The rise of oxygen and the hydrogen hourglass

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Abstract

Oxygenic photosynthesis appears to be necessary for an oxygen-rich atmosphere like Earth's. But available geological and geochemical evidence suggest that at least 200 Myr, and possibly more than 700 Myr, 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_2 needed to be met. Here we argue that the second condition was the oxidation of the surface and crust to the point where O_2 became more stable than competing reduced gases such as CH_4. The cause of Earth's surface oxidation would be the same cause as it is for other planets with oxidized surfaces: hydrogen escape to space. The duration of the interregnum would have been determined by the rate of hydrogen escape and by the size of the reduced reservoir that needed to be oxidized before O_2 became favored. We suggest that continental growth has been influenced by hydrogen escape, and we speculate that, if there must be an external bias to biological evolution, hydrogen escape can be that bias.

Keywords:
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Preamble

Professor Heinrich D. Holland's first major study of the evolution of Earth's atmosphere appeared in 1962 in a book titled *Petrologic Studies: A Volume to Honor*

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A. F. Buddington.[1] The paper strayed far beyond petrology. It is here that Holland first divided the story of Earth's atmosphere into three stages that are recognizable today: the first a Hadean-like era of reduced gases, the second an anoxic era suited to detrital uraninite and rounded pebbles of pyrite, the third an oxic era of increasingly breathable air. Of particular interest to us here is his clear statement of how he saw volcanic gases controlling the growth of oxygen in air: "The third stage began when the rate of production of oxygen by photosynthesis exceeded the rate needed to oxidize injected volcanic gases completely." It is this idea, more than any other, that Holland continued to return to in ever more subtle forms through his long career, and it is the central topic of his final major paper, "Why the atmosphere became oxygenated: A proposal." (Holland, 2009). Holland's statement of the problem has dominated modern thought on the subject.

It therefore seems fitting and proper to rephrase Holland's question in a volume to honor H. D. Holland. The language we use is his, because he invented this way of thinking about atmospheric evolution. Our proposal may seem at odds with Holland's proposal — it cannot be denied that we ask a different question with "Why?" — yet it is not clear that there are any other significant points of disagreement between us. It is unfortunate, to say no more, that we will not enjoy the benefit of reading (or hearing, more likely) Dick's gentle but firm corrections of the previous sentence.

1. Introduction

An oxygen atmosphere raises two issues that are not always separated. One is the matter of abundant O_2, which is the distinctive feature of Earth's atmosphere. The other is the oxidation of the surface and atmosphere, a state that is 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 abundant free oxygen in the atmosphere oxidized the surface, or it could be that oxidation of the surface allowed abundant free oxygen to endure. The view taken here is that surface oxidation is prerequisite to O_2. 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

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[1] Holland (1964) provides a more concise and more internet-accessible discussion of many of these ideas in many of the same words; some of the others were incorporated in his 1984 book *The Chemical Evolution of the Atmosphere and Oceans*.

(e.g., Berkner and Marshall, 1965). Where we differ is that we think of oxygen as a consequence of the steady loss of hydrogen to space. Moreover, we explicitly tie the time it took to oxidize the surface through hydrogen escape to the time taken between the origin of oxygenic photosynthesis and the establishment of an oxygen atmosphere (Catling et al., 2001; Claire et al., 2006).

2. Oxidation

Sixty years ago Harold C. Urey (Urey, 1952) 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 is revealed in his next sentence, "This is essentially the argument of Oparin." To Oparin and Urey the 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. Like Oparin, Urey regarded a reduced atmosphere as essential to prebiotic synthesis, but he also regarded the tension between the reduced interior and the oxidized surface as contributing to life's subsequent evolution. We agree.

Space age exploration has shown that the highly oxidized condition is somewhat more common than Urey expected it to be. 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_2 atmospheres derived from splitting water molecules in ice by *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 closer to home. Mars is red because much of the iron at its surface is oxidized. On Earth surfaces like these ("redbeds") first appear in the geological record during the Huronian glaciation ca. 2.32 Ga and are one of the classic indicators of an oxic atmosphere (Holland, 1999; Kump, 2008; Guo et al., 2009). 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_2 in just 10^5 years (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 Mars, most modern 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, measured relative to burial of reduced carbon (from CO_2) in continents, although the detailed mechanism is debated (Kasting et al., 1993; Kump et al., 2001; Holland, 2002; Kump and Barley, 2007; Holland, 2009; Gaillard et al., 2011). The driving force is planetary cooling. Hydrogen escape plays a subsidiary role in these models: it is determined by the difference between mantle degassing and carbon burial, subject to the constraint that the Archean not become too reduced. A variant that is closer to our point of view posits preferential subduction of reduced matter by the mantle (Hayes and Waldbauer, 2006). The variant is easier to understand because, like hydrogen escape, if it worked it would actually oxidize the surface.

It was long hoped that the answer would be provided by a gradual oxidation of the mantle as it aged (Kasting et al., 1993; Holland, 2002), but evidence that the mantle's oxidation state has not changed in any measurable way since 3.8 Ga (Delano, 2001; Canil, 2002; Li and Lee, 2004), a state that may even extend as far back as 4.35 Ga (Trail et al., 2011), has been received as convincing. More recent versions of the hypothesis compare the steady reducing power of volcanic gases to a secular increase in the amount of carbon and sulfur that these gases would have to reduce (Holland, 2009), or to a secular decrease in the reducing power of volcanic gases by erupting them at later times under shallow water or directly into the atmosphere from emergent continents rather than at high pressure under the deep ocean (Kump and Barley, 2007; Gaillard et al., 2011).

