requires O<sub>2</sub> (Frei et al., 2009). Konhauser et al. (2011) suggested instead that conditions may have been acidic enough to mobilize chromium as Cr<sup>+3</sup>. Acid indirectly indicates oxidation. A plausible source of strong acid is oxidation of sulfur or sulfide, but it may not mean O<sub>2</sub>, although Konhauser et al. (2011) preferred both biology and O<sub>2</sub>, as today at Rio Tinto. Whatever the details, it seems clear that by 2.6 Ga at the latest, H<sub>2</sub>O was being used as the hydrogen source in photosynthesis, and the oxidized product was mobile and regionally abundant. Although O<sub>2</sub> need not have been the product, toxic plumes of biogenic O<sub>2</sub> might account for things nicely.

The best date to divide the Archean from the Proterozoic is ca. 2.45 Ga, defined by the seemingly sudden end to an extraordinary isotopic fractionation history of sedimentary sulfur (Farquhar and Johnston, 2008). This was followed quickly by Earth’s plunge into the first of a series of stupendous ice ages (Papineau et al., 2007). There remains some uncertainty regarding when these events took place. We have placed the end of MIF-S at 2.45 Ga following Farquhar and Johnston (2008), but

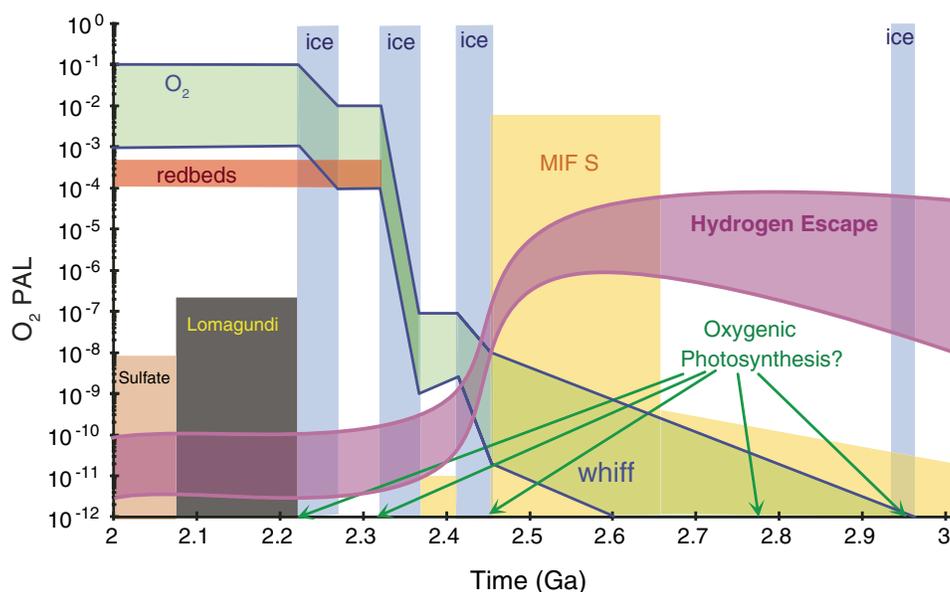


Figure 1. A cartoon history of the Great Oxidation Event. Hydrogen escape rates and the range of mass-independent fractionations of sedimentary isotopes (MIF-S) are indicative of general trends. Approximate tropospheric O<sub>2</sub> levels are estimated but should not be taken too literally. Below ~10<sup>-5</sup> present atmospheric levels (PAL), O<sub>2</sub> levels are ill-defined because the molecule would not in general be well mixed in the troposphere. Key dates are taken from Papineau et al. (2007), Scott et al. (2008), and Guo et al. (2009). “Whiff” [of O<sub>2</sub>] refers to geochemical hints that free O<sub>2</sub> was present in the late Archean environment (Anbar et al., 2007).

dates as early as 2.48 Ga and as late as 2.38 Ga are possible (James Farquhar, 2013, personal commun.). Both events signal profound changes in the composition of the atmosphere that are almost certainly linked to the atmosphere's oxygenation. It is notable that these dates record the disappearance of things that were remarkable about the Archean environment—the mechanism for fractionating sulfur isotopes, thermal blanketing by unidentified greenhouse gases—rather than the advent of abundant  $O_2$  in the atmosphere.

