Availability of O_2 and H_2O_2 on Pre-Photosynthetic Earth

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Abstract

Old arguments that free O_2 must have been available at Earth's surface prior to the origin of photosynthesis have been revived by a new study that shows that aerobic respiration can occur at dissolved oxygen concentrations much lower than had previously been thought, perhaps as low as $0.05\,nM$, which corresponds to a partial pressure for O_2 of about 4×10^{-8} bar. We used numerical models to study whether such O_2 concentrations might have been provided by atmospheric photochemistry. Results show that disproportionation of H_2O_2 near the surface might have yielded enough O_2 to satisfy this constraint. Alternatively, poleward transport of O_2 from the equatorial stratosphere into the polar night region, followed by downward transport in the polar vortex, may have brought O_2 directly to the surface. Thus, our calculations indicate that this "early respiration" hypothesis might be physically reasonable. Key Words: Early Earth—Oxygen—Respiration—Tracer transport—General circulation. Astrobiology 11, 293–302.

1. Introduction

O VER THE PAST 40 YEARS, both biologists (Schwartz and Dayhoff, 1978; Castresana *et al.,* 1994; Pereira *et al.,* 2001; Ducluzeau *et al.,* 2008; Brochier-Armanet *et al.,* 2009) and paleontologists (Cloud, 1972; Schopf, 1975; Towe, 1978, 1988, 1990, 1996) have argued that free O_2 must have been available, at least in small quantities, prior to the origin of oxygenic photosynthesis. These arguments have been considered highly speculative because free O_2 is generally considered to have been absent near Earth's surface prior to the origin of oxygenic photosynthesis (Walker, 1977; Kasting, 1993). Indeed, significant amounts of free O_2 did not appear in the atmosphere until about 2.4 Ga (Holland, 1994, 2006; Farquhar *et al.,* 2000). Before this major rise of atmospheric oxygen, even photosynthetically produced O_2 would have existed only locally within surface water and in short-lived plumes of gas that escaped into the otherwise anoxic atmosphere (Kasting, 1992; Pavlov *et al.,* 2001).

The arguments that some free oxygen must have existed before photosynthesis are almost all biologically based. Cloud (1972) pointed out that early O_2 producers would have needed chemical electron acceptors to protect themselves against the O_2 they created. He suggested that ferrous iron in the early oceans could have provided such a sink. However, the O_2 would have been produced internally within cells, whereas the ferrous iron was external, so it is not obvious that this solution would have worked. Schopf (1975) recognized this and suggested that early photosynthesizers must have had at least rudimentary mecha-

nisms for coping with oxygen. Towe (1978, 1988, 1996) elaborated on this idea by examining the evolutionary history of specific enzymes for O_2 protection, notably the superoxide dismutases, and arguing that they must have evolved at a very early stage.

Molecular phylogenists have added to the strength of these arguments over the years. Based on an early composite protein/rRNA evolutionary tree, Schwartz and Dayhoff (1978) reasoned that aerobic respiration must have preceded oxygenic photosynthesis because of its wide distribution among different organisms. Their analysis included genes for different cytochrome oxidases, which are key enzymes in aerobic metabolism. More recent studies (Castresana *et al.,* 1994; Pereira *et al.,* 2001; Ducluzeau *et al.,* 2008; Brochier-Armanet *et al.,* 2009) have examined the history of cytochrome oxidases in increasing detail. The current consensus is that at least some members of this enzyme family had a monophyletic origin that preceded the origin of oxygenic photosynthesis. Nitric oxide reduction, that is, oxidation of organic matter using NO (the key step in denitrification), may also have been an early evolutionary invention (Castresana and Saraste, 1995). Whether aerobic respiration or nitric oxide reduction came first, and whether one of these metabolisms evolved from the other, remains unresolved (Hendriks *et al.,* 2000; Pereira *et al.,* 2001; Ducluzeau *et al.,* 2008).

Now, a new study (Stolper *et al.,* 2010) has shown that some modern aerobes can respire at extremely low O_2 levels—much lower than previously thought. The prevailing wisdom has been that organisms switch from aerobic

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respiration to anaerobic forms of metabolism (primarily fermentation) below the Pasteur point of ~ 0.01 times the present atmospheric level of O_2. The solubility of O_2 in pure water at 25°C is 1.3×10^{-3} mol/L/bar (Sander, 2009), so this corresponds to a dissolved O_2 concentration of 2.7 μM. (O_2 solubility in seawater is about 20% lower.) By contrast, the new study shows that the common bacterium *E. coli* can grow at dissolved O_2 concentrations of 3 nM or lower, or about 1000 times lower than previously believed. The new work was made possible by the development of O_2-sensing electrodes that are accurate down to 3–5 nM concentrations. (Note of caution: The observed lower limit for respiration in these studies is also the lower limit of accuracy for the electrodes. This suggests that additional confirmation of these results is needed.) A theoretical extrapolation to smaller organisms suggests that a primitive aerobe, only 0.5 μm in diameter, might be able to respire at dissolved O_2 concentrations of 0.05 nM (Stolper *et al.*, 2010). In terms of equivalent atmospheric partial pressure, this lower limit is equivalent to $pO_2 = 4 \times 10^{-8}$ bar, or about 10^{-7} times the present atmospheric level. These limits are summarized in Table 1, where they are compared to calculated O_2 and H_2O_2 sources that might have been available prior to the origin of photosynthesis. The calculations are described below.

Although we ourselves have previously argued that free O_2 was scarce prior to the origin of oxygenic photosynthesis, the new work by Stolper *et al.* (2010) has prompted us to reexamine our assumptions. For example, photochemical models do indeed predict that some free O_2, along with photochemically generated oxidants such as hydrogen peroxide (H_2O_2) and sulfate ($SO_4^=$), should have been generated in small quantities (see, *e.g.*, Kasting *et al.*, 1984; McKay and Hartman, 1991; Liang *et al.*, 2006; Segura *et al.*, 2007). And much larger concentrations of free O_2, up to 0.1% mixing ratio, should have existed at high altitudes, where it was produced by CO_2 photolysis (Kasting *et al.*, 1984; Liang *et al.*, 2006; Segura *et al.*, 2007). The question then is could any of this high-altitude O_2 have made its way down to the surface before it was photochemically destroyed? Our modeling work addresses this question.

