

Atmospheric hydrogen peroxide and Eoarchean iron formations

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ABSTRACT

It is widely accepted that photosynthetic bacteria played a crucial role in Fe(II) oxidation and the precipitation of iron formations (IF) during the Late Archean–Early Paleoproterozoic (2.7–2.4 Ga). It is less clear whether microbes similarly caused the deposition of the oldest IF at ca. 3.8 Ga, which would imply photosynthesis having already evolved by that time. Abiological alternatives, such as the direct oxidation of dissolved Fe(II) by ultraviolet radiation may have occurred, but its importance has been discounted in environments where the injection of high concentrations of dissolved iron directly into the photic zone led to chemical precipitation reactions that overwhelmed photooxidation rates. However, an outstanding possibility remains with respect to photochemical reactions occurring in the atmosphere that might generate hydrogen peroxide (H₂O₂), a recognized strong oxidant for ferrous iron. Here, we modeled the amount of H₂O₂ that could be produced in an Eoarchean atmosphere using updated solar fluxes and plausible CO₂, O₂, and CH₄ mixing ratios. Irrespective of the atmospheric simulations, the upper limit of H₂O₂ rainout was calculated to be <10⁶ molecules cm⁻² s⁻¹. Using conservative Fe(III) sedimentation rates predicted for submarine hydrothermal settings in the Eoarchean, we demonstrate that the flux of H₂O₂ was insufficient by several orders of magnitude to account for IF deposition (requiring ~10¹¹ H₂O₂ molecules cm⁻² s⁻¹). This finding further constrains the plausible Fe(II) oxidation mechanisms in Eoarchean seawater, leaving, in our opinion, anoxygenic phototrophic Fe(II)-oxidizing micro-organisms the most likely mechanism responsible for Earth's oldest IF.

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CURRENT MODELS FOR IRON FORMATION DEPOSITION

Precambrian iron formations (IF) are chemical sedimentary rocks composed of layered, bedded, or laminated rocks that contain 15% or more iron, in which the iron minerals are commonly interlayered with quartz or carbonate (see Bekker *et al.*, 2010). Two types of IF have been recognized with respect to their depositional setting. Algoma-type IF are interlayered with or stratigraphically linked to submarine-emplaced volcanic rocks in greenstone belts and, in some cases, with volcanogenic massive sulfide deposits. These IF contain oxide, silicate and carbonate facies, and commonly grade into sulfidic sediments, which

can be enriched in copper, zinc, lead, silver, and gold. They apparently formed close to volcanic arcs and spreading centers and were produced by exhalative hydrothermal processes related to volcanism (e.g., Goodwin, 1962). They range in age from Eoarchean to Late Paleoproterozoic (Isley & Abbott, 1999; Huston & Logan, 2004), which possibly reflects the absence of large, stable cratons at that time (Bekker *et al.*, 2010).

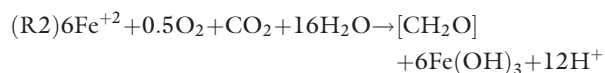
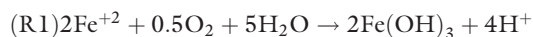
In contrast, larger Superior-type IF developed in near-shore continental-shelf environments where they are typically interbedded with carbonates, quartz arenite, and black shale, but with only minor amounts of volcanic rocks (Gross, 1980). Unlike most Algoma-type IF, which rarely extend for more than 10 km along strike and are usually

not more than 50 m thick, the Superior-type IF can be extremely laterally extensive, with original aerial extents estimated in some cases to be over 100 000 km² (Isley, 1995). Superior-type IF first appear in the Late Archean, when construction of large continents first began. From *ca.* 2.6 to *ca.* 2.4 Ga, global mafic magmatism culminated in the deposition of giant Superior-type IF in South Africa, Australia, Brazil, Russia, and Ukraine (Bekker *et al.*, 2010).

The timing of IF deposition spans major evolutionary changes in the Earth's surface composition, from an early anoxic atmosphere, in which CO₂ and CH₄ were important greenhouse gases, to an atmosphere that became partially oxygenated. Therefore, it is likely that IF formed via different mechanisms throughout the Precambrian. These mechanisms are briefly discussed below.

Cyanobacterially generated O₂

Some of the earliest models of IF deposition posit that the abiotic oxidation of dissolved Fe(II) took place in the presence of free oxygen derived from oxygenic photosynthesis via the evolution of cyanobacteria (Cloud, 1973). Once oxygen was present, aerobic chemolithoautotrophic bacteria could also have contributed to ferric iron precipitation (Holm, 1989).

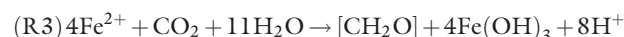


Direct evidence in support of oxygenic photosynthesis during the Archean is rare, and even in those few cases, not without alternate interpretations. Examples include the 2.7 Ga stromatolites of the Tumbiana Formation in Western Australia where the microbial mat community was believed to have been dominated by cyanobacteria (Buick, 1992; Bosak *et al.*, 2009; Flannery & Walter, 2012), and the presence of ¹³C-depleted kerogens in *ca.* 2.7 Ga shales and carbonates that would suggest a microbial community comprised of phototrophs and methanotrophs (Eigenbrode *et al.*, 2008; Thomazo *et al.*, 2009, 2011). However, sulfur mass-independent isotope fractionation (S-MIF) of associated sulfides indicate that atmospheric oxygen levels must have been lower than 10⁻⁵ times the present atmospheric level (PAL) during deposition of Tumbiana sediments (Thomazo *et al.*, 2009). In addition, Sforza *et al.* (2014) recently showed that anoxygenic phototrophs using As(III) as electron donors appear the most likely metabolism to power the prolific Tumbiana microbiota. Nevertheless, Mo and Cr isotope compositions, as well as U

enrichment data, from a banded iron formation of the Pongola Supergroup appear to reflect some partial oxygenation at *ca.* 3.0 Ga, most probably in association with localized oxygen oases in marginal marine settings (Crowe *et al.*, 2013; Planavsky *et al.*, 2014). Hence, on a dominantly anoxic Eoarchean Earth, the role of oxygen in terms of IF deposition, if it existed, would have been limited.

Anoxygenic phototrophic Fe(II)-oxidizing bacteria - the photoferrotrophs

Under anoxic conditions, the oxidation of Fe(II) to Fe(III) can occur via anoxygenic Fe(II)-oxidizing photosynthesis (photoferrotrophy). Here, photosynthetic bacteria (e.g., green and purple bacteria) use Fe(II) as an electron donor for carbon assimilation rather than water, and they produce Fe(III) instead of dioxygen (Garrels *et al.*, 1973; Hartman, 1984; Widdel *et al.*, 1993).