Red beds may be the highest fidelity and most directly pertinent of the classic geological indicators of the atmosphere's changing redox state (Kump, 2008). Red beds record conditions at or near the surface that oxidized sediments in fluvial deposits. It is inferred that the oxygen came from the atmosphere. Figure 1 places the gray bed–red bed transition at 2.32 Ga and after the second of the three Paleoproterozoic ice ages that began ca. 2.45 Ga following Papineau et al. (2007) and Guo et al. (2009).

The latest date that has been considered for the GOE, ca. 2.22 Ga, refers to the onset of the Lomagundi  $\delta^{13}C$  carbonate isotope excursion (Karhu and Holland, 1996; Bekker et al., 2006; Melezhik et al., 2007; Bekker and Holland, 2012) and to the massive Hotazel manganese deposit that followed the last of the great Paleoproterozoic ice ages. This—the last possible moment—is where Kopp et al. (2005) placed the origin of oxygenic photosynthesis. This is also around the time that the first massive sulfate deposits appear (Holland, 2002; Schroeder et al., 2008). The Lomagundi isotope excursion suggests that a great deal of isotopically light reduced carbon was buried, which on the modern Earth would imply that a great deal of  $O_2$  was left behind in the atmosphere, in obedience to the net reaction  $CO_2 = C + O_2$  (Bekker and Holland, 2012). Kopp et al. (2005) suggested that the third ice age was the biggest and baddest and therefore the best ice age to link to the origin of oxygenic photosynthesis.

## SULFUR

Sulfur is particularly important to oxygen because it is, with carbon and iron, one of the three abundant elements that can easily change oxidation state at ordinary conditions. The record of sulfur's ordinary mass fractionation (denoted  $\delta^{34}S$ ) is consistent with increasing oxidation of the surface beginning in the late Archean (Fig. 2). The widening envelope bounding the scattered data indicates that greater amounts of sulfur were becoming biologically available, presumably as soluble sulfate in the seas, which afforded biology the opportunity to be more choosy about which sulfur isotopes they used (Canfield, 2005). The result is a progressively increasing scatter in  $\delta^{34}S$  from 2.7 Ga to 2.1 Ga.

The extraordinary fractionations that characterize the Archean are recorded with sulfur's third isotope. This fractionation, denoted  $\Delta^{33}S$  (often called mass-independent fractionation of sulfur, or MIF-S for short), is the difference between the mass-dependent fractionation of  $^{33}S$  that would be expected from the  $\delta^{34}S$  (were this mass dependent in the ordinary sense) and what is actually observed. Very large nonzero values of  $\Delta^{33}S$  seem to

disappear ca. 2.48 Ga, with more modest but still significant  $\Delta^{33}S$  persisting until ca. 2.38 Ga (Farquhar and Johnston, 2008; James Farquhar, 2013, personal commun.).

The only known way to get MIF-S big enough to give the observed  $\Delta^{33}S$  signal invokes atmospheric photochemistry driven by solar UV (Farquhar et al., 2000; Farquhar and Johnston, 2008). An atmospheric source has two requirements. First, the UV cannot be absorbed by ozone. Ozone becomes abundant when the atmosphere contains more than 0.1%  $O_2$ . Thus, there cannot have been much  $O_2$  in the atmosphere. Second, there have to be at least two channels available to remove sulfur from the atmosphere (Pavlov and Kasting, 2002), in order to keep the two