2. Photochemical Production of O_2 and H_2O_2

Oxygen should have been produced abiotically in the sunlit portions of the early stratosphere. Following the atmospheric photochemistry explored by Kasting *et al.* (1979), Kasting and Walker (1981), and Kasting *et al.* (1984), the production of O_2 in the stratosphere begins with the photolysis of CO_2, which is by far the most abundant oxygen-bearing species in these model atmospheres:
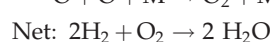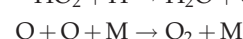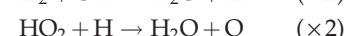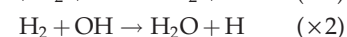
$$CO_2 + h\nu \rightarrow CO + O \qquad (1)$$

Here, ν is frequency of the photon and h is Planck's constant. The products of Reaction 1 then combine to form O_2:
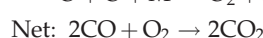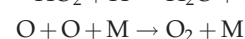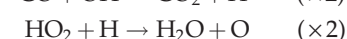
$$O + O + M \rightarrow O_2 + M \qquad (2)$$

where M is a third molecule, required to carry off the excess energy of the collision. O_2 can also be produced in the troposphere by Reaction 1, along with
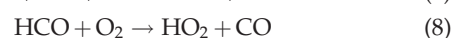
$$H_2O + h\nu \rightarrow H + OH \qquad (3)$$

$$O + OH \rightarrow O_2 + H \qquad (4)$$

Little of this O_2 makes its way down to the surface, though, because it is destroyed almost immediately by reaction sequences such as

$$
\begin{aligned}
H_2O + h\nu \rightarrow\ & H + OH && (\times 2) && (5)\\
H + O_2 + M \rightarrow\ & HO_2 + M && (\times 2)\\
H_2 + OH \rightarrow\ & H_2O + H && (\times 2)\\
HO_2 + H \rightarrow\ & H_2O + O && (\times 2)\\
O + O + M \rightarrow\ & O_2 + M\\
\text{Net: } 2H_2 + O_2 \rightarrow\ & 2\,H_2O
\end{aligned}
$$

along with

$$
\begin{aligned}
H_2O + h\nu \rightarrow\ & H + OH && (\times 2) && (6)\\
H + O_2 + M \rightarrow\ & HO_2 + M && (\times 2)\\
CO + OH \rightarrow\ & CO_2 + H && (\times 2)\\
HO_2 + H \rightarrow\ & H_2O + O && (\times 2)\\
O + O + M \rightarrow\ & O_2 + M\\
\text{Net: } 2CO + O_2 \rightarrow\ & 2CO_2
\end{aligned}
$$

The formyl radical, HCO, also contributes to O_2 destruction by the reactions

$$H + CO + M \rightarrow HCO + M \qquad (7)$$

$$HCO + O_2 \rightarrow HO_2 + CO \qquad (8)$$

TABLE 1. MEASURED AND CALCULATED LIMITS
ON RESPIRATION AND O_2/H_2O_2 AVAILABILITY

Limit	[O_2] nM*	pO_2 (bar)
Observed lower growth limit	3	2×10^{-6}
Extrapolated lower growth limit[†]	0.05	4×10^{-8}
Average surface O_2 (2-bar CO_2 model)	8×10^{-6}	6×10^{-12}
Transient surface O_2 (equinox model)	7×10^{-4}	5×10^{-10}
Transient surface O_2 (winter solstice model)	3×10^{-3}	2×10^{-9}
Maximum transient surface O_2	4	3×10^{-6}

Limit	[H_2O_2] nM	pH_2O_2 (bar)
Average surface H_2O_2 (2-bar CO_2 model)	0.16	2×10^{-15}

Henry's Law constants at 25°C:
O_2: 1.3×10^{-3} mol/L/bar
H_2O_2: 8.2×10^4 mol/L/bar
*1 n$M = 10^{-9}$ mol/L.
[†]For 0.5 μm diameter cells (Stolper *et al.*, 2010).

Once converted to HO_2, O_2 can readily react with other species by reactions such as those shown in sequences (5) and (6). The net effect of this tropospheric photochemistry is to recombine O_2 with H_2 and CO through reactions that are catalyzed by the by-products of H_2O photolysis.

Other reduced gases, CH_4 for example, may also have served as O_2 sinks on early Earth. CH_4 should have become abundant once methanogens evolved (Walker, 1977; Kharecha et al., 2005). But CH_4 would have been produced at the expense of H_2 by the reaction

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (9)$$

Alternatively, CH_4 could have been produced by fermentation of organic matter, followed by production of methane from by-products such as acetate. But much of this organic matter itself would presumably have been generated from H_2-based anoxygenic photosynthesis (Kharecha et al., 2005). Thus, for our purposes here, it is sufficient to think of H_2 as a surrogate for all such reduced gases.

Because of catalytic cycles such as (5) and (6), the O_2 content of the early atmosphere would have depended inversely on the H_2 and CO concentrations. The H_2 mixing ratio of the early atmosphere should have been determined by the balance between volcanic outgassing and escape of hydrogen to space (Walker, 1977; Kasting and Catling, 2003) and is expected to have been of the order of 100–1000 ppmv for H_2 outgassing rates of $(0.7–7)\times10^{12}$ mol/yr. These outgassing rates bracket the range considered by Holland (2002) and Canfield et al. (2006).