Laboratory experiments demonstrated that this form of metabolism could generate sufficient quantities of Fe(III) to account for all the oxidized iron in IF even at rapid accumulation rates (Konhauser *et al.*, 2002; Kappler *et al.*, 2005). Crucially, Fe(II) oxidation by anoxygenic phototrophs can be sustained in relatively deep waters (as much as one hundred meters of water depth) (Kappler *et al.*, 2005), and their growth is not hindered by high concentrations of dissolved silica (Posth *et al.*, 2008; Wu *et al.*, 2014). Therefore, these organisms could easily have oxidized all of the upwelling Fe(II) before it made contact with the overlying oxygenated waters (if these existed) in the Archean oceans (Czaja *et al.*, 2013).

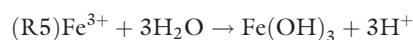
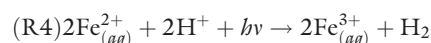
Despite the absence of fossilized remains of photoferrotrophs in the Archean, numerous lines of evidence suggest their presence on the early Earth (e.g., Posth *et al.*, 2013a). Perhaps most importantly, of the seven known strains of anoxygenic Fe(II)-oxidizing phototrophs, six have been classified as *Proteobacteria*; the seventh is a green sulfur bacterium. The *Proteobacteria* are a large and diverse phyla of bacteria consisting of five major classes, all of which may have diversified from one ancestral phototroph (Woese, 1987) that is almost certainly more deeply rooted than the oxygenic cyanobacterial lineages (Xiong, 2006).

Moreover, modern anoxygenic phototrophs are able to utilize multiple substrates (Croal *et al.*, 2009; Melton *et al.*, 2014). In Archean oceans, phototrophic bacteria would not have had access to large quantities of dissolved sulfide as an electron donor because any hydrothermally sourced sulfide would have reacted with Fe(II) near the vent, and thus precipitated as solid-phase sulfide minerals.

In the case of limited HS^- supply, the ability of bacteria to use Fe(II) as a reductant is predictable. In fact, even considering higher hydrogen concentrations (Tian *et al.*, 2005; Kump & Barley, 2007), Fe(II) oxidation by modern analogue anoxygenic phototrophs still proceeds at significant rates under an atmosphere containing approximately three times the maximum predicted concentration of H_2 (300 000 ppm) in the Archean atmosphere (Croal *et al.*, 2009). The input of dissolved Fe(II) from mid-ocean ridges was almost certainly greater during the Archean, a view supported by the presence of excess Fe in sandstones and shales of that time (Kump & Holland, 1992). Thus, it seems likely that these organisms applied enzymatic systems to use abundantly available electron donors, such as Fe^{2+} . In addition, it has been suggested that Fe(II) oxidation and Fe(III) precipitation may even have provided an external UV protecting shield for planktonic bacterial cells (Pierson, 1994; Phoenix *et al.*, 2001).

UV photooxidation

Prior to the rise of oxygen and the development of a protective ozone layer, the Earth's surface was subjected to high levels of ultraviolet radiation. The absorption of ultraviolet radiation in the 200–400 nm range by either Fe(II) or $\text{Fe}(\text{OH})^+$ in the water column causes the oxidation of these species and the subsequent precipitation of ferric oxyhydroxides, such as ferrihydrite and $\text{Fe}(\text{OH})_3$ (Cairns-Smith, 1978; Braterman *et al.*, 1983).



Extrapolation of the experimental photochemical oxidation rates suggested that this oxidative process could have generated enough Fe(III) to account for all the ferric iron in IF (Braterman & Cairns-Smith, 1986).

A more recent study using complex solutions simulating Precambrian ocean water chemistry (i.e., high dissolved Fe^{2+} , Si, and HCO_3^-) showed that the oxidation effects of either UVA or UVC are negligible when compared to the much faster precipitation of the ferrous silicate (greenalite) and ferrous carbonate (siderite) minerals directly out of seawater at chemical disequilibrium (Konhauser *et al.*, 2007). Conversely, in experiments where Fe(II) was exposed either to phototrophic Fe(II)-oxidizing bacteria or to O_2 , ferric oxyhydroxide formed rapidly, and the precipitation of ferrous iron phases was not observed. If, as suggested on mass-balance grounds, IF deposition required that Fe be sourced from shallow seamount-type systems, Konhauser *et al.* (2007) further suggested that oxide-facies IF are the product of a rapid, non-photochemical oxidative

process. It is, however, important to note that the experiments of Konhauser *et al.* (2007) do not negate the possibility that some photooxidation could have occurred in the uppermost levels of the water column where dilution of hydrothermal fluids (either from rising plumes or upwelling currents) would have reduced dissolved Fe(II) concentrations to bulk seawater values (~ 0.03 mM as dictated by equilibrium with siderite and calcite; Holland, 1984): High-precision Fe isotope analysis will likely be required to fully confirm that photooxidation-induced MIF-Fe isotopes was a viable process in these environments. While the shoaling of such equilibrated fluids in marginal settings, far removed from seamounts and other hydrothermal sources, might explain the deposition of Superior-type IF on continental shelves, it is not clear if such models hold true for the precipitation of Algoma-type IF. Indeed, the recognition by Huston & Logan (2004) that shale-normalized Eu anomalies of Algoma-type IF are generally much larger than those of Superior-type IF led these workers to suggest that the latter contained a smaller hydrothermal component. This interpretation is consistent with the large dilution of hydrothermal fluids by seawater in modern plumes (typical dilution factor of 10^4 ; German & Von Damm, 2004) and a decrease in the magnitude of Eu anomalies with distance from ancient hydrothermal vents (Peter *et al.*, 2003). As a result of these factors, the distribution and composition of Algoma-type IF are considered to more accurately reflect local volcanic or hydrothermal conditions, rather than being representative of the large-scale chemistry of the oceans (Huston & Logan, 2004).

If Algoma-IF were proximal to volcanic arcs and spreading centers, then it is likely that they precipitated under conditions similar to that of the experiments by Konhauser *et al.* (2007), that is, under geochemical disequilibrium. Therefore, in the absence of oxygen the ferric oxyhydroxide precursors to Algoma-type IF would seemingly be the result of anoxygenic phototrophs. At first glance, this is a major conclusion that would solve a long-standing issue regarding the origin of IF before the oxygenation of the oceans. But, is oxygen the only effective atmospheric oxidant capable of generating Eoarchean IF? In other words, what about other potential oxidants that may have existed before the rise of oxygen? Here, we explore one such alternative that naturally occurring hydrogen peroxide (H_2O_2), a powerful oxidant capable of oxidizing inorganic reductants, reacted with dissolved Fe(II) to precipitate ferric iron in IF.

