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 (H_2O_2), a recognized strong oxidant for ferrous iron. Here, we modeled the amount of H_2O_2 that could be produced in an Eoarchean atmosphere using updated solar fluxes and plausible CO_2, O_2, and CH_4 mixing ratios. Irrespective of the atmospheric simulations, the upper limit of H_2O_2 rainout was calculated to be $<10^6$ 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 H_2O_2 was insufficient by several orders of magnitude to account for IF deposition (requiring $\sim10^{11}$ H_2O_2 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.

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 sulfitic 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).
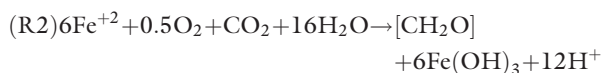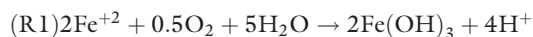
In contrast, larger Superior-type IF developed in near-shore continental-shelf environments where they are typically interbedded with carbonates, quartz arenite, and black shale, but with only minor amounts of volcanic rocks (Gross, 1980). Unlike most Algoma-type IF, which rarely extend for more than 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 km^2 (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 CO_2 and CH_4 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 O$_2$

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).

$$(R1) 2Fe^{+2} + 0.5O_2 + 5H_2O \rightarrow 2Fe(OH)_3 + 4H^+$$

$$(R2) 6Fe^{+2} + 0.5O_2 + CO_2 + 16H_2O \rightarrow [CH_2O] + 6Fe(OH)_3 + 12H^+$$

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 ^{13}C-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, Sforna *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).

$$(R3) 4Fe^{2+} + CO_2 + 11H_2O \rightarrow [CH_2O] + 4Fe(OH)_3 + 8H^+$$
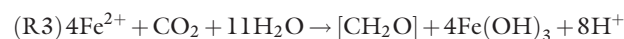
Laboratory experiments demonstrated that this form of metabolism could generate sufficient quantities of Fe(III) to account for all the oxidized iron in IF even at rapid accumulation rates (Konhauser *et al.*, 2002; Kappler *et al.*, 2005). Crucially, Fe(II) oxidation by anoxygenic phototrophs can be 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).
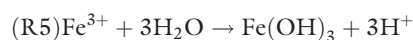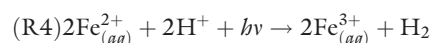
Despite the absence of fossilized remains of photoferrotrophs in the Archean, numerous lines of evidence suggest their presence on the early Earth (e.g., Posth *et al.*, 2013a). Perhaps most importantly, of the seven known strains of anoxygenic Fe(II)-oxidizing phototrophs, six have been classified as *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 $Fe(OH)^+$ in the water column causes the oxidation of these species and the subsequent precipitation of ferric oxyhydroxides, such as ferrihydrite and $Fe(OH)_3$ (Cairns-Smith, 1978; Braterman *et al.*, 1983).

$$(R4) \quad 2Fe^{2+}_{(aq)} + 2H^+ + hv \rightarrow 2Fe^{3+}_{(aq)} + H_2$$

$$(R5) \quad Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

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 the 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 O_2 derived from cyanobacteria, we consider whether H_2O_2 played a significant role in Fe(II) oxidation prior to this time, or perhaps even afterward. For example, photochemically derived H_2O_2 stored in ice caps and glaciers may have been released after the Makganyene Snowball Earth event *ca.* 2.3 Ga. This release of H_2O_2 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 H_2O_2 formed by atmospheric photochemical reactions, as it is the only process that can generate significant fluxes.

The formation of H_2O_2 in the ancient atmosphere begins with the photolysis of water vapor:

$$(R6) H_2O + hv \rightarrow H + OH$$
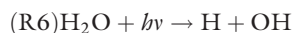
or by the reaction of water vapor with an excited atomic oxygen, $O(^1D)$:

$$(R7) H_2O + O(^1D) \rightarrow 2OH$$

Reaction [R7] may then be followed by:

$$(R8) H + O_2 + M \rightarrow HO_2 + M$$

where, 'M' is any molecule. Both OH and HO_2 are precursors to H_2O_2 formation through the following reactions:

$$(R9) HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

$$(R10) OH + OH + M \rightarrow H_2O_2 + M$$
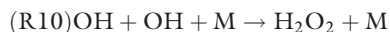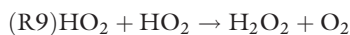
Hydrogen peroxide may then be removed from the atmosphere by photolysis, reaction with OH, or by rainout (Kasting *et al.*, 1985).

Kasting *et al.* (1984) used a photochemical model of a CO_2-rich anoxic atmosphere (surface pO_2 ~10^{-11} bar) to calculate a H_2O_2 rainout rate of ~10^9–10^{10} 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 O_2, CH_4, and CO_2 in the Eoarchean

atmosphere would have affected the rainout rate of H_2O_2.

In the Archean atmosphere, O_2 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 H_2O_2 would have been lower than it is today because the formation of its precursor, HO_2, requires O_2 [see R8]. For example, Haqq-Misra *et al.* (2011) calculated a H_2O_2 rainout rate of ~10^6 molecules cm^{-2} s^{-1} for a pre-photosynthetic atmosphere with 0.2 bar CO_2. Despite the low concentrations of O_2, in the pre-photosynthetic atmosphere, it would have been reaction [R9], not reaction [R10] that was the main formation pathway for H_2O_2. Haqq-Misra *et al.* (2011) erroneously reported that reaction [R10] was more important (J. Kasting, personal communication).

When O_2 is a trace constituent, higher pCO_2 tends to increase the H_2O_2-rainout flux. As discussed in Kasting *et al.* (1984), CO_2 promotes the formation of O_2 [R11 through R13] and, when followed by reactions [R8 and R9], the production of H_2O_2:

$$(R11) CO_2 + hv \rightarrow CO + O$$

$$(R12) O + O + M \rightarrow O_2 + M$$

$$(R13) O + OH \rightarrow O_2 + H$$
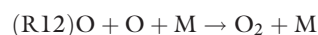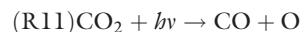
Methane affects H_2O_2 production in an opposite manner in the modern atmosphere compared to the Archean atmosphere. Methane, like CO_2, is posited to have been more abundant in the Archean (see Discussion in following section). In the modern atmosphere, if CH_4 concentrations were to increase, H_2O_2 production would increase. This is because photochemical reactions involving CH_4 produce higher-order hydrocarbon gases, such as ethane (C_2H_6) and formaldehyde (H_2CO) (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 (HO_2) (Thompson *et al.*, 1989; Gunz & Hoffmann, 1990; Willey *et al.*, 1996) through reactions such as:

$$(R14) CH_3O_2 + O_2 \rightarrow CH_2O + HO_2$$
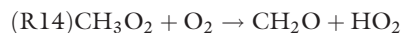
Hydroperoxyl radicals are then available to make H_2O_2 [R9].