2.1. Model scenarios

Vertical profiles of O_2 in the early atmosphere have been calculated by a number of different authors (e.g., Kasting et al., 1979, 1984; Pavlov et al., 2001; Segura et al., 2007). We used the model of Segura et al. (2007) to calculate O_2 mixing ratio profiles for three different atmospheric CO_2 partial pressures: 0.02, 0.2, and 2 bar (Fig. 1). These choices of pCO_2 are meant to span the range of plausible CO_2 concentrations during the Late Hadean/Early Archean, $\sim 4.0–3.0$ Ga. At the two lower CO_2 concentrations, the atmospheric surface pressure was taken to be 1 bar, and the surface temperature was set equal to 278 K. For the 0.2-bar atmosphere, that surface temperature would be appropriate for 4.0 Ga and 75 percent of current solar luminosity (Kasting, 1990). The 0.02-bar CO_2 atmosphere would have needed help from other greenhouse gases to reach this surface temperature during this time period. For the 2-bar CO_2 calculation, the surface pressure was taken to be 2.8 bar, and the surface temperature was set at 317 K, which is again consistent with conditions at 4.0 Ga (Kasting, 1990). No new one-dimensional climate simulations were performed for this study. The eddy diffusion profile in the latter case was changed to be self-consistent with this warmer, thicker troposphere by increasing the vertical range over which high (10^5 cm^2 s^{-1}) eddy coefficients applied (Kasting, 1990).

The hydrogen outgassing rate in each model was assumed to be 1×10^{10} H_2 molecules cm^{-2} s^{-1}, or about 2.7×10^{12} mol/yr. This is close to the H_2 outgassing rate (2.4×10^{12} mol/yr) estimated by Holland (2009). This produced atmospheric H_2 mixing ratios close to 300 ppmv in all three cases. Some
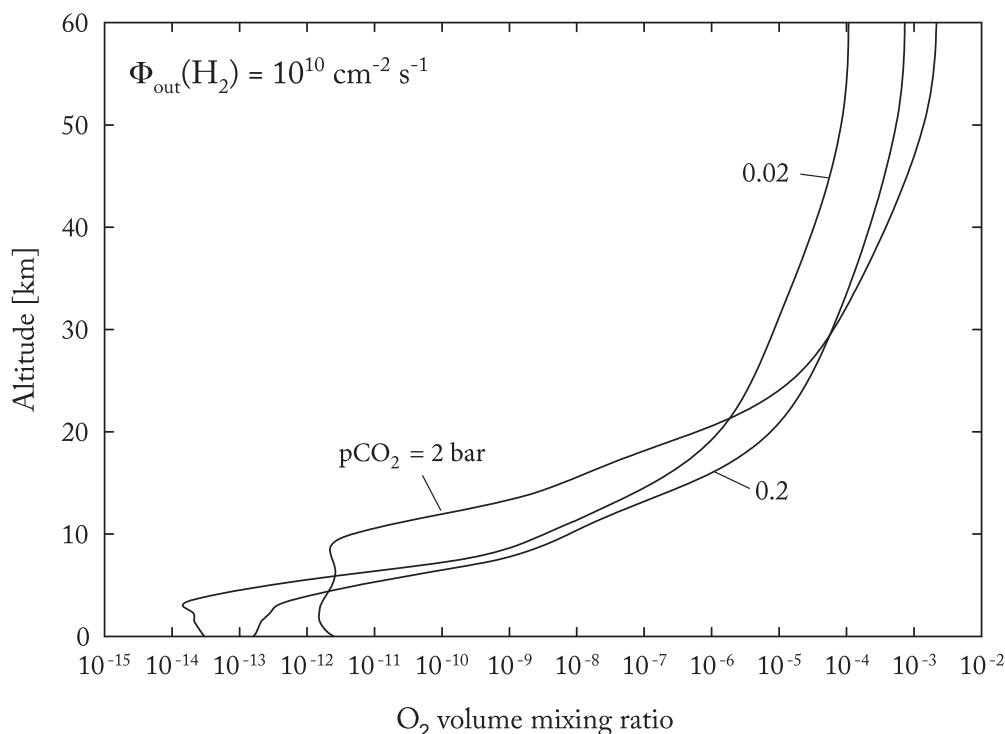

FIG. 1. Vertical profiles of O_2 volume mixing ratio at CO_2 partial pressures of 0.02, 0.2, and 2.0 bar. These profiles are calculated with a one-dimensional photochemical model with an H_2 outgassing rate $\Phi_{out}(H_2) = 10^{10}$ cm^{-2} s^{-1}.

sensitivity studies, described below, were also performed with an outgassing rate that was 10 times smaller. SO_2 outgassing was fixed at $3.5 \times 10^8 \, cm^{-2} \, s^{-1}$, or $\sim 9.4 \times 10^{10} \, mol/yr$, following Ono et al. (2003). CO outgassing (which is smaller than H_2 outgassing) was neglected. CH_4 was held to negligible values. NO was assumed to have been produced by lightning at a rate of $5.85 \times 10^8 \, cm^{-2} \, s^{-1}$, or $\sim 1.6 \times 10^{11} \, mol/yr$ for the 0.2-bar CO_2 case. O_2 production was 2.5 times higher. All lightning production rates were scaled to a value of $2.7 \times 10^{11} \, mol \, NO/yr$ for modern Earth, which is slightly higher than the value of $2.1 \times 10^{11} \, mol/yr$ estimated by Martin et al. (2002).

2.2. Predicted O_2 concentrations

Figure 1 shows that the concentration of O_2 in the model atmosphere increases with pCO_2, as expected. The O_2 mixing ratio in the stratosphere, near 50 km, reaches a maximum of about 2×10^{-3} in the high-CO_2 case. This, of course, would be more than enough to sustain aerobic respiration were the same O_2 concentration to exist at the surface. The O_2 mixing ratio at the surface, however, is 9 orders of magnitude lower, about 2×10^{-12}, because it is being consumed by Reactions 5–9 above. Indeed, the little O_2 that exists near the surface is sustained by lightning in this model, which breaks down CO_2 according to

$$2CO_2 \rightarrow 2CO + O_2 \tag{10}$$

But this surface O_2 concentration is still far too low to sustain respiration, even in the most optimistic case defined by Stolper et al. (2010). Given that the total surface pressure is 2.8 bar in this model, pO_2 near the surface is $\sim 6 \times 10^{-12}$ bar.