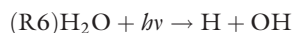
POTENTIAL SOURCE OF H_2O_2 IN THE EOARCHEAN

The propensity for H_2O_2 to oxidize Fe(II) has important implications for the Eoarchean, a time where the oceans

were highly ferruginous with dissolved Fe(II) concentrations estimated to range between 0.05 and 0.5 mM (Holland, 1973; Morris, 1993). Although IF that formed after the Late Archean likely originated from the reaction of O₂ derived from cyanobacteria, we consider whether H₂O₂ played a significant role in Fe(II) oxidation prior to this time, or perhaps even afterward. For example, photochemically derived H₂O₂ stored in ice caps and glaciers may have been released after the Makganyene Snowball Earth event *ca.* 2.3 Ga. This release of H₂O₂ during deglaciation has been used to explain the oxidation of Fe(II) and Mn(II) in Palaeoproterozoic deposits, such as that of the Kalahari manganese field (Liang *et al.*, 2006).

Hydrogen peroxide is generated through several processes and has been measured in a variety of different environments (e.g., Thompson *et al.*, 1989; Zuo & Deng, 1999; Borda *et al.*, 2001, 2003; González-Davila *et al.*, 2005; Amme *et al.*, 2005; Draganic, 2005). For the purpose of this study, however, we only consider H₂O₂ formed by atmospheric photochemical reactions, as it is the only process that can generate significant fluxes.

The formation of H₂O₂ in the ancient atmosphere begins with the photolysis of water vapor:



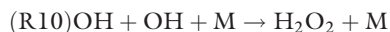
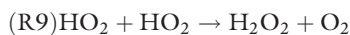
or by the reaction of water vapor with an excited atomic oxygen, O(¹D):



Reaction [R7] may then be followed by:



where, 'M' is any molecule. Both OH and HO₂ are precursors to H₂O₂ formation through the following reactions:



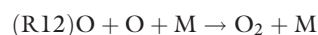
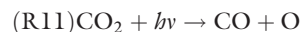
Hydrogen peroxide may then be removed from the atmosphere by photolysis, reaction with OH, or by rainout (Kasting *et al.*, 1985).

Kasting *et al.* (1984) used a photochemical model of a CO₂-rich anoxic atmosphere (surface *p*O₂ ~10⁻¹¹ bar) to calculate a H₂O₂ rainout rate of ~10⁹–10¹⁰ molecules cm⁻² s⁻¹. However, this rate is not applicable to the Eoarchean because the model did not examine levels of methane or volcanic input of gases that consume oxygen. The amounts of O₂, CH₄, and CO₂ in the Eoarchean

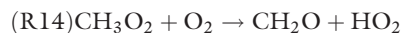
atmosphere would have affected the rainout rate of H₂O₂.

In the Archean atmosphere, O₂ was a trace constituent with a concentration below 10⁻⁵ PAL, as implied by the preservation of mass-independent fractionation of sulfur isotopes (Farquhar *et al.*, 2000; Pavlov & Kasting, 2002; Zahnle *et al.*, 2006). In the Archean, the production of H₂O₂ would have been lower than it is today because the formation of its precursor, HO₂, requires O₂ [see R8]. For example, Haqq-Misra *et al.* (2011) calculated a H₂O₂ rainout rate of ~10⁶ molecules cm⁻² s⁻¹ for a pre-photosynthetic atmosphere with 0.2 bar CO₂. Despite the low concentrations of O₂, in the pre-photosynthetic atmosphere, it would have been reaction [R9], not reaction [R10] that was the main formation pathway for H₂O₂. Haqq-Misra *et al.* (2011) erroneously reported that reaction [R10] was more important (J. Kasting, personal communication).

When O₂ is a trace constituent, higher *p*CO₂ tends to increase the H₂O₂-rainout flux. As discussed in Kasting *et al.* (1984), CO₂ promotes the formation of O₂ [R11 through R13] and, when followed by reactions [R8 and R9], the production of H₂O₂:



Methane affects H₂O₂ production in an opposite manner in the modern atmosphere compared to the Archean atmosphere. Methane, like CO₂, is posited to have been more abundant in the Archean (see Discussion in following section). In the modern atmosphere, if CH₄ concentrations were to increase, H₂O₂ production would increase. This is because photochemical reactions involving CH₄ produce higher-order hydrocarbon gases, such as ethane (C₂H₆) and formaldehyde (H₂CO) (Kasting *et al.*, 1983; Zahnle, 1986; Ogura *et al.*, 1988; Pavlov *et al.*, 2001; Kasting, 2005). The photochemical decomposition of these gases, in turn, may produce hydroperoxyl radicals (HO₂) (Thompson *et al.*, 1989; Gunz & Hoffmann, 1990; Willey *et al.*, 1996) through reactions such as:



Hydroperoxyl radicals are then available to make H₂O₂ [R9].

Reaction [R14] is a slow reaction and augments the production of HO₂ by reaction [R8], a faster reaction (Thompson *et al.*, 1989). In contrast, in the Archean,

when O₂ was a trace gas, the O₂ mixing ratio would have declined with increasing CH₄ concentration. In other words, in a methane-rich Archean atmosphere (Pavlov *et al.*, 2000), H₂O₂ production would have been limited by the availability of O₂.

There are also constraints on the range of CO₂ and CH₄ in the Archean atmosphere, which can be used to define the limits of our model boundary conditions in calculating H₂O₂ fluxes. Based on theoretical climate calculations, Kasting (1987) concluded that more CO₂ in the ancient atmosphere could counteract the effect of a faint young Sun and keep the planet's surface warm. According to their calculations, a 2-bar CO₂ atmosphere would have been sufficient to keep the planetary surface above freezing at 4.0 Ga. For the Late Archean, ~2.8 Ga, recent calculations made using a general circulation model are able to produce hospitable climates with 0.06–0.2 bar CO₂ (Wolf & Toon, 2013), or perhaps or even lower (0.01 bar) when coupled to a slab ocean (Le Hir *et al.*, 2014).

Several authors have argued for geologic constraints on ancient CO₂ levels. Based on paleosol geochemistry, *p*CO₂ has been limited to a maximum of ~0.009 bar at 2.2 Ga (Sheldon, 2006), updating previous results of Rye *et al.* (1995). Driese *et al.* (2011) applied the same paleosol methodology as Sheldon to obtain a constraint of 0.004–0.019 bar on older paleosols at 2.69 Ga. Rosing *et al.* (2010) argued for a very low limit on Archean *p*CO₂ of 0.001 bar based on iron formation mineralogy; however, the validity of using IF as CO₂ paleobarometers has been disputed (Dauphas & Kasting, 2011; Reinhard & Planavsky, 2011; Posth *et al.*, 2013b).