Reaction [R14] is a slow reaction and augments the production of HO_2 by reaction [R8], a faster reaction (Thompson *et al.*, 1989). In contrast, in the Archean,

when O_2 was a trace gas, the O_2 mixing ratio would have declined with increasing CH_4 concentration. In other words, in a methane-rich Archean atmosphere (Pavlov et al., 2000), H_2O_2 production would have been limited by the availability of O_2.

There are also constraints on the range of CO_2 and CH_4 in the Archean atmosphere, which can be used to define the limits of our model boundary conditions in calculating H_2O_2 fluxes. Based on theoretical climate calculations, Kasting (1987) concluded that more CO_2 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 CO_2 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 CO_2 (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 CO_2 levels. Based on paleosol geochemistry, pCO_2 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 pCO_2 of 0.001 bar based on iron formation mineralogy; however, the validity of using IF as CO_2 paleobarometers has been disputed (Dauphas & Kasting, 2011; Reinhard & Planavsky, 2011; Posth et al., 2013b).

A relatively high level of CH_4 and/or H_2 is required for the anoxic conditions that produce mass-independent fractionation (MIF) in sulfur isotopes (Zahnle et al., 2006). Biological thermodynamics predicts CH_4/H_2 ratios in the range 10–30 (Kasting et al., 2001), so the CH_4 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 CH_4 concentration to accumulate to ~10^{-3} bar. The theoretical requirements for a clement climate also suggest similar pCH_4 levels. Haqq-Misra et al. (2008) calculated that 0.01 bar CO_2 and 10^{-5} bar CH_4 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 H_2O_2 in the Eoarchean atmosphere, given the constraints on CO_2 and CH_4 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 CH_4:CO_2 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): H_2 = 3×10^{10} molecules cm^{-2} s^{-1}; CO = 3×10^9 molecules cm^{-2} s^{-1}; H_2S = 1×10^9 molecules cm^{-2} s^{-1}; and SO_2 = 1×10^{10} 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) pCO_2 = 0.01 bar and negligible CH_4; (ii) pCO_2 = 0.01 bar and a range of CH_4 mixing ratios; and (iii) pCO_2 = 0.1 bar and a range of CH_4 mixing ratios. In all model cases, we allow pO_2 to be calculated by the model (i.e., we do not fix the surface mixing ratio or impose a biological input). The concentration of O_2 is always well below 10^{-5} PAL, an upper limit on pO_2 prior to 2.3 Ga (Pavlov & Kasting, 2002).

In *Case 1* (pCO_2 = 0.01 bar), to set a lower limit on the H_2O_2 rainout rate, we model a completely abiotic atmosphere with the CO_2 mixing ratio set to 1% or 33 PAL. As noted previously, this pCO_2 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 CH_4. The deposition velocities – which describe the dry deposition of gases from the atmosphere to ocean – for H_2 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, pCO_2, and solar flux.

In *Case 2* (pCO_2 = 0.01 bar and a range of CH_4 mixing ratio), we vary the mixing ratio of CH_4 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 CH_4:CO_2 = 0.1 when the formation of organic haze kicks in. Non-negligible CH_4 assumes a source from a surface biosphere. To simulate the uptake of H_2 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 H_2 and CO, respectively, following Kharecha et al. (2005). To be fully consistent, we would need to ensure that at each CH_4 mixing ratio, the flux of CH_4 into the model from the lower boundary (i.e., microbial output) equaled the flux of CO and H_2 out of the lower boundary of the model (i.e., micro-

bial input) in terms of H_2-equivalents. This constraint is approximately satisfied for the range of parameters considered.

In *Case 3* (pCO_2 = 0.1 bar or 10% (330 PAL)), we consider an upper limit on H_2O_2-rainout fluxes across a range of CH_4 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 H_2O_2 formation.

For *Case 1*, the H_2O_2-rainout flux is ~3×10^5 molecules cm^{-2} s^{-1}. This is comparable in magnitude to the ~10^6 molecules cm^{-2} s^{-1} rainout flux calculated in Haqq-Misra *et al.* (2011). The mixing ratio profiles for H_2O_2 and O_2 are shown in Fig. 1A. In *Case 2* and *3*, the H_2O_2-rainout flux is maximized at the lowest CH_4 mixing ratio we consider, 5×10^{-5} bar. For both cases (CO_2 mixing ratio of 1% and 10%, respectively), this corresponds to a rainout rate of ~8×10^5 molecules cm^{-2} s^{-1}. The mixing ratio profiles of H_2O_2 and O_2 for the model runs corresponding to this upper limit are shown in Fig. 1B,C. As the mixing ratio of CH_4 is increased from 5×10^{-5} bar to 10^{-3} bar, the H_2O_2-rainout flux decreases by around two orders of magnitude. The rainout flux directly tracks the decreasing column density of atmospheric O_2 (Fig. 2).