But, stepping back from the details, the idea that the mantle should oxidize 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, or by any other interaction with the mantle. 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 exports via 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 Waldbauer mechanism is not immune from this criticism. LeChatelier's principle would not hold. By contrast hydrogen escape is categorically oxidizing.

3. 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 ultraviolet irradiation, to the best of our knowledge no one has yet succeeded in demonstrating this with an actual photochemical model.[2] The thermodynamics of typical planetary materials favor O_2 only at very high temperatures. Photosynthesis makes O_2 from 5800 K sunlight. Even under Mars's favorable circumstances — weak gravity, an oxidized surface, extremely limited weathering owing to extremely low water activities, low surface temperatures, and minimal volcanism and crustal recycling — abiotic processes produce an O_2 partial pressure that is only 4×10^{-5} that of Earth. Detailed photochemical models show that for an Earth-like planet the abiotic photochemical source of O_2 would be overwhelmed by Earth's volcanic gases, resulting in O_2 partial pressures at the surface on the order of 10^{-12} bar (Kasting and Walker, 1981; Kasting, 1993; Haqq-Misra et al., 2009).

Oxygenic photosynthesis uses sunlight to split water molecules into hydrogen and oxygen. The O_2 is released to the atmosphere as a byproduct. The hydrogen is used to reduce CO_2 to water and organic matter. Under an oxygenated atmosphere most of the organic matter is aerobically respired, closing the cycle, but a small 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_2 or sulfate) before it reaches the atmosphere. On long time scales the net effect of oxygenic photosynthesis today is approximately $CO_2 \rightarrow C + O_2$. This is why carbon burial is often treated as the source of O_2 (Hayes et al., 1983). Many models focus on biological and geological controls on carbon burial to reconstruct Phanerozoic histories of O_2 (Berner, 2001).

Under an anoxic atmosphere, aerobic respiration might still be possible locally where O_2 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; Catling et al., 2001; Kasting and Siefert., 2002). Most of the

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[2] It has very recently been shown in unpublished work (by us and by others) that it is possible to generate an O_2-rich atmosphere abiotically by photochemistry of an Earth-like planet in the habitable zone of a very *uv*-quiet M dwarf. A distinctive and inevitable feature of these hypothetical atmospheres is that they are also CO-rich: they have roughly twice as much CO as O_2, because both gases come from CO_2. It is our opinion that such an atmosphere does not resemble Earth's. Technically-speaking, it is not even oxidized. It is also flammable.

CH_4 reaches the stratosphere, where it is oxidized with the help of solar *uv*. Most of the hydrogen that had been in the CH_4 is destined to escape to space. The net is therefore $H_2O \rightarrow \frac{1}{2}O_2 + H_2\,(\rightarrow \text{space})$. When oxygenic photosynthesis leads to methane, hydrogen escape becomes a source of O_2 (Catling et al., 2001).

Methane is much less reactive than O_2. If both are vented to the atmosphere by an oxygenic photosynthetic ecosystem, the O_2 and free radicals that are made from O_2 will react with rocks and such (Berkner and Marshall, 1965) while the CH_4 reacts only with free radicals generated from O_2. As a result one would expect the atmosphere after the origin of oxygenic photosynthesis to be CH_4-rich rather than O_2-rich, and that this would remain the state of the atmosphere for as long as chemical sinks for O_2 remained easy and plentiful. Methane itself leaves few geological traces, but it can polymerize to soots, possibly nitrogenous or sulfurous (Pavlov et al., 2001; Domagal-Goldman et al., 2008; Trainer et al., 2006; Zahnle, 2008; Zerkle et al., 2012), that 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 through its influence on the sulfur cycle, a topic we have speculated on elsewhere (Zahnle et al., 2006).

It is sometimes argued that the advent of oxygenic photosynthesis was a sufficient condition to create an O_2 atmosphere (e.g., Kopp et al., 2005). The appeal here is to brute force: photosynthesis using H_2O is presumed to be so much more 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 (cf. Sleep and Bird, 2008). It is not obvious *a priori* that the hydrogen source was enormously more limiting to biological productivity than all other nutrients (cf. Kharecha et al., 2005). A second presumption is that the flux of biogenic O_2 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 best debatable. But the bigger problem with this hypothesis is not its logic but rather that it has not proved possible to identify exactly when in the geological record the one true revolution took place (Holland, 1962; 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 $\sim$0.6 Ga (Yin et al., 2007; Love et al., 2009; Maloof et al., 2010), an innovation often explained as heralding the advent of breathable levels of O_2 (Knoll, 2004).

4. Where does oxygen come from?

Excess oxygen in the crust and atmosphere derive ultimately from splitting H_2O followed by H escape to space or from splitting CO_2 and subsequent burial of reduced carbon. Both are possible on a planet with oxygenic photosynthesis. Most discussions of the history of oxygen on Earth focus on CO_2 and carbon burial because H escape today is negligible.

It was briefly debated in the early 1950s (see Holland, 1962, for a discussion) whether oxygen came from water photolysis followed by hydrogen escape or from photosynthesis followed by incomplete decay of organic matter. This matter was resolved in favor of photosynthesis shortly after the question was asked (Holland, 1962, 1964), but the clear bifurcation in thinking remained after the reason for it had gone. It is to this day implicitly assumed that hydrogen escape is in a one-to-one correspondance to abiotic water photolysis, while carbon burial is in a one-to-one correspondance to biotic water photolysis. The dichotomy is false, as is obvious from the way we have stated it: it is water photolysis in either case. The sum of all water photolyses can be balanced by the sum of hydrogen escape plus incomplete decay of organic matter. To these oxidation and reduction of iron and sulfur must be added.