A relatively high level of CH₄ and/or H₂ is required for the anoxic conditions that produce mass-independent fractionation (MIF) in sulfur isotopes (Zahnle *et al.*, 2006). Biological thermodynamics predicts CH₄/H₂ ratios in the range 10–30 (Kasting *et al.*, 2001), so the CH₄ level was probably 10⁻²–10⁻³ bar, according to this line of argument coupled with MIF constraints. Indeed, Kharecha *et al.* (2005) calculated that in the anoxic Archean atmosphere, methanogens may have caused the CH₄ concentration to accumulate to ~10⁻³ bar. The theoretical requirements for a clement climate also suggest similar *p*CH₄ levels. Haqq-Misra *et al.* (2008) calculated that 0.01 bar CO₂ and 10⁻⁵ bar CH₄ would have kept Earth's surface above freezing at 2.8 Ga.

A REVISED EOARCHEAN PHOTOCHEMICAL MODEL

Here, we use the photochemical model of Zerkle *et al.* (2012), derived from that of Zahnle *et al.* (2006), to calculate the formation and rainout rate of H₂O₂ in the

Eoarchean atmosphere, given the constraints on CO₂ and CH₄ from above. However, in our model, we make a few changes compared to Zerkle *et al.* (2012) so that our simulations are appropriate for the Early Archean. For simplicity, we do not consider hazy atmospheres, which cause us to limit atmospheric CH₄:CO₂ to less than 0.1 (Zerkle *et al.*, 2012). To model the Eoarchean, we use the solar spectral energy density for 3.8 Ga calculated by Claire *et al.* (2012). Additionally, the model input of volcanic fluxes are set to values appropriate for the Early Archean as defined in Zahnle *et al.* (2006): H₂ = 3 × 10¹⁰ molecules cm⁻² s⁻¹; CO = 3 × 10⁹ molecules cm⁻² s⁻¹; H₂S = 1 × 10⁹ molecules cm⁻² s⁻¹; and SO₂ = 1 × 10¹⁰ molecules cm⁻² s⁻¹. For completeness, we test the sensitivity of our model to the solar flux input and the volcanic input. We explore three cases: (i) *p*CO₂ = 0.01 bar and negligible CH₄; (ii) *p*CO₂ = 0.01 bar and a range of CH₄ mixing ratios; and (iii) *p*CO₂ = 0.1 bar and a range of CH₄ mixing ratios. In all model cases, we allow *p*O₂ to be calculated by the model (i.e., we do not fix the surface mixing ratio or impose a biological input). The concentration of O₂ is always well below 10⁻⁵ PAL, an upper limit on *p*O₂ prior to 2.3 Ga (Pavlov & Kasting, 2002).

In *Case 1* (*p*CO₂ = 0.01 bar), to set a lower limit on the H₂O₂ rainout rate, we model a completely abiotic atmosphere with the CO₂ mixing ratio set to 1% or 33 PAL. As noted previously, this *p*CO₂ is consistent with paleosol data (Sheldon, 2006) and recent 3-D climate models (Wolf & Toon, 2013; Le Hir *et al.*, 2014). This photochemical model case includes negligible CH₄. The deposition velocities – which describe the dry deposition of gases from the atmosphere to ocean – for H₂ and CO are set to low values (0 and 10⁻⁸ cm s⁻¹) following Kharecha *et al.* (2005). This is roughly the same calculation performed by Haqq-Misra *et al.* (2011), except with different volcanic input rates, *p*CO₂, and solar flux.

In *Case 2* (*p*CO₂ = 0.01 bar and a range of CH₄ mixing ratio), we vary the mixing ratio of CH₄ from 5 × 10⁻⁵ to 10⁻³ in a 1-bar atmosphere. The lower limit is consistent with the photochemical model results of Haqq-Misra *et al.* (2008), and the upper limit marks CH₄:CO₂ = 0.1 when the formation of organic haze kicks in. Non-negligible CH₄ assumes a source from a surface biosphere. To simulate the uptake of H₂ by methanogens and the uptake of CO by acetogens, we apply deposition velocities of 2.4 × 10⁻⁴ and 1.2 × 10⁻⁴ cm s⁻¹ for H₂ and CO, respectively, following Kharecha *et al.* (2005). To be fully consistent, we would need to ensure that at each CH₄ mixing ratio, the flux of CH₄ into the model from the lower boundary (i.e., microbial output) equaled the flux of CO and H₂ out of the lower boundary of the model (i.e., micro-

bial input) in terms of H₂-equivalents. This constraint is approximately satisfied for the range of parameters considered.

In *Case 3* ($p\text{CO}_2 = 0.1$ bar or 10% (330 PAL)), we consider an upper limit on H₂O₂-rainout fluxes across a range of CH₄ mixing ratios.

For all three cases described above, the rainout fluxes and column-integrated reaction rates for reactions [R9] and [R10] are given in Table 1. In all three simulated atmospheres, reaction [R9] is the main pathway for H₂O₂ formation.

For *Case 1*, the H₂O₂-rainout flux is $\sim 3 \times 10^5$ molecules $\text{cm}^{-2} \text{s}^{-1}$. This is comparable in magnitude to the $\sim 10^6$ molecules $\text{cm}^{-2} \text{s}^{-1}$ rainout flux calculated in Haqq-Misra *et al.* (2011). The mixing ratio profiles for H₂O₂ and O₂ are shown in Fig. 1A. In *Case 2* and 3, the H₂O₂-rainout flux is maximized at the lowest CH₄ mixing ratio we consider, 5×10^{-5} bar. For both cases (CO₂ mixing ratio of 1% and 10%, respectively), this corresponds to a rainout rate of $\sim 8 \times 10^5$ molecules $\text{cm}^{-2} \text{s}^{-1}$. The mixing ratio profiles of H₂O₂ and O₂ for the model runs corresponding to this upper limit are shown in Fig. 1B,C. As the mixing ratio of CH₄ is increased from 5×10^{-5} bar to 10^{-3} bar, the H₂O₂-rainout flux decreases by around two orders of magnitude. The rainout flux directly tracks the decreasing column density of atmospheric O₂ (Fig. 2).