We also considered the sensitivity to denser CO_2 atmospheres, solar flux and volcanic input. An upper limit for pCO_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 H_2O_2-rainout flux calculated in their model: 3×10^4 molecules cm^{-2} 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 pCO_2 causing a larger H_2O_2-rainout flux. However, this is because large amounts of CO_2 shield H_2O 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 H_2O_2 and the column-integrated reaction rates for reaction [R9] $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ and reaction [R10] $OH + OH + M \rightarrow H_2O_2 + M$ for all three model cases

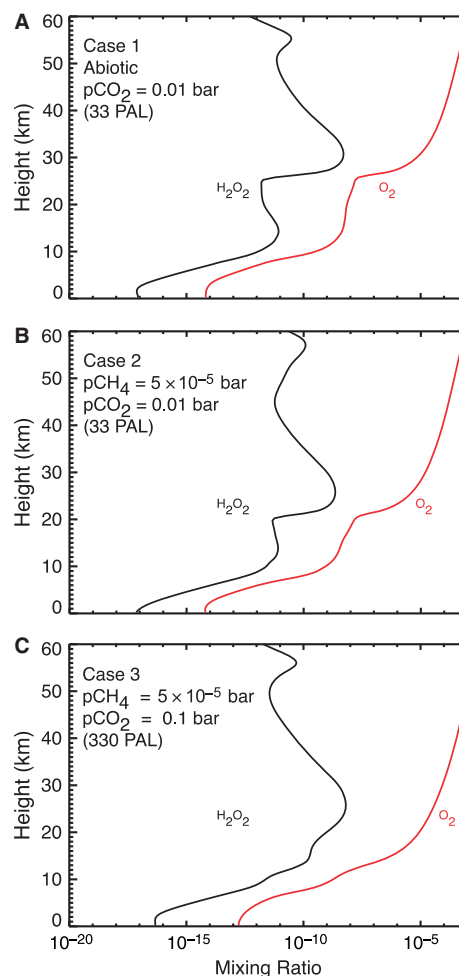|	Case 1	Case 2	Case 3
H_2O_2-rainout flux (molecules per cm^2 per s)	3×10^5	8×10^5	8×10^5
[R9] column-integrated reaction rate (molecules per cm^2 per s)	3×10^{10}	4×10^{10}	1×10^{11}
[R10] column-integrated reaction rate (molecules per cm^2 per s)	3×10^6	1×10^6	2×10^5

Fig. 1 Vertical profiles of H_2O_2 and O_2 for the three model cases described in the text.
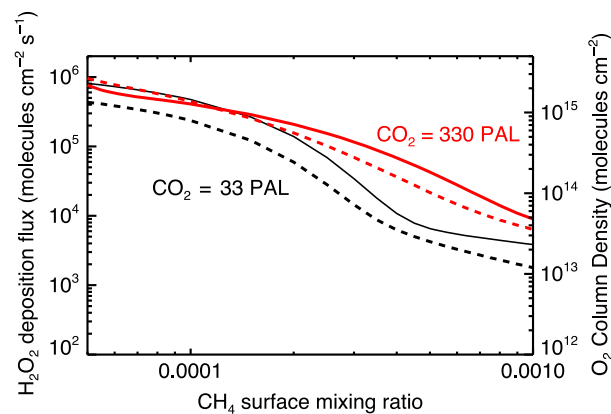

Fig. 2 H_2O_2 deposition (mapped to left axis) versus CH_4 surface mixing ratio for model cases 2 and 3, described in the text. Dashed lines show the O_2 column density for the corresponding CO_2 level.

the solar flux spectrum to a spectrum appropriate for the Late Archean (at 2.5 Ga), and find that the H_2O_2-rainout flux drops from ~8×10^5 molecules cm^{-2} s^{-1} to

$\sim 4 \times 10^5$ molecules cm^{-2} 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:
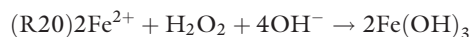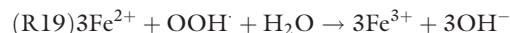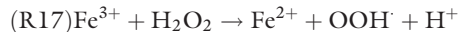
$$(R15) CO + OH \rightarrow CO_2 + H$$

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 $O(^1D)$ 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 cm^{-2} s^{-1} to 3×10^9 molecules cm^{-2} 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 cm^{-2} 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 (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· and OOH· 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 (pH>6), Fenton's reaction becomes inefficient because the Fe^{3+} (from R16) quickly hydrolyses to $Fe(OH)_3$ [R20]; $k_1 \approx 70$ M^{-1} s^{-1}), thereby inhibiting reaction [R17] from taking place (Moffett & Zika, 1987; González-Davila *et al.*, 2005).

$$(R16) Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + OH^{\cdot} + H_2O$$

$$(R17) Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^{\cdot} + H^+$$

$$(R18) Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^-$$

$$(R19) 3Fe^{2+} + OOH^{\cdot} + H_2O \rightarrow 3Fe^{3+} + 3OH^-$$

$$(R20) 2Fe^{2+} + H_2O_2 + 4OH^- \rightarrow 2Fe(OH)_3$$

Similarly, in aqueous environments with increased alkalinity (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):

$$(R21) 2FeHCO_3^+ + H_2O_2 + 2H_2O + 2OH^- \rightarrow 2Fe(OH)_3 + 2H_2CO_3$$
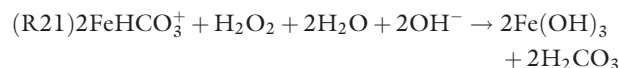
In either reactions [R20 or R21], when Fe^{2+} is abundant, the molar ratio of Fe(II) to H_2O_2 is 2:1. Over a wide range of pH, the overall reaction of Fe(II) with H_2O_2 is first order with respect to the concentration of total Fe(II) and H_2O_2 (k, M^{-1} s^{-1}) (Moffett & Zika, 1987; Millero & Sotolongo, 1989):

$$(R22) d[Fe(II)]/dt = -k_2[Fe(II)][OH^-][H_2O_2]$$

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

Previous thermodynamic modeling under simulated Eoarchean seawater conditions (T = 40°C, saturation with respect to calcite and amorphous silica at pH 7) showed that the aqueous speciation of Fe(II) is largely dominated by Fe^{2+} (88.7% at pCO_2 of $10^{-2.4}$ atm and 70% at pCO_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 3×10^8 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 cm/10^3 year^{-1} (0.006 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 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% $Fe(OH)_3$ and 20% amorphous SiO_2 (which is now found as Fe-rich IF layers containing 80% hematite/magnetite and 20% quartz), we calculate that 5.11×10^7 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 2.55×10^7 mol year^{-1} of H_2O_2 is necessary to deposit all the ferric iron. Converting units, we would need a flux of H_2O_2 ~1.61×10^{11} molecules cm^{-2} s^{-1} (or ~2.48×10^{13} molecules cm^{-2} 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):