There are now 0.37×10^{20} moles of O_2 in the atmosphere. The current rate of carbon burial is estimated to be on the order of 1×10^{13} moles/yr (Holland 2002). At this rate it would take only 4 Myrs to build up the O_2 in the modern atmosphere. The equivalent to another $\sim 5 \times 10^{20}$ moles of O_2 is stored on the continents as sulfates and sedimentary ferric iron (e.g., banded iron formations); these are obvious products of oxic weathering. It would take only 50 Myr at current rates to build up these inventories.

The sedimentary 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 carbon burial is the reason the surface is oxidized. The $\sim 12 \times 10^{20}$ moles of reduced carbon in the continents (Claire et al., 2006) correspond to $\sim$120 Myr of accumulation. Evidently oxic weathering of old continental carbon to CO_2 is a major part of the modern oxygen cycle (Holland, 1984). The final victory of O_2 has sometimes been identified with a pronounced excursion of $\delta^{13}C$ 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. Holland (2009) presents a strawman redox budget for the event, but he also emphasizes that Lomagundi was likely a system out of balance. The $\sim$120 Myr time scale for 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 continental basalts is generally more oxidized than the iron in freshly erupted basalts. The difference suggests that $\sim 20\times10^{20}$ moles of O_2 have gone into oxidizing continental basalts (Lécuyer and Ricard, 1999). This is bigger than the sedimentary buried carbon reservoir, which means that the continental crust as well as the surface are oxidized. This is the relationship to be expected if hydrogen escape is the reason the surface is oxidized. The detailed mechanism of iron oxidation may be abiotic (e.g., $3FeO + H_2O \rightarrow Fe_3O_4 + H_2$), but even so the result would be a net source of H_2 to the atmosphere and biosphere while the continents accumulated. If this H_2 passed directly to space untouched by life it might be possible to keep continental oxidation separated from carbon burial — which would leave the hypothesis that O_2 originates by burying carbon abstracted from CO_2 unchanged — but in reality the H_2 would be utilized biologically, thus entangling continental oxidation with the carbon cycle.

The other big crustal reservoir is CO_2 in carbonates. It may or may not be relevant to this discussion. Although CO_2 can be abundant in comets, most carbon in asteroids, comets, and meteorites is reduced. Earth probably accreted much 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). Holland (2009) emphasizes that there is little evidence that much of the $\sim 50 \times 10^{20}$ moles of CO_2 now in the continents was present in them in the Archean; this observation plays an important role in his proposal. Because carbon can be oxidized by ferric iron in a QFM mantle, carbon oxidation is not necessarily derivative of H escape; it could also be derivative of high pressure disproportionation of ferrous iron followed by export of metallic iron to the core (McCammon, 2005).

The crustal reservoirs are small compared to what could be lost in 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 the Hadean (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) or reduced sulfur rather than by H escape. On the other hand oxidized iron could have been exported to the mantle. The latter might have been especially efficient in the Archean for iron-rich banded iron formations, as these can be dense enough to sink into the mantle without the aid of plate tectonics.

5. When did oxygen first appear?

The geological record of the anoxic-oxic transition between ca. 2.4 Ga and 2.0 Ga is often referred to as the "Great Oxidation Event," usually written "GOE." Authorities differ on what the GOE means, on how broadly it should be defined, on what events should be included in it, or on what geologic indicators should take precedence (in keeping with the theme of this issue, we have used one of Holland's definitions). Figure 1 provides a cartoon summary of some key events. The classical evidence is concisely summarized by Holland (1999); Holland (2006) provides a more recent summary that includes the post-classical evidence found in the isotopes of sulfur. Changes that mark the GOE include the near disappearance of reduced detrital minerals such as sulfides, siderite and uraninite from streambeds (Rasmussen and Buick, 1999; Hofmann et al., 2009); changes in the weathering of redox sensitive continental elements (Anbar et al., 2007; Frei et al., 2009; Reinhard et al., 2009); the appearance of oxidized surfaces (redbeds) in the place of unoxidized surfaces of comparable sediments (greybeds; 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 Proterozoic; Canfield, 2005); fluctuations in iron isotopes that speak of biological meddling (Rouxel et al., 2005); and looming above all, the abrupt end of huge mass independent fractionations (Δ^{33}S) of sedimentary sulfur isotopes after 2.45 Ga, a signal whose 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, but 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 (Eigenbrode and Freeman, 2006; Buick, 2008; Holland, 2009). The earliest evidence that might be taken as evidence of oxygenic photosynthesis refers to Pb isotopes in ~ 3.7 Ga Isua rocks that seem to require separation between U and Th, and thus can be interpreted as implying that U was mobile and thus oxidized (Rosing et al., 2004). Buick (2008) regards 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_2 or CH_4 or both, or even H_2 (Wordsworth and Pierrehumbert, 2013). Cold climates can be interpreted as weak circumstantial evidence for oxygen, the enemy of CH_4 and H_2 (but not of CO_2). On the other hand, the Pongola climate could be explained by an anti-greenhouse organic haze (Domagal-Goldman et al., 2008; Zahnle, 2008) triggered by an increase of biogenic CH_4. 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).

Next oldest are molecular fossils recovered from ca. 2.72 Ga rocks indicative of sterol synthesis (Brocks et al., 2003; Eigenbrode et al., 2008). Biological synthesis of the original molecules demands the presence of O_2 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).