This is still almost 4 orders of magnitude lower than the limit for respiration (Table 1).

2.3. Production of H_2O_2

A second photochemically produced oxidant that has received previous attention (Kasting et al., 1984; McKay and Hartman, 1991; Liang et al., 2006) is hydrogen peroxide, H_2O_2. H_2O_2 is produced from the by-products of H_2O photolysis,

$$OH + OH + M \rightarrow H_2O_2 + M \tag{11}$$
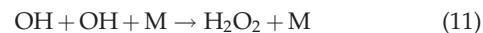
which can yield O_2 by the disproportionation reaction

$$2H_2O_2 \rightarrow 2 \, H_2O + O_2 \tag{12}$$
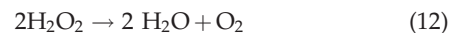
This type of reaction is slow in the gas phase but could be catalyzed in solution by contact with mineral surfaces. Concentrations of H_2O_2 in the troposphere are also very low for the three cases studied (Fig. 2); however, the solubility of H_2O_2 is much higher than that of O_2, about $8.2 \times 10^4 \, mol/L/bar$ at 25°C (Sander, 2009). For the 2-bar CO_2 case, the predicted partial pressure of H_2O_2 at the surface is about 2×10^{-15} bar, so the dissolved H_2O_2 concentration is $1.6 \times 10^{-10} \, mol/L$. A similar ground-level H_2O_2 partial pressure is obtained for the 0.2-bar CO_2 case if the H_2 outgassing rate is divided by 10 (which remains within the plausible range of outgassing rates). Dividing by 2 to account for the stoichiometry of Reaction 13 gives an equivalent dissolved O_2 concentration of $0.08 \, nM$, just above the lower limit for respiration extrapolated by Stolper et al. (2010) for small cells. So, if their calculated threshold is correct, and if H_2O_2 was
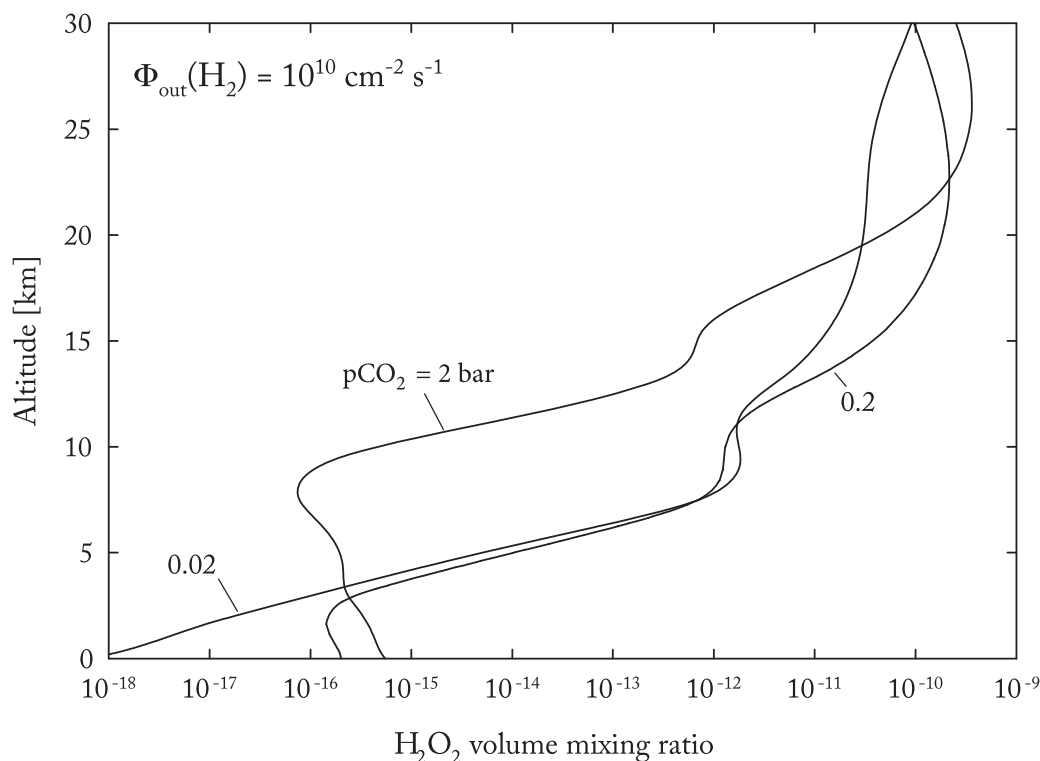

FIG. 2. Vertical profiles of H_2O_2 volume mixing ratio for the three model atmospheres shown in Fig. 1.

converted to O_2 and taken up by organisms before it could react with something else, then this is a possible mechanism for fueling aerobic respiration prior to the invention of oxygenic photosynthesis.

We should note that McKay and Hartman (1991) put forward a hypothesis similar to the one presented here, that is, they argued that the presence of photochemically produced H_2O_2 allowed early organisms to develop defenses against oxygen toxicity. They used numbers from a photochemical model study by Kasting *et al.* (1985). The quoted flux of H_2O_2 to the surface was $\sim 10^{10}\,cm^{-2}\,s^{-1}$, and the maximum dissolved H_2O_2 concentration in surface water, as calculated from a simple box model, was $5 \times 10^{-8}\,mol/L$. That value is about 300 times higher than the one estimated here. But the Kasting *et al.* (1985) model was designed to simulate relatively oxygenated, Proterozoic atmospheres, not the anoxic Archean atmospheres considered here. Our calculated H_2O_2 surface flux (mostly from H_2O_2 dissolved in rainwater) in the present 0.2-bar CO_2 model is of the order of $10^6\,cm^{-2}\,s^{-1}$, which is about 10^4 times less than estimated by McKay and Hartman. With our more modest numbers, H_2O_2 appears to be just marginally capable of fueling early respiration.