$$(R23) HO_2 + Fe^{2+} \rightarrow HO_2^- + 3Fe^{3+}$$
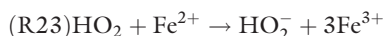
  The reaction stoichiometry requires that 1 mol HO_2 oxidize 1 mol Fe^{2+}; therefore, the surface removal rate of HO_2 must be larger than the needed removal rate of H_2O_2 (1.61×10^{11} molecules cm^{-2} s^{-1}) by a factor of 2. For Case 3 ($pCO_2 = 0.1$ bar, $pCH_4 = 5 \times 10^{-5}$ bar), the surface removal rate of HO_2 is 3×10^5 molecules cm^{-2} s^{-1}, which is less than the 8×10^5 molecules cm^{-2} 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
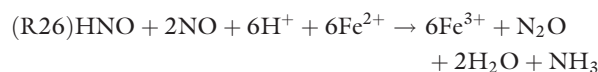
NO_2^- (Mancinelli & McKay, 1988). Then, it can combine with 2 moles of solubilized NO to create 1 mol nitrite (NO_2^-) in the following net reaction:

$$(R24) HNO + 2NO \rightarrow H^+ + N_2O + NO_2^-$$
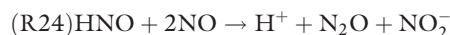
Finally, NO_2^- can react with Fe^{2+} via the following reaction given in Summers & Chang (1993):

$$(R25) NO_2^- + 6Fe^{2+} + 7H^+ \rightarrow 6Fe^{3+} + 2H_2O + NH_3$$

The overall net reaction is as follows:

$$(R26) HNO + 2NO + 6H^+ + 6Fe^{2+} \rightarrow 6Fe^{3+} + N_2O + 2H_2O + NH_3$$

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, 4×10^8 molecules cm^{-2} s^{-1} for Case 3 ($pCO_2 = 0.1$ bar, $pCH_4 = 5 \times 10^{-5}$ bar), is insufficient to account for the HNO flux needed to oxidize 5.11×10^7 mol of Fe(II) to Fe(III) per year. The HNO flux needed would have to be ~140 times larger, 5.4×10^{10} molecules cm^{-2} 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 (4×10^5 molecules N cm^{-2} s^{-1}) is insufficient to account for the NO flux needed to oxidize 5.11×10^7 mol of Fe(II) to Fe(III) per year. The N removal rate would need to be ~3×10^5 times bigger, 1.0×10^{11} molecules cm^{-2} 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 cm^{-2} s^{-1}) is several orders of magnitude smaller than the conservative estimated flux (10^{11} molecules cm^{-2} 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 $Fe(II)_{aq}$ in seawater, meaning that the oxidative capacity at that time was insufficient to process all $Fe(II)_{aq}$ 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 $\delta^{13}C$ values using ferric oxyhydroxides with high $\delta^{56}Fe$, releasing CO_2 and $Fe(II)_{aq}$ in the pore-water that can subsequently form the ferrous-containing minerals (Craddock & 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 $\delta^{13}C$ 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 $\delta^{13}C$ 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 photoferrotrophs we suggest contributed to Eoarchean IF deposition (i.e., before cyanobacteria had evolved). Moreover, based on the range of $\delta^{56}Fe$ 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 photoferrotrophs 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).

$$(R27) 3H_2O_2 + 2Cr(OH)_3 \rightarrow 2HCrO_4^- + 2H^+ + 4H_2O$$
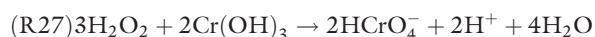
Such reactions can also generate isotopic fractionation in $^{53}Cr/^{52}Cr$, leading to enrichment in the heavier isotope by +0.2‰ (Zink et al., 2010). This is in line with the positively fractionated $\delta^{53}Cr$ values (ranging from +0.04 to +0.29‰) reported in some Neoarchean IF by Frei et al. (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 H_2O_2, 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 H_2O_2 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 H_2O_2 in contact with Cr(III)-bearing soils was on the order of hours, and most H_2O_2 introduced into the soils was disproportionated and lost without participating in Cr(III) oxidation. Therefore, even at H_2O_2:Cr(III) ratios much greater than the 3:2 stoichiometry in reaction [R27], only a fraction of the H_2O_2 deposited onto the soil surface could have facilitated some Cr(III) oxidation. Nonetheless, any attempt to constrain the Archean atmospheric O_2 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 H_2O_2 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 H_2O_2, 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 H_2O_2 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; Bernroitner *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 O_2 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 O_2 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 O_2 concentrations as low as 0.05 nM (Stolper *et al.*, 2010). Previous atmospheric photochemical models suggested that disproportion of H_2O_2 [R28] near the surface might have yielded enough O_2 to satisfy that constraint (Haqq-Misra *et al.*, 2011).

$$(R28)\, 2H_2O_2 \rightarrow 2H_2O + O_2$$
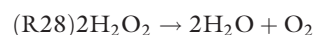
It is thus possible that the hypothetical LUCA (Last Universal Common Ancestor) was equipped with enzymes capable of dealing with O_2/H_2O_2 reactions (Slesak *et al.*, 2012). In the absence of the large amounts of iron (i.e., no hydrothermal plumes or upwelling of Fe-rich waters), which would have overwhelmed all the H_2O_2 generated, disproportionation of H_2O_2 in the water column might have generated similar amounts of O_2, and ultimately facilitated the advent of oxygenic photosynthesis on an otherwise anaerobic Earth.

ACKNOWLEDGMENTS

REFERENCES

Amme M, Bors W, Michel C, Stettmaier K, Rasmussen G, Betti M (2005) Effects of Fe(II) and hydrogen peroxide interaction upon dissolving UO2 under geologic repository conditions. *Environmental Science and Technology* **39**, 221–229.

Asada K, Kanematsu S, Okaka S, Hayakawa T (1980) Phylogenic distribution of three types of superoxide dismutase in organisms and in cell organelles. In *Chemical and Biochemical Aspects of Superoxide and Superoxide Dismutase* (eds Bannister JV, Hill HAO). Elsevier, New York, pp. 136–153.

Barb WG, Baxendale JH, George P, Hargrave PR (1951) Reactions of ferrous and ferric ions with hydrogen peroxide Part 1: the ferrous ion reaction. *Transactions of the Faraday Society* **47**, 462–500.

Bekker A, Slack JF, Planavsky N, Krapez B, Hofmann A, Konhauser KO, Rouxel OJ (2010) Iron formation: the sedimentary product of a complex interplay among mantle, tectonic, oceanic, and biospheric processes. *Economic Geology* **105**, 467–508.