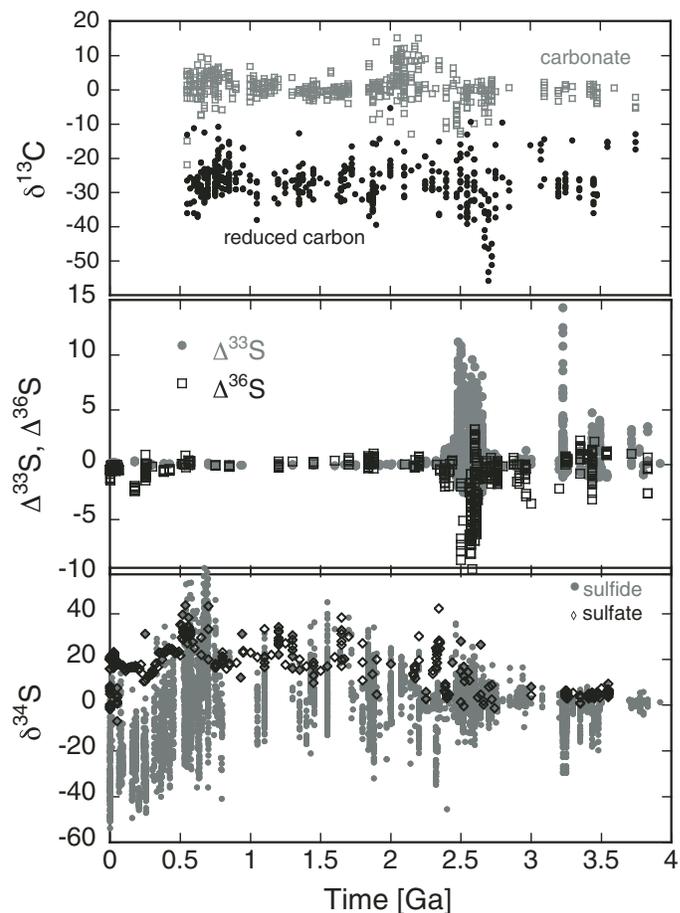


Figure 2. (Top) Carbon isotope history in carbonates ( $\delta^{13}C \approx 0‰$ ) and in reduced carbon ( $\delta^{13}C \approx -30‰$ ). (Bottom) The widening dispersion of ordinary mass-dependent fractionation  $\delta^{34}S$  as a function of time on Earth suggests that sulfur becomes progressively more abundant and less dear to life (Canfield, 2005). (Middle) Mass independent S fractionation  $\Delta^{33}S$  (Farquhar and Johnston, 2008) appears to increase as the biologically accessible sulfur pool grows until the signal vanishes ca. 2.45 Ga, to be followed by a series of major ice ages. The late Archean marks the time when biogenic reduced gases such as  $CH_4$  and  $H_2S$  were abundant and biogenic  $O_2$  suppressed. This figure uses databases compiled by R. Buick, E. Stüeken, and J. Farquhar. Use of their data here does not imply their support for our interpretations of these data.

complementary  $\Delta^{33}\text{S}$  flavors separate (if, as today, nearly all S left the atmosphere as sulfate aerosols, the  $\Delta^{33}\text{S}$  would sum to naught). Laboratory experiments (Farquhar et al., 2001; DeWitt et al., 2010) show and photochemical models predict (Pavlov and Kasting, 2002; Zahnle et al., 2006; Kurzweil et al., 2013) that both sulfate aerosols and elemental sulfur ( $\text{S}_8$ ) aerosols should be generated photochemically in an anoxic atmosphere, and that elemental sulfur does not form in an oxic atmosphere. This mechanism could have generated significant nonzero  $\Delta^{33}\text{S}$  values if the atmosphere were deeply anoxic ( $<10^7$  bars  $\text{O}_2$ ; Zahnle et al., 2006) before 2.4 Ga.

Getting the  $\Delta^{33}\text{S}$  signature out of the atmosphere is only the first step toward preserving it in the sediments (Halevy et al., 2010). At first, elemental sulfur and sulfate are likely to stay apart because  $\text{S}_8$  is insoluble in water. Elemental sulfur will be patchily distributed like a dust, while sulfate will dissolve in raindrops and wash into the sea. The next step is harder. Biology is a threat because it will convert insoluble  $\text{S}_8$  into sulfate or sulfide and vice versa, actions that might be expected to dilute or dissipate the  $\Delta^{33}\text{S}$  signal in the vastness of the ocean. Halevy et al. (2010) therefore concluded that biology made little metabolic use of sulfur before 2.5 Ga. This would be an extreme solution. It would work, but it does not fit easily with other evidence that the sulfate pool was increasing (Holland, 2002), nor does it fit with our own prejudice that extreme values of  $\Delta^{33}\text{S}$  in the late Archean stemmed from the cycling, recycling, and photochemical processing of the many biogenic S-containing gases that would have flourished in the biologically perturbed late Archean anoxic troposphere (Zahnle et al., 2006; Kurzweil et al., 2013). The fluxes of biogenic S-containing reduced gases (such as  $\text{H}_2\text{S}$ ,  $\text{CH}_3\text{SH}$ ,  $[\text{CH}_3]_2\text{SH}$ ,  $\text{OCS}$ , etc.) would likely have greatly exceeded the volcanic sources of  $\text{SO}_2$  and  $\text{H}_2\text{S}$ . This encompasses a set of processes for which Halevy et al. did not account. Massive iron formations deposited ca. 2.45–2.72 Ga imply that  $\text{Fe}^{+2}$  was abundant in the oceans and therefore imply that sulfide could not have been, because iron sulfides are insoluble. The lifetime of sulfur in the late Archean oceans was probably very short, and its transport in the oceans was probably limited. Instead of biology not using sulfur, we suspect that, with S insoluble or in short supply, it was used promptly and locally, thus preserving the temporal and spatial variations of the source.