3. Transport of O₂ by the Brewer-Dobson Circulation

An alternative way of getting O_2 to the surface would be to transport it downwards from the stratosphere in the polar night region where it was protected against photochemical destruction. The calculations shown in Figs. 1 and 2 cannot account for this mechanism because our one-dimensional photochemical model assumes global average conditions, with the sun always shining. O_2 is destroyed within seconds or minutes when it reaches the troposphere in the presence of ultraviolet (UV) photons. In the real, modern atmosphere, ozone (O_3) is produced photochemically in the stratosphere and is transported poleward and downward by the Brewer-Dobson circulation (Brewer, 1949; Holton *et al.*, 1995; Callaghan and Salby, 2002; Austin and Li, 2006). This suggests a mechanism by which photochemically produced O_2 could have been transported to the surface of early Earth.

Exchange of air between the stratosphere and troposphere then occurs through a variety of processes, most of which are dominant in regions outside the tropics. In the absence of physical features (such as topography), some mass exchange occurs by diffusion, while some occurs by a mechanism known as "tropopause folding" (Reed, 1955; Danielsen, 1968; Shapiro, 1980; Wei, 1987; Lamarque and Hess, 1994). Although the time-mean tropopause is approximately symmetric about the equator, tropopause structure in regions with large vertical shear and strong meridional temperature gradients can fold and thereby transport stratospheric air downward (Holton *et al.*, 1995). Such events commonly occur in conjunction with cyclogenesis (*i.e.*, the development of low-pressure circulation systems in the atmosphere). Part of this transport is also described by the influence of breaking waves above the tropopause according to the downward control principle (Haynes *et al.*, 1991). Topographic features also play an important role in troposphere-stratosphere exchange by generating planetary-scale waves that propagate into the stratosphere and then break to induce the mixing of air (McIntyre and Palmer, 1983; Randel *et al.*, 1993). Finally, the stratosphere in the winter hemisphere cools because of the strong equator-to-pole temperature gradient, which intensifies the Brewer-Dobson circulation and causes the formation of a polar vortex. Air that flows from the stratosphere through the polar vortex can mix with air in the troposphere either directly (Bowman, 1993; Mizuta and Yoden, 2001) or from the interaction of planetary waves with the vortex (Waugh, 1993).

3.1. Three-dimensional (3-D) tracer model

We investigated the downward transport of stratospheric oxygen by modeling O_2 as a passive atmospheric tracer in an idealized atmospheric general circulation model (GCM). Our GCM was described by Frierson *et al.* (2006) and Haqq-Misra (2010) and includes a spectral dynamical core (with T42 resolution), gray radiative transfer, latent heat release, and a diffusive boundary layer scheme. This provides a way to estimate the amount of stratospheric O_2 that could reach the surface without the need for an elaborate coupled climate-chemistry model, which would be a far more demanding computational task. Here, we conceptually account for the photochemical loss of O_2 in the troposphere; however, our model contains no actual atmospheric chemistry and should be considered only as a proof of concept for downward oxygen transport on early Earth. We note that surface oxygen does not need to be well mixed because early respiring organisms may have thrived in oxygen oases that only covered a fraction of the surface.

We represent O_2 as a passive tracer that follows the flow determined in our model by solving an advection-diffusion equation. We release this passive tracer instantaneously into the stratosphere of a GCM configuration that has already reached a statistically steady state. By doing so, we simulate photochemical production of O_2 at a single moment in time so that we can observe the amount of tracer that reaches the surface.

Our tracer $\xi = \xi(t,p,\phi,\lambda)$ is a function of time t, pressure p, latitude ϕ, and longitude λ. It is given an initial distribution centered on the equator with the form

$$\xi(0,p,\phi,\lambda) = \begin{cases} \xi_0 & \text{for } 90°S \le \phi \le 60°N \text{ and } 5\,hPa \le p \le 35\,hPa \\ 0 & \text{otherwise} \end{cases}$$

(13)

In terms of altitude, the tracer release area corresponds to a range of about 21–28 km in the modern atmosphere. We set the unitless tracer concentration to a constant value ξ_0 in this region. Because we specify no other sources or sinks of ξ, we do not include reaction rates for O_2 production and destruction. However, a low-oxygen early Earth atmosphere would be susceptible to O_2 loss from water vapor photolysis in the troposphere, so any stratospherically produced O_2 that is transported to the surface will therefore have a lifetime limited by its exposure to sunlight. The longest residence time of such an O_2 molecule would occur in the polar night, where some regions reside in perpetual darkness for up to 6 months. UV photons would be absent or scarce during this season and allow O_2 to accumulate. In the summertime, though, we assume that O_2 could not accumulate in the troposphere because it would be destroyed in the presence of direct sunlight. Thus, we only model the concentration of ξ over a period of 180

days when loss of O_2 would be minimal. Shielding by organic haze could conceivably extend the region where downwelling O_2 might survive in the troposphere (Pavlov *et al.*, 2001; Wolf and Toon, 2010); however, examining this possibility would require a more elaborate model.

Transport of stratospheric tracer to the surface was explored under eight different climate conditions in order to examine the various processes that contribute to stratosphere-troposphere mass exchange. [See Haqq-Misra (2010) for detailed descriptions of these eight climate states.] The first two states consider idealized dry and moist circulations (which we refer to as dry 3-D and moist 3-D) that approximate the structure of the observed atmosphere. In these cases, exchange of tracer between the stratosphere and troposphere occurs through diffusion across the tropopause as well as tropopause folding events generated by baroclinically unstable waves. We next add realistic topographic data to dry 3-D and moist 3-D to generate planetary waves that can propagate into the stratosphere and strengthen the Brewer-Dobson circulation to increase tracer transport. (Realistic mountains and land-water masks are generated by interpolating from a one-sixth degree U.S. Navy mean topography and percent water data set. These data are limited to changes in surface geopotential height only and do not include soil temperature, moisture, or other surface properties.) Transport in the winter hemisphere is also enhanced by a stronger Brewer-Dobson circulation and accompanies the formation of a polar night vortex, so we add a seasonal cycle to the model to calculate dry and moist 3-D states with seasons. Finally, we combine these mechanisms to calculate dry 3-D and moist 3-D states that include both topography and seasons in order to maximize the downward transport of tracer.