Bernroitner M, Zamocky M, Furtmüller PG, Peschek GA, Obinger C (2009) Occurrence, phylogeny, structure, and function of catalases and peroxidases in cyanobacteria. *Journal of Experimental Botany* **60**, 423–440.

Bigda RJ (1996) Fenton's chemistry: an effective advanced oxidation process. *Environmental Technology* **17**, 34–39.

Blankenship RE, Hartman H (1998) The origin and evolution of oxygenic photosynthesis. *Trends in Biochemical Science* **23**, 94–97.

Borda M, Elsetinow A, Schoonen M, Strongin D (2001) Pyrite-induced hydrogen peroxide formation as a driving force in the evolution of photosynthetic organisms on an early Earth. *Astrobiology* **1**, 283–288.

Borda MJ, Elsetinow AR, Strongin DR, Schoonen MA (2003) A mechanism for the production of hydroxyl radical at surface defect sites on pyrite. *Geochimica Cosmochimica Acta* **67**, 935–939.

Bosak T, Liang B, Sim MS, Petroff AP (2009) Morphological record of oxygenic photosynthesis in conical stromatolites. *Proceedings of the National Academy of Sciences of the USA* **106**, 10939–10943.

Braterman PS, Cairns-Smith AG (1986) Photoprecipitation and the banded iron-formations - some quantitative aspects. In *Appel PWU, LaBerge GL).* (ed Iron-Formations P). Theophrastus, Athens, pp. 221–228.

Braterman PS, Cairns-Smith AG, Sloper RW (1983) Photo-oxidation of hydrated Fe^{2+}-significance for banded iron formations. *Nature* **303**, 163–164.

Brochier-Armanet C, Talla E, Gribaldo S (2009) The multiple evolutionary histories of dioxygen reductases: implications for the origin and evolution of aerobic respiration. *Molecular Biology and Evolution* **26**, 285–297.

Buick R (1992) The antiquity of oxygenic photosynthesis: evidence for stromatolites in sulphate-deficient Archaean lakes. *Science* **255**, 74–77.

Burns RG (1988) Gossans on Mars. In *Lunar and Planetary Science Conference, 18th, Houston, TX, Mar. 16-20, 1987, Proceedings (A89-10851 01-91).* Cambridge University Press/Lunar and Planetary Institute, Cambridge and New York/Houston, TX, pp. 713–721.

Cairns-Smith AG (1978) Precambrian solution photochemistry, inverse segregation, and banded iron formations. *Nature* **76**, 807–808.

Castresana J, Lübben M, Saraste M, Higgins DG (1994) Evolution of cytochrome oxidase, an enzyme older than atmospheric oxygen. *EMBO Journal* **13**, 2516–2525.

Cave RR, German CR, Thomson J, Nesbitt RW (2002) Fluxes to sediments underlying the Rainbow hydrothermal plume at 36j14VN on the Mid-Atlantic Ridge. *Geochimica et Cosmochimica Acta* **66**, 1905–1923.

Chown EH, N'Dah E, Mueller WU (2000) The relation between iron-formation and low temperature hydrothermal alteration in an Archean volcanic environment. *Precambrian Research* **101**, 263–275.

Claire MW, Sheets J, Cohen M, Ribas I, Meadows VS, Catling DC (2012) The evolution of solar flux from 2 nm to 160 microns: quantitative estimates for planetary studies. *Astrophysical Journal* **757**, 95. doi:10.1088/0004-637X/757/1/95.

Cloud P (1973) Paleoecological significance of the banded iron-formation. *Economic Geology* **68**, 1135–1143.

Cole CA, Molinski AE, Rieg N, Backus F (1977) Oxidation of iron containing coal mine drainage using hydrogen peroxide. *Journal of Water Pollution Control Federation* **49**, 1616–1624.

Craddock PR, Dauphas N (2011) Iron and carbon isotope evidence for microbial iron respiration throughout the Archean. *Earth and Planetary Science Letters* **303**, 121–132.

Croal LR, Jiao Y, Kappler A, Newman DK (2009) Phototrophic Fe(II) oxidation in an atmosphere of H_2: implications for Archean banded iron formations. *Geobiology* **7**, 21–24.

Crowe SA, Dossing LN, Beukes NJ, Bau M, Kruger SJ, Frei R, Canfield DE (2013) Atmospheric oxygenation three billion years ago. *Nature* **501**, 535–539.

Czaja AD, Johnson CM, Beard BL, Roden EE, Li W, Moorbath S (2013) Biological Fe oxidation controlled deposition of banded iron formation in the ca. 3770 Ma Isua Supracrustal Belt (West Greenland). *Earth and Planetary Science Letters* **363**, 192–203.

Dauphas N, Kasting JF (2011) Low pCO_2 in the pore water, not in the Archean air. *Nature* **474**(7349), E2–E3.

Dauphas N, van Zuilen M, Wadhwa M, Davis AM, Marty B, Janney PE (2004) Clues from Fe isotope variations on the origin of early Archean BIFs from Greenland. *Science* **306**, 2077–2080.

Dauphas N, Cates NL, Mojzsis SJ, Busigny V (2007) Identification of chemical sedimentary protoliths using iron isotopes in the >3750 Ma Nuvvuagittuq supracrustal belt, Canada. *Earth and Planetary Science Letters* **254**, 358–376.

Draganic IG (2005) Radiolysis of water: a look at its origin and occurrence in the nature. *Radiation Physics and Chemistry* **72**, 181–186.

Driese SG, Jirsa MA, Ren M, Brantley SL, Sheldon ND, Parker D, Schmitz M (2011) Neoarchean paleoweathering of tonalite and metabasalt: implications for reconstructions of 2.69 Ga early terrestrial ecosystems and paleoatmospheric chemistry. *Precambrian Research* **189**, 1–17.

Ducluzeau AL, Ouchane S, Nitschke W (2008) The cbb3 oxidases are an ancient innovation of the domain Bacteria. *Molecular Biology and Evolution* **25**, 1158–1166.

Dymond J, Veeh HH (1975) Metal accumulation rates in the southeast Pacific and the origin of metalliferous sediments. *Earth and Planetary Science Letters* **28**, 13–22.

Eigenbrode JL, Freeman KH, Summons RE (2008) Methylhopane biomarker hydrocarbons in Hamersley Province sediments provide evidence for Neoarchean aerobiosis. *Earth and Planetary Science Letters* **273**, 323–331.