Theory has been used to suggest that the rise of oxygen in the atmosphere should have taken place in a geological instant (Kasting, 1993; Goldblatt et al., 2006). This is because the atmosphere's reservoirs of reduced or oxidized species would have been quite small, and hence rapidly responsive to environmental forces. The one oxygen indicator that shows this expected behavior is MIF-S. Detailed atmospheric photochemical models show that the disappearance of the MIF-S signal is directly consequent to removing reducing gases from the troposphere—probably by reaction with biogenic  $\text{O}_2$ —but does not mean that  $\text{O}_2$  levels were necessarily consistently appreciable at the surface (Zahnle et al., 2006). Steady-state  $\text{O}_2$  abundant enough to stain red beds came later.

## WHY WOULD AN ATMOSPHERE SWITCH TO $\text{O}_2$ ?

It is useful to review a legacy model (Kump et al., 2001) that blamed the rise of oxygen on the changing redox state of volcanic gases.<sup>1</sup> This model is a useful foil to illustrate the concepts in play in their simplest form. The model makes two postulates: (1) that the mantle became more oxidized over time, i.e., that the mantle's  $f_{\text{O}_2}$  (oxygen fugacity) has been secularly increasing; and (2) that on average ~20% of the  $\text{CO}_2$  outgassed from volcanoes has been buried as C and the rest as carbonate—the  $\delta^{13}\text{C}$  record indicates that this ratio has held approximately for the entire sweep of Earth's history.

The model's key idea is to compare the flux of reduced volcanic gases into the atmosphere to the rate at which reduced carbon is buried. If the fluxes of  $\text{H}_2$  and  $\text{CO}$  exceed the reduced carbon burial rate, there is enough  $\text{H}_2$  and  $\text{CO}$  to consume all the  $\text{O}_2$  generated by reduced carbon burial, and the atmosphere remains reduced. The  $\text{H}_2/\text{H}_2\text{O}$  and  $\text{CO}/\text{CO}_2$  ratios in volcanic gases both go as  $f_{\text{O}_2}^{-0.5}$ . As the mantle's  $f_{\text{O}_2}$  increases, the ratios of  $\text{H}_2$  and  $\text{CO}$  to  $\text{CO}_2$  in volcanic gases decrease until they drop below the reduced carbon burial rate. At this point, free  $\text{O}_2$  appears.

This particular model fell from favor because it relies on changing the oxidation state of the mantle. There is evidence that  $f_{\text{O}_2}$  of the upper mantle has not changed to at least as far back as 3.8 Ga (Canil, 2002; Delano, 2001; Li and Lee, 2004), and there is no compelling evidence that  $f_{\text{O}_2}$  of the lower mantle has changed either. One may protest that surely the Archean was more volcanically active than today, and as volcanic gases are reducing, the Archean atmosphere should have been more reduced than today, but by itself this gains us nothing if the ratios of  $\text{H}_2$  and  $\text{CO}$  to  $\text{CO}_2$  in volcanic gases did not change. In this theory, it is the ratio of  $\text{H}_2$  and  $\text{CO}$  to  $\text{CO}_2$  in volcanic gases that is important. Simply changing the rate of volcanic degassing does not work, because the burial rates of C and  $\text{CO}_2$  must both keep pace with the volcanic supply of  $\text{CO}_2$  if  $\delta^{13}\text{C}$  is to remain constant. Some other change is required.