We also considered the sensitivity to denser CO₂ atmospheres, solar flux and volcanic input. An upper limit for $p\text{CO}_2$ in the Eoarchean is 2 bar, a value calculated by Kasting (1987). Haqq-Misra *et al.* (2011) have already performed this calculation, so we simply refer to the H₂O₂-rainout flux calculated in their model: 3×10^4 molecules $\text{cm}^{-2} \text{s}^{-1}$ (J. Kasting, pers. comm.). This value is lower than the rainout rates calculated in all three of our simulated atmospheres, which apparently contradicts our earlier statement about higher $p\text{CO}_2$ causing a larger H₂O₂-rainout flux. However, this is because large amounts of CO₂ shield H₂O from photolysis, which limits the rate of reaction [R6].

In all model cases, we use the solar flux for 3.8 Ga derived in Claire *et al.* (2012). For *Case 2*, we change

Table 1 Rainout rate of H₂O₂ and the column-integrated reaction rates for reaction [R9] HO₂ + HO₂ → H₂O₂ + O₂ and reaction [R10] OH + OH + M → H₂O₂ + M for all three model cases

	Case 1	Case 2	Case 3
H ₂ O ₂ -rainout flux (molecules per cm ² per s)	3×10^5	8×10^5	8×10^5
[R9] column-integrated reaction rate (molecules per cm ² per s)	3×10^{10}	4×10^{10}	1×10^{11}
[R10] column-integrated reaction rate (molecules per cm ² per s)	3×10^6	1×10^6	2×10^5

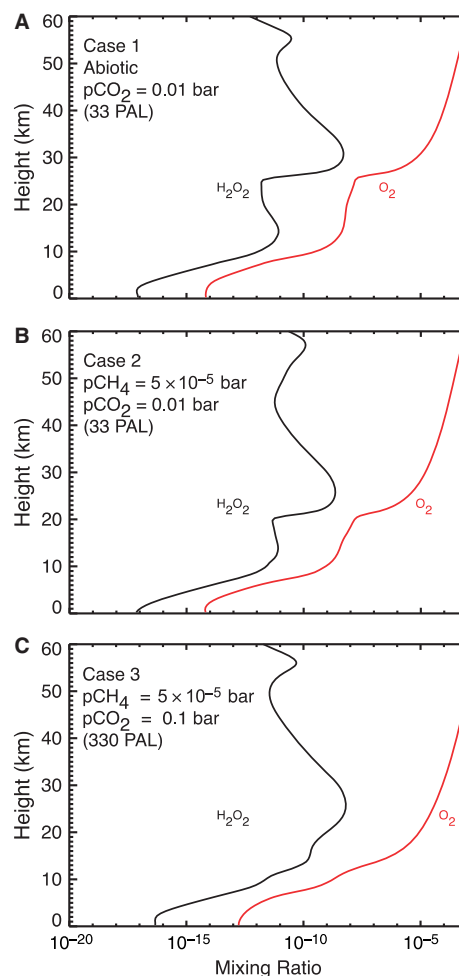


Fig. 1 Vertical profiles of H₂O₂ and O₂ for the three model cases described in the text.

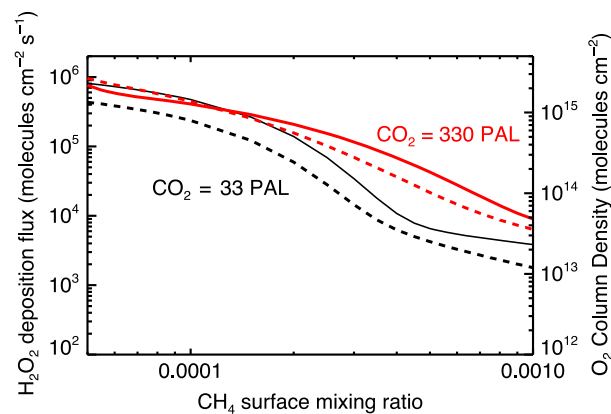


Fig. 2 H₂O₂ deposition (mapped to left axis) versus CH₄ surface mixing ratio for model cases 2 and 3, described in the text. Dashed lines show the O₂ column density for the corresponding CO₂ level.

the solar flux spectrum to a spectrum appropriate for the Late Archean (at 2.5 Ga), and find that the H₂O₂-rainout flux drops from $\sim 8 \times 10^5$ molecules $\text{cm}^{-2} \text{s}^{-1}$ to

$\sim 4 \times 10^5$ molecules $\text{cm}^{-2} \text{s}^{-1}$. This is because the column-integrated rates of CO_2 photolysis, H_2O photolysis, and O_3 photolysis are lower at 2.5 Ga than 3.8 Ga. Following Kasting *et al.* (1985), decreased photolysis of CO_2 limits the production of CO. Carbon monoxide converts OH to H by:

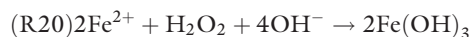
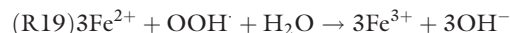
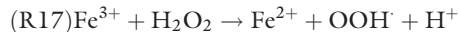


Accordingly, H may enter into reaction [R8] to make H_2O_2 . Similarly, H_2O photolysis [R8] creates H and OH that may make H_2O_2 . Ozone photolysis is critical for a different reason: It produces $\text{O}(^1\text{D})$ that may then be used in reaction [R7]. These reaction sequences are described further in Kasting *et al.* (1985).

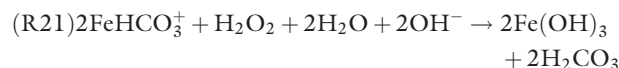
We test the volcanic emission rates in our model by decreasing the H_2 volcanic outgassing flux by a factor of 10, from 3×10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$ to 3×10^9 molecules $\text{cm}^{-2} \text{s}^{-1}$ for *Case 2* (following a similar sensitivity test in Haqq-Misra *et al.*, 2011). As the H_2 mixing ratio decreases, the O_2 column abundance increases and the overall H_2O_2 -rainout flux increases slightly by $\sim 1\%$. Of all the atmospheric simulations we have completed, the upper limit of H_2O_2 rainout is $\sim 10^6$ molecules $\text{cm}^{-2} \text{s}^{-1}$.