3.2. Tracer model results

Initially, we performed calculations for models that lacked a seasonal cycle. The tracer ξ was released into the strato-sphere at some initial time, t_0, and its subsequent evolution was followed for 180 model days. At this point, we calculated the fraction of tracer, ξ/ξ_0, that had reached the surface. Our calculations show that tracer transport in the dry 3-D case is greater than in moist 3-D because poleward transport by the stratospheric Brewer-Dobson circulation is stronger in the absence of moisture. (In general, meridional circulations are weaker in moist atmospheres because the condensation of water vapor in ascending air causes a decrease in the lapse rate—the vertical rate of cooling—so that air parcels rise more slowly.) This produces a maximum polar tracer abundance of $\xi/\xi_0 \approx 3\times10^{-6}$ for dry 3-D and $\xi/\xi_0 \approx 2\times10^{-6}$ for moist 3-D. When we include realistic topography, planetary waves are generated that propagate into the stratosphere and provide a modest increase in surface tracer. Here, we find that our dry and moist simulations with topography give us maximum polar tracer abundances of $\xi/\xi_0 \approx 9\times10^{-6}$ and $\xi/\xi_0 \approx 5\times10^{-6}$, respectively.

The more interesting, and more realistic, cases are those in which a seasonal cycle is included. The seasonal cycle enhances downward transport by inciting a polar vortex in the winter hemisphere and also provides a region of darkness in which downwelling stratospheric O_2 might survive. The most efficient downward transport occurs when both topography and seasons are included, because in this case topographic planetary waves are generated in the winter hemisphere where surface westerly winds are strong. Results from two initial simulations with a dry model atmosphere are shown in Fig. 3. In the left-hand panel, the simulation begins at northern autumnal equinox, while the right-hand panel shows a simulation that began at northern winter solstice. The two panels show relative tracer abundance ξ/ξ_0 at the surface after 180 days of evolution. In both cases, the tracer tends to accumulate toward the equator, but our winter solstice case shows an increase of about a factor of 10 in surface tracer abundance at the northern pole.
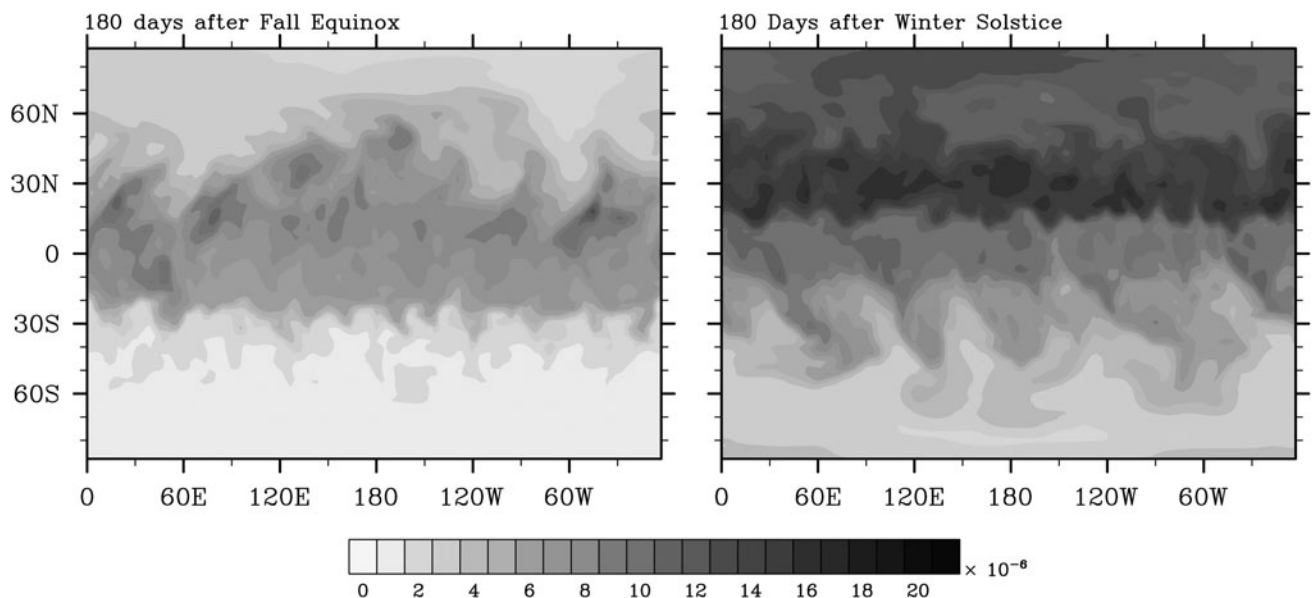

FIG. 3. Fraction of tracer ξ/ξ_0 at the surface 180 days after northern autumnal equinox (left panel) and northern winter solstice (right panel). Both simulations assume dry conditions and include topography.

We first consider the results for the equinox simulation (left-hand panel). This simulation may be the most applicable to our O$_2$ transport problem, because the North Pole would remain shaded throughout the calculation. In this case, the maximum tracer abundance in the northern polar region is about $\xi/\xi_0 \approx 5 \times 10^{-6}$. To calculate a surface O$_2$ concentration, this number must be multiplied by the O$_2$ mixing ratio at the height at which the tracer was released, roughly 20–30 km. According to Fig. 1, the O$_2$ mixing ratio at these altitudes is about 10^{-4} for both the 0.2-bar and 2-bar CO$_2$ simulations. Hence, the calculated ground-level O$_2$ partial pressure is about 5×10^{-10} bar. (This number should correspond to the 0.2-bar CO$_2$ case, as the dynamical transport calculation is not valid for atmospheres with surface pressures greater than 1 bar.) This pO$_2$ value is about 1000 times greater than the average surface pO$_2$ calculated for the 0.2-bar CO$_2$ case (Fig. 1), but it remains a factor of 100 lower than the lowest limit for respiration estimated by Stolper *et al.* (2010; see Table 1). So we see that this particular simulation does not succeed in explaining the early appearance of respiration.