The simplest change would be to postulate a higher  $\text{H}_2\text{O}/\text{CO}_2$  ratio in Archean volcanic gases. This would give a higher  $\text{H}_2/\text{CO}_2$  at a fixed  $f_{\text{O}_2}$ , and thus leave more reducing power in the atmosphere (Holland, 2009). A change in the  $\text{H}_2\text{O}/\text{CO}_2$  ratio coming out of volcanoes implies a proportionate change in the  $\text{H}_2\text{O}/\text{CO}_2$  ratio in the rocks that go into the volcanoes. Holland (2009) showed that it is possible to get the sought-for behavior from a model that divides volcanic  $\text{CO}_2$  emissions into a declining juvenile component and a growing component stemming from recycled crust. Possible evidence for this is that massive carbonates are rare in continental sediments before 2.8 Ga (Holland, 2009), but changes in the way in which carbonates are deposited can also be associated with biological innovation (e.g., Nisbet and Nisbet, 2008).

<sup>1</sup>Kump et al. (2001) also address mantle oxidation by subduction and mantle overturn ca. 2.5 Ga as specific mechanisms for changing the redox state of volcanic gases, and thus link the model to secular cooling of Earth.

Two recent models suggest that volcanic gases were effectively more reducing in the Archean than in the Proterozoic without changing  $f_{O_2}$  of the mantle. Both appeal to the growth of continents. Kump and Barley (2007) suggested that the rise of continents increased the role of high-temperature subaerial volcanism and diminished the role of low-temperature submarine volcanism; the low-temperature volcanism is more strongly reducing. Gaillard et al. (2011) reached a similar conclusion but from changing the pressure rather than temperature; they argued that high-pressure volcanism favors  $H_2S$  over  $SO_2$ , and submarine volcanism is more reducing. This latter work has been criticized (Kasting et al., 2012).

Holland (2002) left  $H_2O/CO_2$  fixed but added sulfur to the system. The evolution of the envelope of  $\delta^{34}S$  in the sedimentary record suggests that sulfur was scarce before 2.7 Ga and became abundant by 2.2 Ga, and thus that its role grew from tracer to major player in the redox budget at roughly the same time that  $O_2$  took over. Holland accepted a constant mantle  $f_{O_2}$  and fixed the C burial rate to 20% of the volcanic  $CO_2$  flux. The redox budget when sulfur is included gives a more complicated relation between volcanic fluxes and C burial, the gist of which is that, while volcanoes mostly emit S as  $SO_2$ , Holland argues that S is removed from the anoxic atmosphere mostly as  $FeS_2$ . Thus,  $H_2$  and CO are tasked with reducing  $SO_2$  to  $FeS_2$  in addition to reducing the  $O_2$  that comes from C burial and H escape. As the amount of sulfur in the crustal rock cycle increased with time, the amount of S-containing volcanic gases increased, and so the burden of reducing  $SO_2$  increased until it overcame the ability of  $H_2$  and CO to reduce it all. At this point,  $O_2$  wins. Holland (2009) modified the argument to allow  $H_2O/CO_2$  to decrease during the Archean, which enhances the effect produced by increasing sulfur.

Holland's model has many points to recommend it, but it cannot be the whole story because it leaves the rough constancy of  $f_{org}$  unexplained, it does not explain why carbonate or sulfate accumulate at the surface, and it does not explain why the surface became oxidized. Holland's model resembles a titration, with sulfur being added to the system until the buffer sustaining the reducing atmosphere (volcanic  $H_2$  and CO vs. C burial) is overcome. Holland explicitly included H escape in his budgets, but as a global oxidizing force, considered it only in relation to the mantle. We have attributed the buildup of a biologically accessible sulfur pool in the late Archean to oxid weathering of igneous sulfides ultimately caused by H escape (Zahnle et al., 2006). Our story fits well with Holland's model, although it may not require it.