FLUX OF H_2O_2 NEEDED TO PRECIPITATE ARCHEAN IRON FORMATION

The oxidation of Fe(II) by H_2O_2 (or its by-products) occurs in a variety of environments and has been experimentally characterized over a range of conditions (Millero & Sotolongo, 1989; King & Farlow, 2000; González-Davila *et al.*, 2005). Under acidic conditions ($\text{pH} < 6$), the oxidation of Fe(II) by H_2O_2 , also known as Fenton's reaction [R16], is employed in the treatment of acidic municipal and industrial wastewaters because the radicals produced are efficient oxidants of organic pollutants while the Fe^{2+} gets recycled [reaction R17] to serve as an electron donor in further reactions (e.g., Bigda, 1996; Neyens & Baeyens, 2003). In the net reaction, 2 moles of H_2O_2 are converted into 2 moles of reactive radicals that engage in secondary organic oxidation reactions. Depending on the supply of Fe^{2+} , however, some OH^\cdot and OOH^\cdot radicals may instead get consumed in the further oxidation of Fe^{2+} when the latter is in abundance [R18–19], and, if the alkalinity were allowed to increase ($\text{pH} > 6$), Fenton's reaction becomes inefficient because the Fe^{3+} (from R16) quickly hydrolyses to $\text{Fe}(\text{OH})_3$ [R20]; $k_1 \approx 70 \text{ M}^{-1} \text{ s}^{-1}$), thereby inhibiting reaction [R17] from taking place (Moffett & Zika, 1987; González-Davila *et al.*, 2005).



Similarly, in aqueous environments with increased alkalinity ($\text{pH} > 8$), the addition of HCO_3^- (or CO_3^{2-}) was found to linearly increase the rate of Fe(II) oxidation because FeHCO_3^+ reacts faster with H_2O_2 than Fe^{2+} (Cole *et al.*, 1977; Millero & Sotolongo, 1989):



In either reactions [R20 or R21], when Fe^{2+} is abundant, the molar ratio of Fe(II) to H_2O_2 is 2:1. Over a wide range of pH, the overall reaction of Fe(II) with H_2O_2 is first order with respect to the concentration of total Fe(II) and H_2O_2 (k , $\text{M}^{-1} \text{ s}^{-1}$) (Moffett & Zika, 1987; Millero & Sotolongo, 1989):

$$(R22) d[\text{Fe(II)}]/dt = -k_2[\text{Fe(II)}][\text{OH}^-][\text{H}_2\text{O}_2]$$

where, $k_2 = k/[\text{OH}^-] = k[\text{H}^+]/K_w^*$. The term K_w^* is the dissociation product of water.

Previous thermodynamic modeling under simulated Eoarchean seawater conditions ($T = 40^\circ\text{C}$, saturation with respect to calcite and amorphous silica at $\text{pH} 7$) showed that the aqueous speciation of Fe(II) is largely dominated by Fe^{2+} (88.7% at $p\text{CO}_2$ of $10^{-2.4}$ atm and 70% at $p\text{CO}_2$ of $10^{-0.4}$ atm); FeHCO_3^+ increases to 21% as carbonate alkalinity increases (Konhauser *et al.*, 2007). Given that oxidation of Fe^{2+} by H_2O_2 is kinetically possible, even under high concentrations of HCO_3^- (or CO_3^{2-}) (Cole *et al.*, 1977; Millero & Sotolongo, 1989; González-Davila *et al.*, 2005), the question then becomes, was the amount of hydrogen peroxide generated in the Eoarchean atmosphere sufficient to account for all the ferric iron precipitated as iron formations?

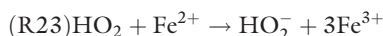
As discussed above, Algoma-type IF are typical in the rock record before 2.6 Ga. They are also smaller than 10 km along strike, although most have been severely deformed and dismembered, suggesting that their true size and extent were larger (Bekker *et al.*, 2010). To test the plausibility of H_2O_2 being the oxidant that caused the precipitation of Algoma IF, we consider an area of $3 \times 10^8 \text{ m}^2$, similar to that represented by the Malawi Lake in the Great Rift Valley Sys-

tem of East Africa, as a good approximation of the depositional basin. Although sedimentation rates for Algoma-type IF are poorly constrained, we apply a very conservative sedimentation rate of $0.6 \text{ cm}/10^3 \text{ year}^{-1}$ ($0.006 \text{ mm year}^{-1}$), which represents the average recorded in hydrothermal sediments near the East Pacific Rise (Dymond & Veeh, 1975); in the fall-out zone beneath some neutrally buoyant plumes today, such as the Rainbow vent field on the Mid-Atlantic Ridge, ferric hydroxides can accumulate faster, at a rate of $0.03 \text{ mm year}^{-1}$ (Cave *et al.*, 2002). By contrast, sedimentation rates previously assumed for some Superior-type IF are nearly three orders of magnitude higher, that is, 1 mm year^{-1} (Konhauser *et al.*, 2002, 2005). Using an initial composition of 80% $\text{Fe}(\text{OH})_3$ and 20% amorphous SiO_2 (which is now found as Fe-rich IF layers containing 80% hematite/magnetite and 20% quartz), we calculate that $5.11 \times 10^7 \text{ mol}$ of Fe(III) was precipitated during periods of high iron deposition.

Considering that 1 mole of Fe(II) oxidation requires 0.5 mole of H_2O_2 to be fully oxidized, and Fe(II) is the most important contributing species to the overall oxidation rate, a total of $2.55 \times 10^7 \text{ mol year}^{-1}$ of H_2O_2 is necessary to deposit all the ferric iron. Converting units, we would need a flux of $\text{H}_2\text{O}_2 \sim 1.61 \times 10^{11} \text{ molecules cm}^{-2} \text{ s}^{-1}$ (or $\sim 2.48 \times 10^{13} \text{ molecules cm}^{-2} \text{ s}^{-1}$ if a sedimentation rate of 1 mm year^{-1} is considered).

For completeness, we note that in addition to H_2O_2 , other oxidized atmospheric species rained out of the early atmosphere and may have been able to oxidize dissolved Fe(II). In the photochemical model of Segura *et al.* (2007), HO_2 , HNO, and H_2SO_4 form more rapidly than H_2O_2 in the prebiotic atmosphere. We note the relative contributions of these oxidants, as follows:

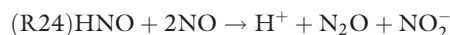
- HO_2 may oxidize Fe(II) by the following reaction from Barb *et al.* (1951):



The reaction stoichiometry requires that 1 mol HO_2 oxidize 1 mol Fe^{2+} ; therefore, the surface removal rate of HO_2 must be larger than the needed removal rate of H_2O_2 ($1.61 \times 10^{11} \text{ molecules cm}^{-2} \text{ s}^{-1}$) by a factor of 2. For Case 3 ($p\text{CO}_2 = 0.1 \text{ bar}$, $p\text{CH}_4 = 5 \times 10^{-5} \text{ bar}$), the surface removal rate of HO_2 is $3 \times 10^5 \text{ molecules cm}^{-2} \text{ s}^{-1}$, which is less than the $8 \times 10^5 \text{ molecules cm}^{-2} \text{ s}^{-1}$ rainout rate of H_2O_2 . Therefore, H_2O_2 is more important in producing an Fe(III) flux.