These results may be overly pessimistic, however. The simulation that begins at winter solstice predicts high-latitude tracer levels that are about 4 times higher, $\xi/\xi_0 \approx 2 \times 10^{-5}$ (Fig. 3, right-hand panel). Furthermore, tracer transport in our model can be shown to depend on spatial (spectral) resolution. When we doubled the spectral resolution of our winter solstice model (to T85), the relative tracer abundance increased locally to as much as 3×10^{-4} (Fig. 4).

The largest accumulations occurred near large mountain ranges such as the Himalayan and Rocky mountains. The reason for this accumulation can be understood in terms of the mechanism of Taylor columns (*e.g.*, Hogg, 1973; Huppert, 1975). Much of this tracer occupies a region over land, where it could not dissolve into seawater, but some of it extends into the Bay of Bengal, the Arabian Sea, and perhaps even the Great Salt Lake. Of course, we do not know what topographic features were present on early Earth, but it appears that large mountain ranges can cause surface tracer to accumulate to concentrations from 10 to 50 times greater than the average hemispheric abundance. If these mountain ranges existed in the polar regions where O$_2$ could have been protected from sunlight, then lakes or seas within these regions might have been exposed to relatively high surface O$_2$ concentrations.

Abundances of O$_2$ in the stratosphere may also be underestimated in the above calculations. The O$_2$ mixing ratio continues to increase above 30 km in all our photochemical simulations, reaching values as high as 2×10^{-3} in the 2-bar CO$_2$ case (Fig. 1). Stratospheric O$_2$ could have been enhanced by another factor of 3 or more by the increased UV flux from the young Sun (Segura *et al.*, 2007). (The calculations shown here assume present-day solar UV fluxes.) If our tracer model had extended higher into the stratosphere, some of this higher-O$_2$ air may have been brought down to the surface as well. An approximate upper limit on surface O$_2$ can be estimated by multiplying the maximum surface tracer
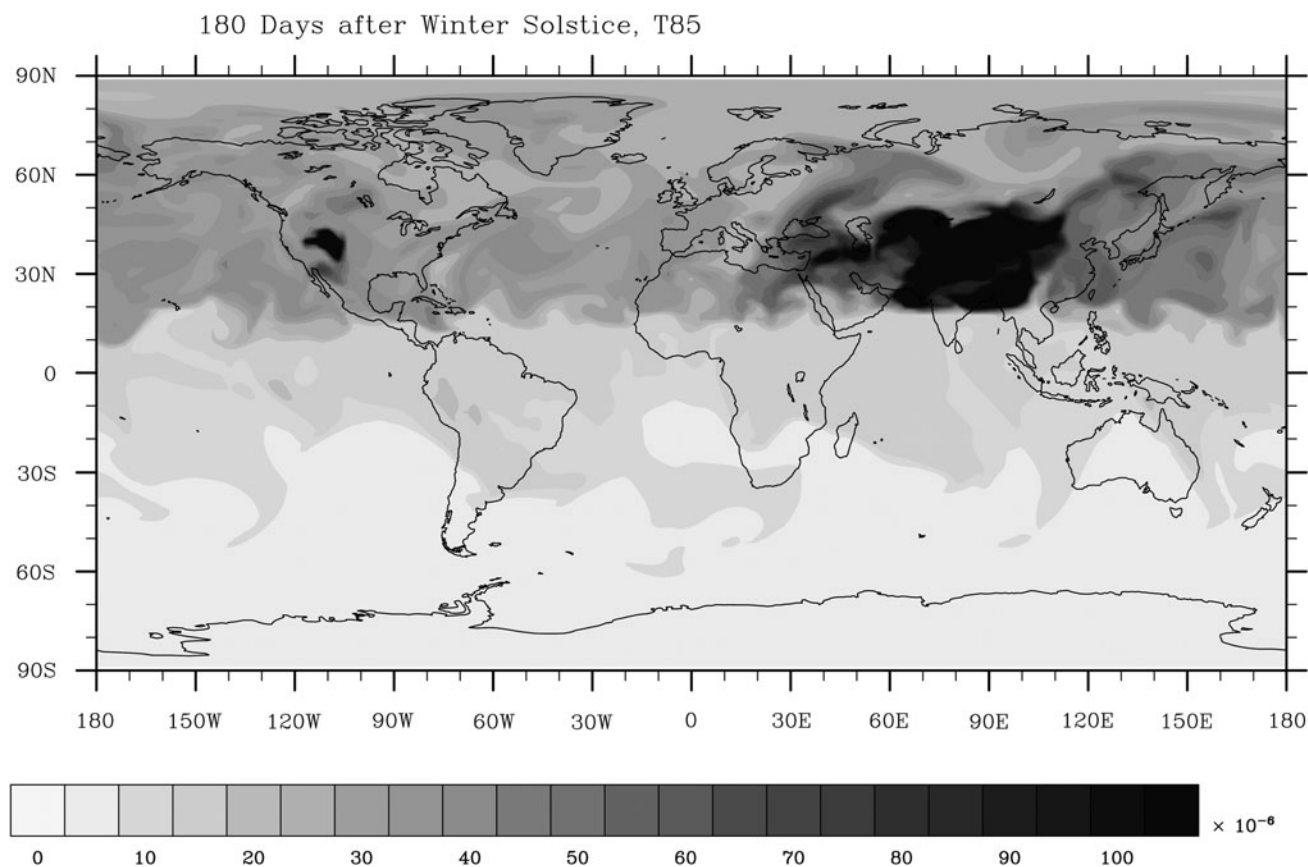