## HYDROGEN ESCAPE

Hydrogen escape oxidizes planets, beginning at the surface. Earth is no exception. The pertinent questions are by how much and at what rate. Our hypothesis is quite simple: Hydrogen escape oxidizes the surface and atmosphere until they become oxidized enough that  $O_2$  can accumulate (Catling et al., 2001, 2005). It applies directly and clearly to a model like Holland's (2002), where the key oxidized material to be accumulated is sul-

fate (Zahnle et al., 2006). It can be applied to Guo et al.'s. (2009) suggestion that the delay between the end of MIF-S at 2.45 Ga and the appearance of red beds at 2.32 Ga was determined by titration of oceanic iron. It can also be applied to the oxidation of continental igneous rocks, which as stated earlier, appear to hold the largest reservoir of oxidized material at the surface (Lecuyer and Ricard, 1999; Claire et al., 2006).

To quantify things, we can ask how long it takes for plausible levels of hydrogen escape to oxidize representative crustal inventories. The rate at which hydrogen escapes from Earth is well approximated by Hunten's diffusion limit (Hunten and Donahue, 1976), which can be evaluated as

$$\phi_{lim} = (5.7 \times 10^{15}) f_{tot}(H_2) \text{ moles/yr}, \quad (1)$$

where  $f_{tot}(H_2) = f(H_2) + f(H_2O) + 2f(CH_4)$  is the total mixing ratio of  $H_2$  equivalents in the stratosphere. Currently, H escape is small, and the effective  $H_2$  mixing ratio is  $f_{tot} = 7.1$  ppmv, to which  $CH_4$  and  $H_2O$  contribute equally (Nassar et al., 2005). The diffusion-limited escape rate corresponds to the loss of 1 m of water per billion years, or equivalently the production of 0.1 bar of  $O_2$  per billion years.

Hydrogen escape rates in the anoxic Archean atmosphere were probably not negligible (Hunten and Donahue, 1976). Through methane, H escape would be at least in part under biological control (Hunten and Donahue, 1976). The modern-day biogenic  $CH_4$  flux vented into an anoxic atmosphere would support a methane mixing ratio of 1000 ppmv (Kharecha et al., 2005; Zahnle et al., 2006; Haqq-Misra et al., 2008). In the diffusion limit, this corresponds to an  $H_2$  escape rate of  $10^{13}$  moles/yr. This corresponds to a crustal oxidation rate half that generated today by C burial. Other ways to express this are as the loss of 400 m of water over 1 b.y., or as the creation of 40 bars of  $O_2$  over 1 b.y. This is enough bleaching power to oxidize the continents (basalts + sediments – buried carbon) in some 300 m.y. In all likelihood, the biogenic methane flux and the consequent oxidation rates would have been bigger than this following the advent of oxidative photosynthesis, but the present biogenic methane flux would be big enough to do the job.

Judging the importance of escape solely by the magnitude of the term misses the second key point: that H escape is irreversible. Carbon buried in the continents will over the course of the rock cycle be lifted up, exposed to weathering, consume its equivalent of oxygen, and be reborn as  $CO_2$ . The oxidation generated by carbon burial is provisional. The oxidation generated by hydrogen escape is permanent.

## DISCUSSION

If the surface is to oxidize as the influence of the mantle wanes, there must exist some innate tendency of the surface to oxidize. Hydrogen escape is such a tendency. This is our position.

This is not a position that one often encounters in earth science. The more common argument is based on comparing the amount of

reducing power coming from the mantle to a fixed sink of reduced matter. The reduced matter is either buried in the continents or subducted back into the mantle. It is usually thought of as organic carbon made from CO<sub>2</sub>, and thus is often expressed for accounting purposes as a photosynthetic flux of O<sub>2</sub> into the atmosphere (where it does combat with the reduced volcanic gases); more generally, the reduced matter can include metal sulfides made from volcanic SO<sub>2</sub>, which makes the accounting more complicated.

The implicit presumption behind this model is that the production and sequestration of reduced matter can be treated as a background rate that is only weakly dependent on the redox state of the surface environment. The rate may be enforced by biological activity; it may be enforced by the limited availability of a nutrient such as phosphorous. If the mantle supplies more reducing power than is needed to meet the burial rate, the excess hydrogen can be vented to space. Thus, to the extent that hydrogen escape plays a role, its role is fundamentally passive, determined by geological and probably biological evolution. If the mantle supplies less reducing power than needed for the fixed burial rate, the surface and atmosphere become oxidized. If by this point oxygenic photosynthesis had been invented, the atmosphere accumulates O<sub>2</sub>.