- HNO dissociates in water, ultimately forming nitrate (NO_3^-) and nitrite (NO_2^-) ions (Summers & Khare, 2007), the latter of which can oxidize dissolved Fe^{2+} (Summers & Chang, 1993; Klueglein & Kappler, 2013). To get the correct reaction stoichiometry, we follow 1 mole of HNO through to nitrite after it rains into the ocean. First, HNO dissociates into H^+ and

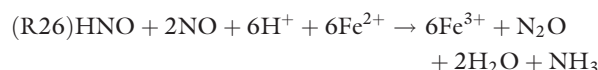
NO_2^- (Mancinelli & McKay, 1988). Then, it can combine with 2 moles of solubilized NO to create 1 mol nitrite (NO_2^-) in the following net reaction:



Finally, NO_2^- can react with Fe^{2+} via the following reaction given in Summers & Chang (1993):



The overall net reaction is as follows:



The stoichiometry dictates that 1/6 mole HNO and 1/3 mole NO are needed to oxidize 1 mol Fe(II). The limiting source of N, either HNO or NO, determines the maximum rate of reaction [R26]. If we first assume that HNO is the limiting reactant, and we assume an ambitious 100% yield for reaction [R25] (not achieved during any of the experiments in Summers & Chang, 1993), the surface loss of HNO, $4 \times 10^8 \text{ molecules cm}^{-2} \text{ s}^{-1}$ for Case 3 ($p\text{CO}_2 = 0.1 \text{ bar}$, $p\text{CH}_4 = 5 \times 10^{-5} \text{ bar}$), is insufficient to account for the HNO flux needed to oxidize $5.11 \times 10^7 \text{ mol}$ of Fe(II) to Fe(III) per year. The HNO flux needed would have to be ~ 140 times larger, $5.4 \times 10^{10} \text{ molecules cm}^{-2} \text{ s}^{-1}$. We next assume that NO is the limiting reactant and all other nitrogen species removed at the lower boundary of our model (HNO_3 , NO, and NO_2) are a source of NO. Once again, the total surface removal rate of those three species ($4 \times 10^5 \text{ molecules N cm}^{-2} \text{ s}^{-1}$) is insufficient to account for the NO flux needed to oxidize $5.11 \times 10^7 \text{ mol}$ of Fe(II) to Fe(III) per year. The N removal rate would need to be $\sim 3 \times 10^5$ times bigger, $1.0 \times 10^{11} \text{ molecules cm}^{-2} \text{ s}^{-1}$. Results from our model show that the flux of NO would have been the limiting factor, but regardless of the limiting factor, nitrogen species could not have oxidized enough dissolved Fe(II) to account for IF precipitation.

The fate of H_2SO_4 in the early anoxic ocean would have depended upon the exact chemical state and microbiology of the ocean. In the presence of O_2 , H_2SO_4 can oxidize Fe(II) to make the ferric iron species jarosite at low pH (equation 18 in Burns, 1988). In the absence of O_2 – consistent with conditions we assume in this study – Fe(II) remains stable against abiotic reaction with H_2SO_4 or the sulfate is reduced, biologically, to pyrite (Burns, 1988). Therefore, little oxidation of Fe(II) to Fe(III) by H_2SO_4 would be expected.

Because of these reasons, we only have focused on the oxidation of Fe(II) by H_2O_2 . These two species have well-characterized reactions in solution [R16-R21].

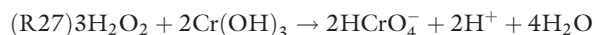
IMPLICATIONS FOR THE EOARCHEAN EARTH

Biotic processes, either directly or indirectly, have traditionally been put forward as the most parsimonious explanation for the origin of IF; either cyanobacteria generated oxygen which inorganically reacted with Fe^{2+} in seawater to form ferric oxyhydroxide minerals or anoxygenic photosynthetic bacteria utilized Fe^{2+} in their metabolism and thereby directly caused the formation of ferric iron. Evidence supporting either of these proposed mechanisms, however, is inconclusive for Eoarchean IF, and thus, their ultimate origin remains highly speculative. Here, we hypothesized that H_2O_2 , a powerful naturally occurring oxidant, could have formed in geochemically significant quantities to precipitate, most, if not all the Eoarchean IF. Our simple model relies on a comprehensive view in the evolution of the early Earth consistent with previous findings, whereby photochemical reactions of UV light in a CH_4 - and CO_2 -dominated atmosphere, which lacked oxygen and an ozone layer, could produce abundant H_2O_2 to oxidize the Fe^{2+} present in the ocean. Our results show that the rainout flux of H_2O_2 ($<10^6$ molecules $\text{cm}^{-2} \text{s}^{-1}$) is several orders of magnitude smaller than the conservative estimated flux (10^{11} molecules $\text{cm}^{-2} \text{s}^{-1}$) required for Fe(II) oxidation in IF.

The implications from this modeling exercise are quite profound because they further constrain the Fe(II) mechanisms required for the precipitation of the ferric iron component in Algoma-type IF. Their close association with volcanic rocks suggests that they were deposited from the settling of Fe(III)-rich particles in the central part of submarine volcanic centers (Chown *et al.*, 2000) or along their flanks, similar to the model invoked by Krapež *et al.* (2003). In these scenarios, it would seem that the hydrothermal sources must have been relatively shallow to allow Fe(III) accumulation near the vent, that is, before significant lateral dispersion. It is also important to note that in the Eoarchean IF studied, including the *ca.* 3.8 Ga Nuvvuagittuq Supracrustal Belt in northern Quebec, the Nulliak Supracrustal Association in northern Labrador, and the Isua and Akilia Supracrustal Belt in southern west Greenland (e.g., Mloszewska *et al.*, 2013), magnetite (Fe_3O_4) is one of the main iron minerals. The magnetite tends to have heavy iron isotopic compositions relative to other minerals, consistent with the view that Fe(III) in the IF was derived from partial oxidation of $\text{Fe}(\text{II})_{\text{aq}}$ in seawater, meaning that the oxidative capacity at that time was insufficient to process all $\text{Fe}(\text{II})_{\text{aq}}$ available (Dauphas *et al.*, 2004, 2007; Planavsky *et al.*, 2011; Mloszewska *et al.*, 2012; Czaja *et al.*, 2013). Although various mechanisms exist that can account for magnetite formation in IF (e.g., Li *et al.*, 2013), the C and Fe isotopic compositions of coexisting iron-oxides and carbonates in Isua is best explained by