Farquhar J, Bao HM, Thiemens M (2000) Atmospheric influence of Earth's earliest sulfur cycle. *Science* **289**, 756–758.

Flannery DT, Walter MR (2012) Archean tufted microbial mats and the Great Oxidation Event: new insights into an ancient problem. *Australian Journal of Earth Sciences* **59**, 1–11.

Frei R, Gaucher C, Canfield DE, Poulton SW (2009) Fluctuations in Precambrian atmospheric oxygenation recorded by chromium isotopes. *Nature* **461**, 250–253.

Garrels RM, Perry EA Jr, Mackenzie FT (1973) Genesis of Precambrian iron-formations and the development of atmospheric oxygen. *Economic Geology* **68**, 1173–1179.

German CR, Von Damm KL (2004) Hydrothermal processes. *Treatise on Geochemistry* **6**, 181–222.

González-Davila M, Santana-Casiano JM, Millero FJ (2005) Oxidation of iron (II) nanomolar with H_2O_2 in seawater. *Geochimica Cosmochimica Acta* **69**, 83–93.

Goodwin AM (1962) Structure, stratigraphy, an origin of iron formations, Michipicoten Area, Algoma District, Ontario, Canada. *Geological Society of America Bulletin* **73**, 561–586.

Gross GA (1980) A classification of iron-formation based on depositional environments. *Canadian Mineralogist* **18**, 215–222.

Gunz DW, Hoffmann MR (1990) Atmospheric chemistry of peroxides: a review. *Atmospheric Environment* **24A**, 1601–1633.

Haqq-Misra JD, Domagal-Goldman SD, Kasting PJ, Kasting JF (2008) A revised, hazy methane greenhouse for the Archean Earth. *Astrobiology* **8**, 1127–1137.

Haqq-Misra J, Kasting JF, Lee S (2011) Availability of O_2 and H_2O_2 on Pre-Photosynthetic Earth. *Astrobiology* **11**, 293–302.

Hartman H (1984) The evolution of photosynthesis and microbial mats: a speculation on banded iron formations. In *Microbial Mats: Stromatolites* (eds Cohen Y, Castenholz RW, Halvorson HO). Alan Liss, New York, pp. 451–453.

Holland HD (1973) The oceans: a possible source of iron in iron-formations. *Economic Geology* **68**, 1169–1172.

Holland HD (1984) *The Chemical Evolution of the Atmosphere and Oceans*. Princeton University Press, New Jersey.

Holm NG (1989) The $^{13}C/^{12}C$ ratios of siderite and organic matter of a modern metalliferous hydrothermal sediment and their implications for banded iron formations. *Chemical Geology* **77**, 41–45.

Huston DL, Logan GA (2004) Barite, BIFs and bugs: evidence for the evolution of the Earth's early hydrosphere. *Earth and Planetary Science Letters* **220**, 41–55.

Isley AE (1995) Hydrothermal plumes and the delivery of iron to banded iron formation. *Journal of Geology* **103**, 169–185.

Isley AE, Abbott DH (1999) Plume-related mafic volcanism and the deposition of banded iron formation. *Journal of Geophysical Research* **104**(B7), 15461–15477.

Kappler A, Pasquero C, Konhauser KO, Newman DK (2005) Deposition of banded iron formations by anoxygenic photo-trophic Fe(II)-oxidizing bacteria. *Geology* **33**, 865–868.

Kasting JF (1987) Theoretical constraints on oxygen and carbon dioxide concentrations in the Precambrian atmosphere. *Precambrian Research* **34**, 205–229.

Kasting JF (2005) Methane and climate during the Precambrian era. *Precambrian Research* **137**, 119–129.

Kasting JF, Zahnle KJ, Walker JCG (1983) Photochemistry of methane in the Earth's early atmosphere. *Precambrian Research* **20**, 121–148.

Kasting JF, Pollack JB, Crisp D (1984) Effects of high CO_2 levels on surface temperature and atmospheric oxidation state of the early earth. *Journal of Atmospheric Chemistry* **1**, 403–428.

Kasting JF, Holland HD, Pinto JP (1985) Oxidant abundances in rainwater and the evolution of atmospheric oxygen. *Journal of Geophysical Research* **90**, 10497–10510.

Kasting JF, Pavlov AA, Siefert JL (2001) A coupled ecosystem-climate model for predicting the methane concentration in the Archean atmosphere. *Origins of Life and Evolution of Biospheres* **31**, 271–285.

Kharecha P, Jasting J, Siefert J (2005) A coupled atmosphere-ecosystem model of the early Archean Earth. *Geobiology* **3**, 53–76.

King DW, Farlow R (2000) Role of carbonate speciation on the oxidation of Fe(II) by H_2O_2. *Marine Chemistry* **70**, 201–209.

Klueglein N, Kappler A (2013) Abiotic oxidation of Fe(II) by reactive nitrogen species in cultures of the nitrate-reducing Fe(II)-oxidizer *Acidovorax* sp. BoFeN1 - questioning the existence of enzymatic Fe(II) oxidation. *Geobiology* **11**, 180–190.

Konhauser KO, Hamade T, Raiswell R, Morris RC, Ferris FG, Southam G, Canfield DE (2002) Could bacteria have formed the Precambrian banded iron formations? *Geology* **30**, 1079–1082.

Konhauser KO, Newman DK, Kappler A (2005) Fe(III) reduction in BIFs: the potential significance of microbial Fe(III) reduction during deposition of Precambrian banded iron formations. *Geobiology* **3**, 167–177.

Konhauser KO, Amskold L, Lalonde SV, Posth NR, Kappler A, Anbar A (2007) Decoupling photochemical Fe(II) oxidation from shallow-water BIF deposition. *Earth and Planetary Science Letters* **258**, 87–100.

Konhauser KO, Lalonde SV, Planavsky N, Pecoits E, Lyons T, Mojzsis S, Rouxel OJ, Barley M, Rosiere C, Fralick PW, Kump LR, Bekker A (2011) Chromium enrichment in iron formations record Earth's first acid rock drainage during the Great Oxidation Event. *Nature* **478**, 369–373.

Krapez B, Barley ME, Pickard AL (2003) Hydrothermal and resedimented origins of the precursor sediments to banded iron-formation: sedimentological evidence from the Early Palaeoproterozoic Brockman Supersequence of Western Australia. *Sedimentology* **50**, 979–1011.