The earliest evidence that water was used as the hydrogen source in photosynthesis is found at 2.72 Ga in lacustrine stromatolites. The Tumbiana stromatolites 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_2 cannot be ruled out (Kharecha et al., 2005), evidence of bubbles in the stromatolites, plausibly interpreted as bubbles of O_2 (Bosak et al., 2009), and the presence of structural features that are claimed to be characteristic of cyanobacterial mats (Flannery and Walter, 2012), strengthen the case for oxygenic photosynthesis. Extremely low δ^{13}C suggest both methanogenesis and methanotrophy (Hayes, 1994). Methanotrophy suggests that O_2 was consumed metabolically, as anaerobic methanotrophy using sulfate would seem unlikely given the dearth of sulfur in these rocks. A similar but more widespread prevalence of low δ^{13}C in deepwater carbonates paired with modern photosynthetic δ^{13}C in shallow water suggests a more far-reaching impact of aerobic ecosystems between 2.45 and 2.7 Ga, perhaps achieving global reach by 2.45 Ga (Eigenbrode and Freeman, 2006).

Between $\sim$2.8 Ga and 2.45 Ga there are several reports of otherwise insoluble elements and minerals such as molybdenum and rhenium (Anbar et al., 2007), chromium (Frei et al., 2009), and pyrite (Stüeken et al., 2012) being weathered from continents and washed into the sea. These elements are more soluble when more highly oxidized. It is interesting that the signature is seen in Mo and Re but not U, a pattern that strongly suggests that the source of Mo and Re was oxidative weathering of sulfide minerals in particular (Buick, 2008). 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_2-rich atmosphere (Scott et al., 2008). Oxidation of Cr to the Cr^{+6} of soluble chromate probably requires O_2 (Frei et al., 2009). Konhauser et al. (2011) suggest instead that strongly acidic conditions would suffice to mobilize chromium as Cr^{+3}. Acid indirectly indicates oxidation, as the plausible source of acid is oxidation of iron, sulfur or sulfide, but it may not mean O_2, although Konhauser et al. (2011) prefer both biology and O_2, as today at Rio Tinto. Whatever the details, it seems clear that by 2.6 Ga at the latest H_2O was being used as a hydrogen source in photosynthesis in settings by the sea and that the oxidized product was mobile and locally or regionally abundant. Although O_2 need not have been the product, toxic plumes of biogenic O_2 might account for things nicely.

Redbeds are probably the highest fidelity and most directly pertinent of the classic geological indicators of the atmosphere's changing redox state (Holland, 2006; Kump, 2008). Redbeds indicate an oxidizing atmosphere at the surface but, as we have seen with Mars, not necessarily a lot of free O_2. Figure 1 places the greybed-redbed transition at 2.32 Ga and after the second of the three Paleoproterozoic ice ages that began ca. 2.45 Ga (Papineau et al., 2007; 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) and to the massive Hotazel MnO_2 deposit that follows the last of the great Paleoproterozoic ice ages. This — the last possible moment — is where Kopp et al. (2005) place the origin of oxygenic photosynthesis. This is also around the time that the first massive sulfate deposits appear (Melezhik et al., 2005; Holland, 2006; Schröder 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 $CO_2 \rightarrow C + O_2$. Kopp et al. (2005) suggest that the third ice age was the biggest and therefore the best ice age to link to the origin of oxygen photosynthesis, but this is a weak argument given that at least two great ice ages had come and gone over the previous 200 Myr.

If there is one date to divide the Archean from the Proterozoic, the best choice would be the sudden end of an extraordinary isotopic fractionation history of sedimentary sulfur, which was followed immediately by Earth's plunge into the first of a series of stupendous ice ages. On the other hand, there remains some uncertainty regarding when these events took place. We have placed it at 2.45 Ga, which is the earliest plausible date for the event and the one most often cited, but a date as late as 2.32 Ga is possible (Bekker et al., 2004; Bekker and Holland, 2012). Both isotopes and climate signal major changes in the composition of the atmosphere.

Sulfur is particularly important because it is, with carbon and iron, one of the three abundant elements that 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 (Figure 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 δ^{34}S from 2.7 Ga to 2.0 Ga.

The extraordinary fractionations that highlight the date of 2.45 Ga are recorded with sulfur's third isotope. This fractionation, denoted Δ^{33}S, (often called mass independent fractionation of sulfur, or MIF-S for short) is the difference between the fractionation of ^{33}S expected from δ^{34}S and what is actually observed. Large nonzero values of Δ^{33}S vanish abruptly at $\sim$2.45 Ga, although weak signals somewhat comparable to what can be found on Earth today in Antarctica continue for another 400 Myrs (Farquhar and Johnston, 2008).