Here, we place hydrogen escape at the center of the story. We argue that crustal oxidation is caused by hydrogen escape, that biological evolution is pushed in the direction of inventing an oxygen economy by hydrogen escape, and that therefore oxygen in the atmosphere is a consequence of hydrogen escape. The hundreds of millions of years that elapsed between the invention of oxygenic photosynthesis and the establishment of an oxygen atmosphere would then be the measure of how long it took to oxidize the continents by hydrogen escape. To order of magnitude, the amount of excess oxygen stored in continents is consistent with this picture.

It can be asked whether oxidation of continental igneous rocks is related to the story of O<sub>2</sub>, if the oxidant were in fact water. One can then argue that, if igneous-rock oxidation is exactly balanced by H<sub>2</sub> escape to space, the whole process is entirely abiotic, and therefore does not involve O<sub>2</sub> or any other biological product. Thus, the length of time it took to oxidize the continents is not related to the time interval between the invention of oxygenic photosynthesis and the advent of the O<sub>2</sub>-rich atmosphere.

This argument indirectly raises a good point. It is not O<sub>2</sub> per se that is responsible for oxidizing the crust. The advent of oxygenic photosynthesis by itself does not change the oxidation state of the surface and crust, rather it means more production of both oxidized and reduced materials in equal amounts. Thus, the important point about oxygenic photosynthesis is that it made biology more productive, which can lead to higher H escape rates if it leads to more CH<sub>4</sub> in the atmosphere.

In any event, continental oxidation is not disconnected from biology, even if the oxidant is water. Biology entangles the water-rock-H<sub>2</sub> cycle with CO<sub>2</sub>, organic carbon, and biogenic O<sub>2</sub>. With biology, there is no particular reason to expect near equality between H<sub>2</sub> generated by oxidizing the continents and H<sub>2</sub> escape, and thus it is too simple to treat biology as just canceling out.

Second, continents may be dependent on Earth's oxidation, if we can take continents being oxidized as a clue. Continents are often thought to have grown faster in the Archean or early Proterozoic than afterward (Dhuime et al., 2012), although there is a considerable range of opinion about when, or even if, continents grew (Condie, 1997). It is interesting to ask if the stories of oxygen and granite are related.

Reasonable hypotheses are (1) that continental growth is a direct consequence of Earth's secular cooling, or (2) continents provide a record of how much water-weathered rock has been subducted. Growing continents might promote the growth of atmospheric oxygen by providing bigger sinks for carbon burial, either directly as platforms for storing organic carbon, or indirectly if weathering of emergent continents is the source of phosphorous and if phosphorous is the limiting nutrient that regulates carbon burial (for a mildly skeptical discussion of governance by phosphorous, see Bekker and Holland, 2012). Or, it could go the other way: Bigger continents might delay O<sub>2</sub>, because they must be oxidized as they form.

Here, we suggest that continental growth depends on planetary oxidation and therefore on hydrogen escape. This would be the case if continents need to be oxidized in order to be continents as we know them. For example, Jagoutz (2013) suggested that continent composition ("granitoids") was changed by increasing  $f_{O_2}$  in weathered subducted materials. The subducted oxides include oxidized seafloor (e.g., serpentinization) as well as oxidized continental materials. O<sub>2</sub> itself can have a role if O<sub>2</sub> plumes and O<sub>2</sub> oases played a part in producing oxidized sediments from older continents. In this story, modern continents are a response to planetary oxidation. Continental growth would be expected to have slowed down after the advent of the oxygenated atmosphere ca. 2.3 Ga throttled back the rate of hydrogen escape, and continents would have stopped growing in the Phanerozoic after O<sub>2</sub> jumped to modern values and H escape was effectively shut off. It is even possible that Earth's long slow slog through the Proterozoic was frustrated by the modest levels of hydrogen escape possible in an oxic atmosphere. If so, the Proterozoic, like the Archean, was just another eon waiting for O<sub>2</sub>.

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