FIG. 4. Fraction of tracer ξ/ξ_0 at the surface 180 days after northern winter solstice under dry conditions with doubled spectral resolution.

abundance from our transport model, 3×10^{-4}, by the O_2 concentration at 50 km in the 2-bar CO_2, high-UV case from Segura *et al.* (2007), $\sim 10^{-2}$. This yields a surface pO_2 value of 3×10^{-6} bar and a corresponding dissolved O_2 concentration of 4 nM. The latter value exceeds the observed threshold for aerobic growth in *E. coli* (Stolper *et al.,* 2010). Although this upper limit is admittedly optimistic, it demonstrates that this mechanism might also have allowed aerobic organisms to evolve in an otherwise anoxic world.

Further discussion should be added to the above calculations because of the uncertain conditions of early Earth. In particular, planetary formation models predict that younger planets rotate faster, and it has been suggested that early Earth rotated with a day as short as 14 to 18 hours (*e.g.,* Walker and Zahnle, 1986; Williams, 2000). Because the vertical penetration depth of the overturning circulation is proportional to rotation rate (Hoskins *et al.,* 1985), a faster rotator will be more effective at downward transport. As a result, downward transport may be somewhat enhanced on a rapidly rotating planet. Additionally, deviations in the axial tilt of Earth would change the latitudinal distribution of sunlight so that the wintertime Brewer-Dobson circulation strengthens as obliquity increases and weakens as obliquity decreases. The continental configuration of early Earth is also unknown, which means that topographically generated planetary waves could have been more active or less active in the past, depending on the size and position of the continents. For all three of these parameters, we have chosen present-day Earth values because of the uncertainty in the conditions of early Earth. Our model calculations can therefore be understood as a demonstration of an atmospheric transport mechanism that can be scaled appropriately as we continue to learn about the early history of Earth.

4. Discussion

All the "successful" simulations for delivery of either O_2 or H_2O_2 to Earth's surface require high-CO_2 early atmospheres. This is because high CO_2 concentrations lead to greater production of O_2 in the stratosphere from photolysis (Reactions 1 and 2). Additionally, high CO_2 creates a warmer atmosphere by way of its greenhouse effect, which increases the concentrations of H_2O and its photolysis by-product, OH, that is instrumental in forming H_2O_2 (Reaction 11).

Recently published estimates of paleo-CO_2 concentration, however, suggest that it may have been very low. Rosing *et al.* (2010) estimated an upper limit of 1×10^{-3} bar, or 3 times the present atmospheric level, based on an analysis of banded iron formations. According to these authors, CO_2 partial pressures higher than this value would have caused all the magnetite to be quantitatively converted to siderite, and this of course is not observed. If Rosing *et al.* are correct, then CO_2 concentrations must have been low during the entire time between 1.8 and 3.8 Ga when banded iron formations are known to have formed. However, the Rosing *et al.* (2010) paper is controversial, and several critical comments (not yet published) have been submitted regarding their conclusions. We hypothesize that conversion of magnetite to siderite was limited by the supply of organic matter, not by atmospheric or dissolved CO_2. Support for this hypothesis is provided by the presence of isotopically light carbon in the siderite, which indicates that

organic matter was involved in its formation (Becker and Clayton, 1972; Heimann *et al.,* 2010). So, this particular argument for low CO_2 does not appear to be valid.

Other published estimates for pCO_2 in the Archean are also much lower than we require here. Rye *et al.* (1995) estimated that pCO_2 was less than 0.03 bar at 2.8 Ga, based on an analysis of paleosols. Their estimate, however, has been criticized by Sheldon (2006). Sheldon argued that the thermodynamic data they used were out of date and that if their analysis were repeated it would predict pCO_2 values lower than today, which is not at all consistent with the need for higher greenhouse warming in the past (Kasting, 1987; von Paris *et al.,* 2008). Sheldon's own analysis of paleosols also led to low values, ~ 0.008 bar, but this estimate applies to the time around 2.2 Ga. Furthermore, his analysis assumed that every CO_2 molecule that enters the soil reacts with silicate minerals. If this is not true, then atmospheric CO_2 partial pressures could have been much higher than he calculated. Thus, there is nothing to preclude high CO_2 concentrations during the early to mid-Archean, which is presumably when respiration first evolved.

Theoreticians have made different predictions for CO_2 partial pressures on early Earth, with Walker (1985) favoring values as high as 10 bar prior to the origin of the continents and Sleep and Zahnle (2001) favoring values not much higher than today. We favor pCO_2 values ≥ 0.2 bar prior to the origin of methanogenesis, as this is approximately the amount of CO_2 that was needed to keep the surface from freezing in the absence of additional greenhouse warming from CH_4 (Kasting, 1987; Haqq-Misra *et al.,* 2008). So, we consider the CO_2 partial pressures assumed here to be plausible for the time period we are considering.

5. Conclusions

Trace amounts of oxidants, including free O_2 and H_2O_2, could have been supplied to organisms living on Earth's surface prior to the origin of oxygenic photosynthesis. If the threshold for aerobic respiration (0.05 nM dissolved O_2) estimated by Stolper *et al.* (2010) is correct, then these trace oxidant levels might have permitted the early evolution of respiration. Production of both O_2 and H_2O_2 is enhanced in warm, dense atmospheres that are rich in CO_2.

Although the availability of H_2O_2 at the surface is reasonably well estimated by the models employed here, the problem of stratospheric O_2 delivery deserves more detailed treatment. A fully coupled chemistry-climate GCM would allow for a more robust treatment of this problem by providing accurate temporal and spatial variations in O_2 concentration and by allowing the inclusion of phenomena such as the presence of UV-screening organic haze.

Author Disclosure Statement

No competing financial interests exist.

Abbreviation

GCM, general circulation model.

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