The only known way to get MIF-S big enough to give the observed Δ^{33}S signal invokes atmospheric photochemistry driven by solar *uv* (Farquhar et al., 2000). An atmospheric source has two requirements. First, the *uv* cannot be absorbed by ozone. Thus there cannot be much O_2 in the atmosphere. Second, there have to be at least two channels to remove sulfur from the atmosphere (Pavlov and Kasting, 2002), in order to keep the two complementary Δ^{33}S signals separate (if, as today, nearly all S left the atmosphere as sulfate aerosols, the Δ^{33}S would sum to zero). Laboratory experiments (Farquhar et al., 2001; DeWitt et al., 2010) show and photochemical models predict (Pavlov and Kasting, 2002; Zahnle et al., 2006) that both sulfate aerosols and elemental sulfur (S_8) aerosols can be generated photochemically in an anoxic atmosphere, but that elemental sulfur cannot form if the atmosphere is not sufficiently reduced. Hence significant nonzero Δ^{33}S demands an effectively anoxic atmosphere ($pO_2 < 10^{-7}$ bars; Zahnle et al., 2006) before 2.45 Ga. Getting Δ^{33}S into the sedimentary record raises additional issues in the presence of oceans and biology. Separation is maintained at first because S_8 is insoluble in water, but if oxidized or reduced — either abiologically or biologically — its products need not be. Halevy et al. (2010) consider the simple but extreme expedient of suggesting that biology did not cycle sulfur, thus preserving the atmosphere's signature. But the explanation could also be that, with S in short supply, all available S was used locally. Insoluble elemental sulfur would be globally precipitated but patchily distributed on land like dust, while soluble sulfate is washed into the sea. Another factor to consider is that S-containing gases may have played a more immediate role in sulfur cycling than today. Photochemistry acting on these gases would re-imprint, and potentially amplify through distillation, the Δ^{33}S signal.

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 geologic 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 reduced gases such as CH_4 or H_2 from the troposphere — probably by reaction with biogenic O_2 — but does not mean that O_2 levels were necessarily consistently appreciable at the surface (Zahnle et al., 2006). Steady-state O_2 abundant enough to stain redbeds may have come later. It is not required that MIF-S end at the same moment that redbeds begin because these record different things.

6. Why would an atmosphere switch to O_2?

It is useful to review a legacy model that blamed the rise of oxygen on the changing redox state of volcanic gases. As mentioned above, the idea is from Holland (1962): "[The oxygen age] began when the rate of production of oxygen by photosynthesis exceeded the rate needed to oxidize injected volcanic gases completely." The particular model we discuss (Kump et al., 2001), although since superceded, gives a clear presentation of the concepts in play[3]. The model makes two postulates: (i) that the mantle's f_{O_2} (oxygen fugacity) has been secularly increasing; and (ii) that on average about 20% of the CO_2 outgassed from volcanoes has been buried as C and the rest as carbonate — the $\delta^{13}C$ record indicates that this ratio has held approximately for the entire sweep of Earth's history.

The key concept is to compare the flux of reduced volcanic gases into the atmosphere to the rate that carbon is buried. If the fluxes of H_2 and CO exceed the carbon burial rate, there is enough H_2 and CO to consume all the O_2 generated by carbon burial and the atmosphere remains reduced. The H_2/H_2O and CO/CO_2 ratios in volcanic gases both go as $f_{O_2}^{-0.5}$. As the mantle's f_{O_2} increases, the ratios of H_2 and CO to CO_2 in volcanic gases decrease until they drop below the carbon burial rate. At this point free O_2 appears. The role of hydrogen escape is limited to venting off excess reductant in the Archean, otherwise the continents would grow progressively more reduced, for which evidence is lacking.

As mentioned above, this particular model fails because there is no evidence that f_{O_2} of the mantle has changed to at least as far back as 3.8 Ga (Canil, 2002; Delano, 2001; Li and Lee, 2004; Holland, 2009), and possibly even 4.35 Ga Trail et al. (2011). One may protest that surely the Archean was more volcanically active than today,

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[3] 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 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 H_2 and CO to CO_2 in volcanic gases did not change: in this theory, it is the ratio of H_2 and CO to CO_2 in volcanic gases that is important. Simply changing the rate of volcanic degassing while holding the composition of the gases fixed does not work, because the burial rates of C and carbonate (CO_2) must both keep pace with the volcanic supply of CO_2 if $\delta^{13}C$ be constant. Some other change is required.

The simplest change is to postulate a higher H_2O/CO_2 ratio in Archean volcanic gases (Holland, 2009). This would give a higher H_2/CO_2 at a fixed f_{O_2}, and thus leave more reducing power in the atmosphere. A change in the H_2O/CO_2 ratio coming out of volcanoes implies a proportionate change in the H_2O/CO_2 ratio in the rocks that go into the volcanoes. The evidence for this is massive carbonates being rare in continental sediments before 2.8 Ga (Holland, 2009). Against this is the expectation (prejudice) that, as the mantle cools, it will degas less CO_2 and incorporate a greater fraction of the carbonate and organic carbon entering subduction zones, which makes a true dearth of CO_2 in the Archean a bit of a surprise. Holland (2009) shows that it is possible to get the sought-for behavior from a model that divides volcanic CO_2 emissions into a declining juvenile component and a growing component stemming from recycled crust.

A bigger effect of the same sort can be obtained from sulfur gases, which are now a major player in the redox budget of volcanic gases, but may not have been if sulfur were scarce in subducting zones. Holland (2002) developed a model that left H_2/H_2O fixed but added progressively increasing amounts of sulfur gases to the system. The evolution of the envelope of δ^{34}S in the sedimentary record suggests that sulfur was scarce before 2.7 Ga and became abundant by 2.0 Ga, and thus that its role grew from a trace element to a major player in the redox budget at roughly the same time that O_2 took over. In both the 2002 and 2009 models, Holland accepts a constant mantle f_{O_2} and fixes the carbon burial rate to 20% of the volcanic CO_2 flux (i.e., f_{org}, the fraction of volcanic CO_2 buried as C, is 0.2). Adding sulfur creates a more complicated relation between volcanic fluxes and carbon burial, the gist of which is that, while volcanoes mostly emit S as SO_2, Holland (2002) argues that S is removed from the anoxic atmosphere mostly as FeS_2. Thus volcanic H_2 and CO are tasked with reducing SO_2 to FeS_2 in addition to reducing the O_2 that comes from carbon 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) later modified the argument to allow H_2O/CO_2 to decrease as well, which enhances the effect.