Kump L, Barley ME (2007) Increased subaerial volcanism and the rise of atmospheric oxygen 2.5 billion years ago. *Nature* **448**, 1033–1036.

Kump LR, Holland HD (1992) Iron in Precambrian rocks: implications for the global oxygen budget of the ancient Earth. *Geochimica et Cosmochimica Acta* **56**, 3217–3223.

Le Hir G, Teitler Y, Fluteau F, Donnadieu Y, Philippot P (2014) The faint young Sun problem revisited with a 3-D climate-carbon model - Part I. *Climate of the Past* **10**, 697–713.

Lepland A, Van Zuilen M, Philippot P (2011) Fluid-deposited graphite and its geobiological implications in early Archean gneiss from Akilia, Greenland. *Geobiology* **9**, 2–9.

Li Y-L, Konhauser KO, Kappler A, Hao X-L (2013) Experimental low-grade alteration of biogenic magnetite indicates microbial involvement in generation of banded iron formations. *Earth and Planetary Science Letters* **361**, 229–237.

Liang MC, Hartman H, Kopp RE, Kirschvink JL, Yung YL (2006) Production of hydrogen peroxide in the atmosphere of a Snowball Earth and the origin of oxygenic photosynthesis. *Proceedings of the National Academy of Sciences of the USA* **103**, 18896–18899.

Mancinelli RL, McKay CP (1988) The evolution of nitrogen cycling. *Origins of Life and Evolution of the Biosphere* **18**, 311–325.

McKay CP, Hartman H (1991) Hydrogen-peroxide and the evolution of oxygenic photosynthesis. *Origins of Life and Evolution Biospheres* **21**, 157–163.

McKeegan KD, Kudryavtsev AB, Schopf JW (2007) Raman and ion microscopic imagery of graphitic inclusions in apatite from older than 3830 Ma Akilia supracrustal rocks, west Greenland. *Geology* **35**, 591–594.

Melton ED, Schmidt C, Behrens S, Schink B, Kappler A (2014) Metabolic flexibility and substrate preference by the Fe(II)-oxidizing purple non-sulphur bacterium Rhodopseudomonas palustris strain TIE-1. *Geomicrobiology Journal* **9**, 835–843.

Millero FJ, Sotolongo S (1989) The oxidation of Fe(II) with H_2O_2 in seawater. *Marine Chemistry* **53**, 1867–1873.

Mloszewska AM, Pecoits E, Cates NL, Mojzsis SJ, O'Neil J, Robbins LJ, Konhauser KO (2012) The composition of Earth's oldest iron formations: the Nuvvuagittuq Supracrustal Belt (Québec, Canada). *Earth and Planetary Science Letters* **317–318**, 331–342.

Mloszewska AM, Mojzsis SJ, Pecoits E, Papineau D, Dauphas N, Konhauser KO (2013) Chemical sedimentary protoliths in the >3.75 Ga Nuvvuagittuq Supracrustal Belt (Québec, Canada). *Gondwana Research* **23**, 574–594.

Moffett JW, Zika RG (1987) Reaction kinetics of hydrogen peroxide with copper and iron in seawater. *Environmental Science and Technology* **21**, 804–810.

Mojzsis SJ, Arrhenius G, McKeegan KD, Harrison TM, Nutman AP, Friend CRL (1996) Evidence for life on Earth before 3,800 million years ago. *Nature* **384**, 55–59.

Morris RC (1993) Genetic modelling for banded iron-formation of the Hamersley Group, Pilbara Craton, Western Australia. *Precambrian Research* **60**, 243–286.

Neyens E, Baeyens J (2003) A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials* **B98**, 33–50.

Ogura K, Migita KT, Fujita M (1988) Conversion of methane to oxygen-containing compounds by the photochemical reaction. *Industrial and Engineering Chemical Research* **27**, 1387–1390.

Pavlov AA, Kasting JF (2002) Mass-independent fractionation of sulfur isotopes in Archean sediments: strong evidence for an anoxic Archean atmosphere. *Astrobiology* **2**, 27–41.

Pavlov AA, Kasting JF, Brown LL (2000) Greenhouse warming by CH_4 in the atmosphere of early Earth. *Journal of Geophysical Research* **105**, 11981–11990.

Pavlov AA, Brown LL, Kasting JF (2001) UV shielding of NH_3 and O_2 by organic hazes in the Archean atmosphere. *Journal of Geophysical Research* **106**, 23267–23287.

Peter JM, Goodfellow WD, Doherty W (2003) Hydrothermal sedimentary rocks of the Heath Steele belt, Bathurst mining camp, New Brunswick: part 2. Bulk and rare earth element geochemistry and implications for origin. *Economic Geology Monograph* **11**, 391–415.

Phoenix VR, Konhauser KO, Adams DG, Bottrell SH (2001) Role of biomineralization as an ultraviolet shield: implications for Archean life. *Geology* **29**, 823–826.

Pierson BK (1994) The emergence, diversi?cation, and role of photosynthetic eubacteria. In *Early Life on Earth* (ed Bengtson S), Nobel Symposium No. 84, Bjorkborn, Sweden, pp. 161–180.

Planavsky NJ, Asael D, Hofmann A, Reinhard CT, Lalonde SV, Knudsen A, Wang X, Ossa Ossa F, Pecoits E, Smith AJB, Beukes NJ, Bekker A, Johnson TM, Konhauser KO, Lyons TW, Rouxel OJ (2014) Evidence for oxygenic photosynthesis half a billion years before the Great Oxidation Event. *Nature Geoscience* **7**, 283–286.

Posth NR, Hegler F, Konhauser KO, Kappler A (2008) Alternating Si and Fe deposition caused by temperature fluctuations in Precambrian oceans. *Nature Geoscience* **10**, 703–708.

Posth N, Konhauser KO, Kappler A (2013a) Microbiological processes in banded iron formation deposition. *Sedimentology* **60**, 1733–1754.

Posth N, Köhler I, Swanner ED, Schröder C, Wellmann E, Binder B, Konhauser KO, Neumann U, Berthold C, Nowak M, Kappler A (2013b) Simulating Precambrian banded iron formation diagenwsis. *Chemical Geology* **362**, 66–73.