the process of dissimilatory Fe(III) reduction, whereby bacterial respiration oxidizes organic matter with low $\delta^{13}\text{C}$ values using ferric oxyhydroxides with high $\delta^{56}\text{Fe}$, releasing CO_2 and $\text{Fe}(\text{II})_{\text{aq}}$ in the pore-water that can subsequently form the ferrous-containing minerals (Cradock & Dauphas, 2011). Significantly, the presence of organic carbon implies burial of microbial biomass along with the ferric iron-containing IF precursor sediment. At present, evidence in support of Eoarchean life comes mainly from graphite-containing apatite grains from Akilia that show $\delta^{13}\text{C}$ values ranging from -20 to -50‰ (Mojzsis *et al.*, 1996; McKeegan *et al.*, 2007) which are consistent with biological carbon fractionation (but see van Zuilen *et al.*, 2002; Lepland *et al.*, 2011 for an alternative view). Rosing (1999) and Rosing & Frei (2004) also reported 0.4 wt.% reduced carbon, with $\delta^{13}\text{C}$ values as low as -25‰ in metamorphosed pelagic shales from Isua that were interpreted as evidence for cyanobacteria. It is interesting to note that those fractionations lie within the expected range for anoxygenic photosynthetic bacteria (see Schidlowski, 2001), such as the photoferrotophs we suggest contributed to Eoarchean IF deposition (i.e., before cyanobacteria had evolved). Moreover, based on the range of $\delta^{56}\text{Fe}$ in the Isua IF, Czaja *et al.* (2013) argued that the precursor ferric oxyhydroxide precipitated from a low-temperature and essentially anoxic water column, with photoferrotophs being the most likely mechanism.

Regardless of the inability to precipitate IF, this flux of H_2O_2 could have had a measureable effect on the continental weathering. It has been widely accepted that oxygen levels in Earth's atmosphere were very low before the GOE. Despite recent studies reporting geochemical proxies suggestive of oxidative continental weathering at *ca.* 3.0 Ga (Crowe *et al.*, 2013; Planavsky *et al.*, 2014) – the 1st study arguing for the presence of atmospheric oxygen and the 2nd arguing for the presence of localized oxygen oases in the water column – it remains possible that H_2O_2 might have augmented these oxidative weathering reactions. For instance, the oxidation of Cr(III) in residual soil minerals, such as chromium(III) hydroxide, has been demonstrated in the presence of hydrogen peroxide (Rock *et al.*, 2001).

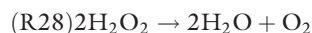


Such reactions can also generate isotopic fractionation in $^{53}\text{Cr}/^{52}\text{Cr}$, leading to enrichment in the heavier isotope by $+0.2\text{‰}$ (Zink *et al.*, 2010). This is in line with the positively fractionated $\delta^{53}\text{Cr}$ values (ranging from $+0.04$ to $+0.29\text{‰}$) reported in some Neoproterozoic IF by Frei *et al.* (2009) who used those positive values as evidence for early oxidative weathering via the reaction of O_2 with Mn(II) to form the MnO_2 catalyst required for Cr(III) oxidation and

Cr(VI) supply to the oceans. The significance of such a reaction is that Cr(VI) – the mobile form of Cr – can be generated under anoxic conditions by oxidation with H₂O₂, and as such, the presence of Cr in pre-GOE marine sediments does not unequivocally imply that oxygen was available to have mobilized Cr from insoluble Cr(III)-bearing minerals in soils (e.g., Frei *et al.*, 2009; Crowe *et al.*, 2013). Whether the reaction of Cr(III) with H₂O₂ was significant enough to mobilize all of the Cr measured in 3.0 Ga IF is unknown given our lack of knowledge about initial concentrations of Cr(III) in the host rocks and subsequent paleosols, the flux of Cr(VI) mobilized in the rivers and groundwater, the actual distance Cr(VI) might have been mobilized given the abundance of reductants capable of driving the reverse reductive reactions (e.g., ferrous iron), and the total amount of Cr immobilized in the IF depositional basin. In addition, based on the experiments of Rock *et al.* (2001), the half-life of H₂O₂ in contact with Cr(III)-bearing soils was on the order of hours, and most H₂O₂ introduced into the soils was disproportionated and lost without participating in Cr(III) oxidation. Therefore, even at H₂O₂:Cr(III) ratios much greater than the 3:2 stoichiometry in reaction [R27], only a fraction of the H₂O₂ deposited onto the soil surface could have facilitated some Cr(III) oxidation. Nonetheless, any attempt to constrain the Archean atmospheric O₂ concentrations based solely on the presence of Cr in marine sediments might need to be reevaluated (e.g., Konhauser *et al.*, 2011).

The flux of H₂O₂ could also have a profound effect on the marine microbiota by triggering the early development of enzymes capable of protecting the indigenous microorganisms against reactive oxygen species, such as H₂O₂, and the products of its decomposition, such as superoxide and hydroxyl radicals. Various enzymatic defense systems (e.g., superoxide dismutase, catalase, and peroxidase) scavenge superoxide radicals and H₂O₂ and convert them into less reactive species preventing damage to some of their biological macromolecules, including DNA (Touati, 2000). Many modern anaerobic bacteria have these key enzymes (e.g., Asada *et al.*, 1980; Towe, 1988; Bernroither *et al.*, 2009), and thus, it has been argued that these enzymes likely evolved in response to an environmental peroxide challenge (McKay & Hartman, 1991; Blankenship & Hartman, 1998). Many previous authors have also supported the idea that some free O₂ must have been available prior the origin of oxygenic photosynthesis (Towe, 1988, 1990, 1996; Castresana *et al.*, 1994; Ducluzeau *et al.*, 2008; Brochier-Armanet *et al.*, 2009). In this regard, a recent study showed that some modern aerobes can respire at dissolved O₂ concentrations of 3 nM or less, that is, about 1000 times lower than previously believed (Stolper *et al.*, 2010). Accordingly, a primitive aerobe of ca. 0.5 mm in diameter might have been able to respire

under O₂ concentrations as low as 0.05 nM (Stolper *et al.*, 2010). Previous atmospheric photochemical models suggested that disproportionation of H₂O₂ [R28] near the surface might have yielded enough O₂ to satisfy that constraint (Haqq-Misra *et al.*, 2011).



It is thus possible that the hypothetical LUCA (Last Universal Common Ancestor) was equipped with enzymes capable of dealing with O₂/H₂O₂ reactions (Slesak *et al.*, 2012). In the absence of the large amounts of iron (i.e., no hydrothermal plumes or upwelling of Fe-rich waters), which would have overwhelmed all the H₂O₂ generated, disproportionation of H₂O₂ in the water column might have generated similar amounts of O₂, and ultimately facilitated the advent of oxygenic photosynthesis on an otherwise anaerobic Earth.

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