Holland's models have many points to recommend them, but they cannot be the whole story because they leave the rough constancy of f_{org} unexplained, they do not explain why carbonate or sulfate accumulate at the surface, and they do not explain why the surface became oxidized. The models resemble a titration, with sulfur and carbonate being added to the volcanoes until the reducing power (volcanic H_2 and CO vs. C burial) is overcome. Indeed, Holland's models fit rather well with hydrogen escape as the driving principle.

7. 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; Claire et al., 2006). It applies directly and clearly to a model like Holland (2002), where the key oxidized material to be accumulated is sulfate (Zahnle et al., 2006). It could be applied to Guo et al's (Guo et al., 2009) suggestion that oceanic Fe^{+2} was titrated between 2.45 Ga and 2.32 Ga. It can also be applied to the oxidation of continental igneous rocks, which as noted above appear to hold the largest reservoir of oxidized material at the surface (Lécuyer and Ricard, 1999; Claire et al., 2006). In all cases what results is a kind of oxidation hourglass.

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

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

where $f_{\mathrm{tot}}(\mathrm{H_2}) = f(\mathrm{H_2}) + f(\mathrm{H_2O}) + 2f(\mathrm{CH_4})\ldots$ is the total mixing ratio of H_2 equivalents in the stratosphere. In the current atmosphere the effective H_2 mixing ratio f_{tot} is 7.1 ppmv, to which CH_4 and H_2O contribute equally (Nassar et al., 2005). Diffusion limited escape today 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.

By contrast, hydrogen escape rates in the anoxic Archean atmosphere were probably not negligible (Hunten and Donahue, 1976). Through methane, hydrogen escape is at least in part under biological control, even today (*ibid*). 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; Haqq-Misra et al., 2008). In the diffusion limit this corresponds to an H_2 escape rate of 10^{13} moles/yr. This corresponds in turn to a crustal oxidation rate half that generated today by carbon burial. Other ways to express this rate are as the loss of 400 m of water over 1 Gyr, or as the creation of 40 bars of O_2 over 1 Gyr. This is enough bleaching power to oxidize the continents (basalts + sediments - buried carbon) in some 300 Myr. The biogenic methane flux and the consequent oxidation rates may 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.

Holland was no enemy of hydrogen escape as a possible major player in the oxidation of the Earth, as he makes clear in his books *The Chemistry of the Atmosphere and Oceans* (Holland, 1978) and *The Chemical Evolution of the Atmosphere and Oceans* (Holland, 1984). Holland (1978, p. 296) wrote, "Hydrogen escape from an anoxic atmosphere containing sizable quantities of reducing gases is probably orders of magnitude more rapid than it is from the atmosphere today, and could have had an important influence on the chemistry of the early atmosphere of the Earth." He always included hydrogen escape in his budgets (as for example in Holland, 2009), but he usually also pointed out that the term was small compared to the other terms in the redox budget. As a global oxidizing force he appears to have considered it only in relation to the mantle's volcanic H_2 emissions and the resulting drift of the mantle's oxygen fugacity. When the latter was found not to have changed over the past 3.8 Gyr, he appears to have given up on hydrogen escape.

But judging the importance of hydrogen escape solely by the magnitude of the term misses the greater point that hydrogen 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. This is a qualitative distinction that makes it misleading to compare the magnitude of the hydrogen escape flux against the other major terms in Earth's redox budget. In a sense, it can only be compared to the oxygen escape flux, which is very nearly zero.

8. 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. The process is general and should apply to all habitable planets of all sizes and types throughout the universe. It is therefore testable by future astronomical observations.

The fundamental importance of hydrogen escape is not a position that one often encounters in Earth science. The most common argument is that oxygen is a secondary consequence of Earth cooling. Arguments derived from Holland's 1962 hypothesis usually compare the flux of reducing power from the mantle to a fixed flux of reduced matter that accumulates on continents or is buried in sediments that are destined to be subducted by the mantle. The reduced matter can be carbon made from CO_2 or metal sulfides made from volcanic SO_2. The implicit presumption is that production and burial of reduced matter can be regarded as constant rates that are independent of the redox state of the surface environment. The constancy may be enforced by biological activity. If the mantle supplies more reducing power than is needed to meet the constant carbon burial rate, the waste hydrogen is vented to space. If the mantle supplies less reducing power than needed for the fixed burial rate, the surface and atmosphere become oxidized. If by this time oxygenic photosynthesis had been invented, the atmosphere would then begin to accumulate O_2. The redox budget can be balanced by such a model, but one is ultimately left with the hypothesis that an oxidized surface environment oxidizes itself by reducing an already reduced mantle.