Reinhard TC, Planavsky NJ (2011) Mineralogical constraints on pCO_2. *Nature* **474**, E1.

Rock ML, James BR, Helz GR (2001) Hydrogen peroxide effects on chromium oxidation state and solubility in four diverse chromium-enriched soils. *Environmental Science and Technology* **35**, 4054–4059.

Rosing MT (1999) C-13-depleted carbon microparticles in >3700-Ma sea-floor sedimentary rocks from west Greenland. *Science* **283**, 674–676.

Rosing MT, Frei R (2004) U-rich Archean sea-floor sediments from Greenland – indications of >3700 Ma oxygenic photosynthesis. *Earth and Planetary Science Letters* **217**, 237–244.

Rosing MT, Bird DK, Sleep NH, Bjerrum CJ (2010) No climate paradox under the faint early Sun. *Nature* **464**, 744–747.

Rye R, Kuo PH, Holland HD (1995) Atmospheric carbon dioxide concentrations before 2.2 billion years ago. *Nature* **378**, 603–605.

Schidlowski M (2001) Carbon isotopes as biogeochemical recorders of life over 3.8 Ga of Earth history: evolution of a concept. *Precambrian Research* **106**, 117–134.

Segura A, Meadows VS, Kasting JF, Crisp D, Cohen M (2007) Abiotic formation of O_2 and O_3 in high-CO_2 terrestrial atmospheres. *Astronomy and Astophysics* **472**, 665–679.

Sforna MC, Philippot P, Somogyi A, van Zuilen MA, Medoudji K, Nitschke W, Schoepp-Cottenet B, Visscher P (2014) Evidence for arsenic metabolism and cycling by microorganisms 2.7 billion years ago. *Nature Geoscience* (in press).

Sheldon ND (2006) Precambrian paleosols and atmospheric CO_2 levels. *Precambrian Research* **147**, 148–155.

Slesak I, Slesak H, Kruk J (2012) Oxygen and hydrogen peroxide in the early evolution of life on Earth: in silico comparative analysis of biochemical pathways. *Astrobiology* **12**, 775–784.

Stolper DA, Revsbech NP, Canfield DE (2010) Aerobic growth at nanomolar oxygen concentrations. *Proceedings of the National Academy of Sciences of the USA* **107**, 18755–18760.

Summers DP, Chang S (1993) Prebiotic ammonia from reduction of nitrite by Fe(II) on the early Earth. *Nature* **365**, 630–633.

Summers DP, Khare B (2007) Nitrogen fixation on early Mars and other terrestrial planets: experimental demonstration of abiotic fixation reactions to nitrite and nitrate. *Astrobiology* **7**, 333–341.

Thomazo C, Pinti DL, Busigny V, Ader M, Hashizume K, Philippot P (2009) Biological activity and the Earth's surface evolution: insights from carbon, sulfur, nitrogen and iron stable isotopes in the rock record. *Comptes Rendus Palevol* **8**, 665–678.

Thomazo C, Ader M, Philippot P (2011) Extreme 15N-enrichments in 2.73 Gyr ago sediments: evidence for a turning point in the nitrogen cycle. *Geobiology* **9**, 107–120.

Thompson A, Owens MA, Stewart RW (1989) Sensitivity of tropospheric hydrogen peroxide to global chemical and climate change. *Geophysical Ressearch Letters* **16**, 53–56.

Tian F, Toon OB, Pavlov AA, De Sterck H (2005) A hydrogen-rich early Earth atmosphere. *Science* **308**, 1014–1017.

Touati D (2000) Iron and oxidative stress in bacteria. *Archives Biochemistry and Biophysics* **373**, 1–6.

Towe KM (1988) Biochemical arguments for early O_2. In *Molecular Evolution and the Fossil Record*. (ed Broad-Heads TW). University of Tennesee, Knoxville, pp. 114–129.

Towe KM (1990) Aerobic respiration in the Archaean? *Nature* **348**, 54–56.

Towe KM (1996) Environmental oxygen conditions during the origin and early evolution of life. *Advances in Space Research* **18**, 127–1215.

Widdel F, Schnell S, Heising S, Ehrenreich A, Assmus B, Schink B (1993) Ferrous iron oxidation by anoxygenic phototrophic bacteria. *Nature* **362**, 834–836.

Willey J, Kieber R, Lancaster R (1996) Coastal rainwater hydrogen peroxide: concentration and deposition. *Journal of Atmospheric Chemistry* **25**, 149–165.

Woese CR (1987) Bacterial evolution. *Microbiological Reviews* **51**, 221–271.

Wolf ET, Toon OB (2013) Hospitable Archean climates simulated by a general circulation model. *Astrobiology* **13**, 656–673.

Wu W, Swanner ED, Hao L, Zeitvogel F, Obst M, Pan Y, Kappler A (2014) Characterization of the physiology and cell-mineral interactions of the marine anoxygenic phototrophic Fe(II)-oxidizer Rhodovulum iodosum - implications for Precambrian banded iron formation deposition. *FEMS Microbiology Ecology* **88**, 503–515.

Xiong J (2006) Photosynthesis: what color was its origin? *Genome Biology* **12**, 245. 1-245.5.

Zahnle KJ (1986) Photochemistry of methane and the formation of hydrocyanic acid (HCN) in the Earth's early atmosphere. *Journal of Geophysical Research* **91**, 2819–2834.

Zahnle K, Claire M, Catling D (2006) The loss of mass-independent fractionation in sulfur due to a Paleoproterozoic collapse of atmospheric methane. *Geobiology* **4**, 271–283.

Zerkle AL, Claire M, Domagal-Goldman SD, Farquar J, Poulton SW (2012) A bistable organic-rich atmosphere on the Neoarchaean Earth. *Nature Geoscience* **5**, 359–363.

Zink S, Schoenberg R, Staubwasser M (2010) Isotopic fractionation and reaction kinetics between Cr(III) and Cr(VI) in aqueous media. *Geochimica Cosmochimica Acta* **74**, 5729–5745.

van Zuilen MA, Lepland A, Arrhenius G (2002) Reassessing the evidence for the earliest traces of life. *Nature* **418**, 627–630.

Zuo Y, Deng Y (1999) Evidence for the production of hydrogen peroxide in rainwater by lightning during thunderstorms. *Geochimica Cosmochimica Acta* **63**, 3451–3455.