In most respects secular cooling is a more important influence on planetary evolution than is hydrogen escape. But cooling does not in itself alter oxidation. Oxygenation by cooling would have to be a by-product, a secondary effect that preferentially pools oxidants at the surface. Speculations abound. In addition to those which closely follow Holland's, which we have discussed, a nonexhaustive list includes (i) declining rates of volcanism (a fact that does not explain why oxygen pools at the surface); (ii) a switch from submarine to subaerial volcanism that diminishes the reducing power of volcanic gases (Kump and Barley, 2007; Gaillard et al., 2011); (iii) increased stability and volume of continents as burial grounds of reduced (or oxidized) materials; (iv) a switch from weathering of more mafic to less mafic matter, driven by the growth of continents, that changes the relative burial rates of reduced and oxidized minerals (Sleep, 2005); (v) increased supply of P (as limiting nutrient) from continental weathering consequent to continental growth; (vi) less or more subduction; (vii) increased stability of relatively volatile reduced (or oxidized) minerals during subduction (Hayes and Waldbauer, 2006, in effect); (viii) and internal differentiation within the mantle (Kump et al., 2001; McCammon, 2005). Several of these change the magnitude but not the sign of surface oxidation; several of these include a measure of knowing in advance what the answer needs to be.

Three other long term trends should be mentioned. (i) The Sun grows monotonically brighter. How this would impact oxygen is unclear, but it could do so indirectly if the climate were moderated by greenhouse gas feedbacks (in which O_2 can play a part). Such an argument is usually associated with biological meddling (Lovelock and Margulis, 1974; Goldblatt et al., 2006; Zahnle, 2008). (ii) The flux of high energy ionizing radiation monotically decreases. The effect is mostly on hydrogen escape, which would be easier in the past than it is today. (iii) Biological evolution might be innately progressive, with a trend to develop more potent metabolisms. Free oxygen is an outstandingly potent and useful fuel for animal metabolism (Catling et al., 2005). The hypothesis that biological evolution is destined to make oxygen is at present best regarded as speculative.

Here we argue that oxidation and oxygen are consequences of hydrogen escape, which is the one process affecting planetary oxidation that always points in the same direction. We do not argue that hydrogen escape acts alone without interaction with biological innovation or planetary evolution. We *do* argue that hydrogen escape determines the direction of things, especially at the planet's surface where its effects are most immediate. This includes the speculation that hydrogen escape provides the bias to biological evolution. We suggest that the hundreds of millions of years that elapsed between the invention of oxygenic photosynthesis and the establishment of an oxygen atmosphere were how long it took to oxidize the continents by hydrogen escape. This is complicated by, and probably linked to, the putative growth of continents between 3 Ga and 2 Ga. Growing continents allow more reduced carbon, sulfate, BIF, and carbonate to be stored on continents, and increase the amount of oxidized igneous rock in the cratons.

It has been argued that continental oxidation as registered in basalts has nothing to do with oxygen, because basalts are oxidized abiotically shortly after eruption by water, not by oxygen or sulfate or any other biogenic oxidant (Kasting, 2001). However, H_2 generated when basalts are oxidized by H_2O is utilized biologically to make organic matter from CO_2. Hence the apparent net oxidation of continents means that more oxygen got stored in continents as continents grew. We expect Earth's surface to have remained reduced while the new sinks for oxygen provided by the growing continents kept pace with hydrogen escape. When continents slowed their growth their potential to store excess oxygen diminished. At this point any further hydrogen escape would lead to a more oxidized surface environment.

It is intriguing to turn all this on its head and ask whether continental oxidation and continental growth are both governed by hydrogen escape — i.e., to ask whether continents as we know them must be relatively oxidized to exist as such, and therefore that hydrogen escape determines the rate of continental growth (cf. Jagoutz, 2013). But whatever the details, oxygen's conquest waited on the exhaustion of the powers of reduction. Hydrogen escape was Earth's hourglass.

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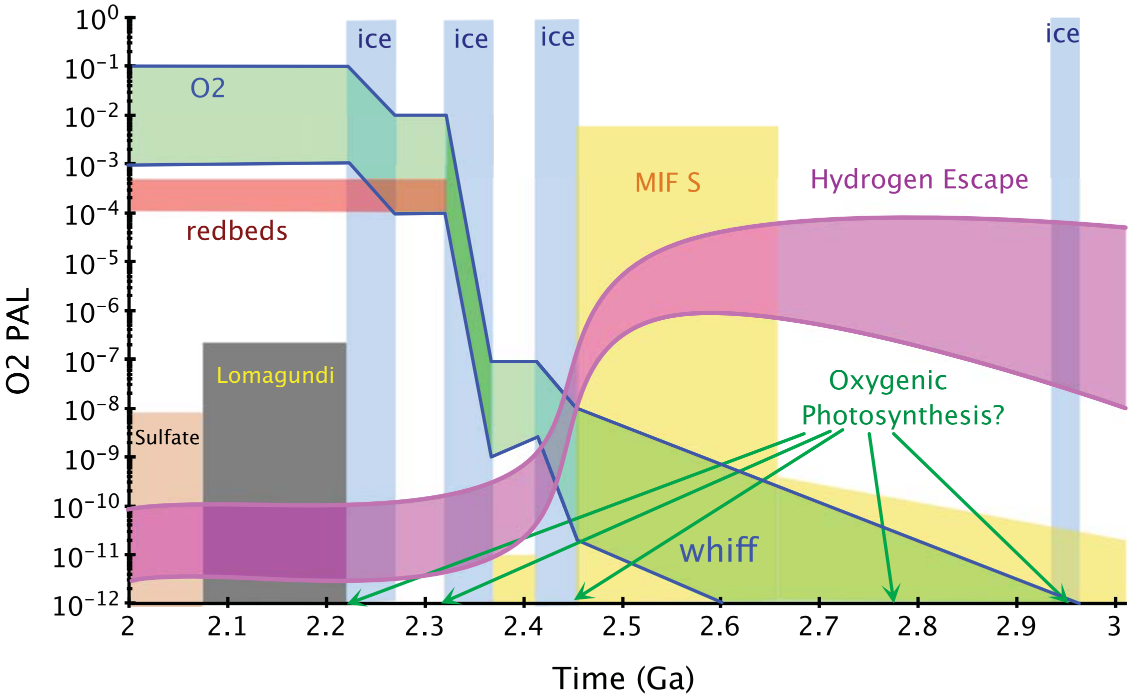
Figure Captions

Figure 1

A cartoon history of the Great Oxidation Event. Hydrogen escape rates and the range of MIF-S values are indicative of general trends. Approximate tropospheric O_2 levels are estimated but should not be taken too literally. Below $\sim 10^{-5}$ PAL (Present Atmospheric Levels), O_2 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).

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 fractionations $\Delta^{33}S$ and $\Delta^{36}S$ (Farquhar and Johnston, 2008) appear to increase as the biologically accessible sulfur pool grows until the signal abruptly vanishes 2.46 Ga. The Late Archean marks the time when biogenic reduced gases such as CH_4 and H_2S were likely abundant and biogenic O_2 suppressed. The figure uses databases compiled by R. Buick, E. Stüecken, and J. Farquhar. Use of their data here does not imply their support for our interpretations of these data.


ice
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2
2.1
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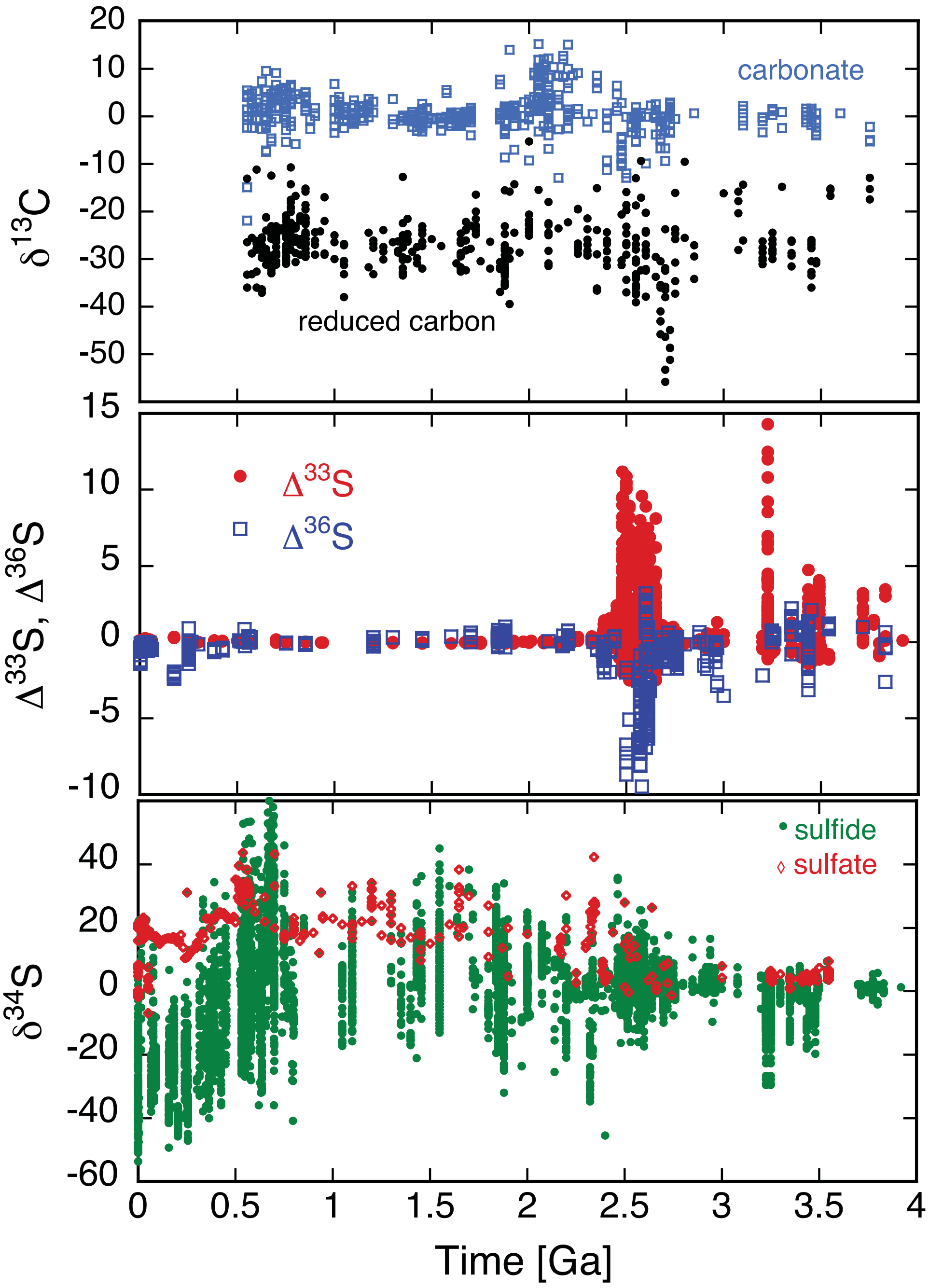
2.9
3
Time (Ga)

Figure 1:



20
10
0
-10
-20
-30
-40
-50
δ13C
carbonate
reduced carbon
15
10
5
0
-5
-10
Δ33S, Δ36S
Δ33S
Δ36S
40
20
0
-20
-40
-60
δ34S
sulfide
sulfate
0
0.5
1
1.5
2
2.5
3
3.5
4
Time [Ga]

Figure 2: