

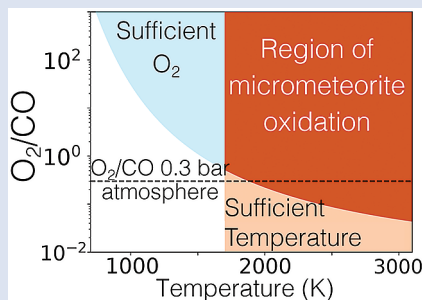
Oxidised micrometeorites as evidence for low atmospheric pressure on the early Earth

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Abstract



Reconstructing a record of the partial pressure of molecular oxygen in Earth's atmosphere is key for understanding macroevolutionary and environmental change over geological history. Recently, the oxidation state of iron in micrometeorites has been taken to imply the presence of modern Earth concentrations of oxygen in the upper atmosphere at 2.7 Ga, and therefore a highly chemically stratified atmosphere (Tomkins *et al.*, 2016). We here explore the possibility that the mixing ratio of oxygen in Earth's upper atmosphere, that probed by micrometeorites, may instead be sensitive to the surface atmospheric pressure. We find that the concentrations of oxygen in the upper atmosphere required for micrometeorite oxidation are achieved for a 0.3 bar atmosphere. In this case, significant water vapour reaches high up in the atmosphere and is photodissociated, leading

to the formation of molecular oxygen. The presence of oxidised iron in micrometeorites at 2.7 Ga may therefore be further evidence that the atmospheric pressure at the surface of the early Earth was substantially lower than it is today.

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Introduction

Reconstructing the history of atmospheric oxygen on Earth has been a longstanding, yet elusive, goal of the geosciences. Constraints from several observations now show that a major transition in atmospheric oxygen occurred in the past, the so called 'Great Oxidation Event' (GOE). The current paradigm places the GOE at 2.33 Ga (Luo *et al.*, 2016), although recent evidence challenges this (Philippot *et al.*, 2018). One of the most stringent constraints on the past abundance of atmospheric oxygen comes from the mass independent fractionation of sulphur isotopes (Farquhar *et al.*, 2000), which limits pre-GOE atmospheric oxygen to $<10^{-5}$ times present levels. However, all the geochemical, isotopic, and sedimentary proxies commonly used to reconstruct past atmospheric oxygen are incorporated into the geological record by processes occurring in the lower atmosphere.

In contrast, Tomkins *et al.* (2016) identified that micrometeorites may sample the upper atmosphere, by reacting with the atmosphere during transient heating on entry. Sixty micrometeorites were recovered from the Pilbara region of Australia by Tomkins *et al.* (2016), with their age estimated at 2.7 Ga. Tomkins *et al.* (2016) examined the FeNi metal in the spherules, and determined that they were oxidised while molten, with much of the iron now contained in magnetite

(Fe_3O_4) and wüstite (FeO). The authors argue that this level of oxidation requires modern earth levels of molecular oxygen in the upper atmosphere, 75–90 km above the surface of the Earth. This would be a remarkable result if verified, given the abundant evidence for anoxic conditions at Earth's surface during this period. The authors explain this observation by appealing to a methane-rich atmosphere, in which an organic haze could have produced a temperature inversion within the mesopause (see Tomkins *et al.*, 2016 and citations therein).

We here suggest an alternative explanation: that low atmospheric pressure in the Archean led to higher concentrations of molecular oxygen in Earth's upper atmosphere. Recent evidence from the measured radii of fossilised rain droplets, from the size of volcanic vesicles, and from nitrogen trapped in quartz, suggests that the atmospheric pressure at the surface of the Earth at 2.7 Ga was less than 0.5 bar (*e.g.*, Som *et al.*, 2016). We find that this low pressure can explain the oxidation of the micrometeoritic iron, with the Pilbara micrometeorites thus providing support for a low pressure atmosphere at 2.7 Ga.

Methods

We model the global chemistry of low pressure atmospheres for the Earth prior to 2.7 Ga. Our atmospheres are dominated

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by N₂, CO₂, CO, and H₂O. If the atmosphere of the Earth at this time had pressure <0.8 bar, then the partial pressure of N₂ must have been lower than it is today. CO as well as CO₂ were plausibly major constituents of volcanic outgassing on the early Earth, with the flux of CO increasing as pressures decreases, to the point that CO becomes the dominant species outgassed when $p \lesssim 0.1$ bar (Gaillard and Scaillet, 2014). The ratio of degassed CO/CO₂ is dependent on both pressure and the redox state of the crust and mantle. H₂O is assumed to be present at vapour pressure.

We seek to describe a plausible long term global quasi-steady state atmospheric condition appropriate for the Earth's atmosphere at 2.7 Ga. To ensure that we have identified a realistic quasi-steady state, we need to account for the global redox balance of the atmosphere and of the atmosphere-ocean system. We follow the approach of Harman *et al.* (2015), with CO₂, N₂, and H₂O as neutral species. The global redox balance is:

$$\Phi_{\text{out}}(\text{Red}) + \Phi_{\text{dep}}(\text{Ox}) = \Phi_{\text{esc}}(\text{H}_2) + \Phi_{\text{dep}}(\text{Red}), \quad \text{Eq.1}$$

where $\Phi_{\text{out}}(\text{Red})$ is the outgassing flux of reduced species, $\Phi_{\text{dep}}(\text{Ox})$ the deposition flux of oxidised species (either *via* dry deposition or rainout), $\Phi_{\text{dep}}(\text{Red})$ the deposition flux of reduced species, and $\Phi_{\text{esc}}(\text{H}_2)$ the escape of H₂ (all with units of cm⁻²s⁻¹). For now, we will stipulate that the outgassing flux of methane is negligible, and so:

$$\Phi_{\text{out}}(\text{Red}) = \Phi_{\text{out}}(\text{CO}) + \Phi_{\text{out}}(\text{H}_2). \quad \text{Eq. 2}$$

Also, we use the standard form for escape (adapted from Kasting, 2013).

$$\Phi_{\text{dep}}(\text{Red}) = v_{\text{dep}}(\text{CO})f_0(\text{CO})n_{\text{gas}} + v_{\text{dep}}(\text{H}_2)f_0(\text{H}_2)n_{\text{gas}}, \quad \text{Eq.3}$$

where $v_{\text{dep}}(X)$ [cm s⁻¹] is the deposition velocity of species X, and $f_0(X)$ is the surface mixing ratio of species X.

Applying these equations to Equation 1, noting that we are interested in atmospheres with surface pressure of 0.3 bar, we note that there are two independent components, dependent on CO and H₂, so we separate these into two independent equations and concentrate on the mixing ratio of CO:

$$\Phi_{\text{out}}(\text{CO}) = v_{\text{dep}}(\text{CO})f_0(\text{CO})n_{\text{gas}}. \quad \text{Eq. 4}$$

As with Harman *et al.* (2015), we will adjust H₂ and $v_{\text{dep}}(\text{H}_2)$ to balance out the hydrogen escape. The deposition velocity of CO during the Archean is driven by acetogens converting CO efficiently into acetate, with an equivalent deposition velocity of $v_{\text{dep}}(\text{CO}) = 1.2 \times 10^{-4}$ cm s⁻¹ (Harman *et al.*, 2015). The CO deposition is compensated for by CO volcanic outgassing.

We consider two cases:

1. Volcanically dominated, with volcanic CO >> volcanic CO₂ (0.3 bar with 33 % N₂, 33 % CO, and 33 % CO₂).
2. Biotically dominated, with negligible CO (0.3 bar with 33 % N₂ and 66 % CO₂)

Case 1 is appropriate for a >3.5 Ga atmosphere. During this period three effects would have combined to lead plausibly to an atmosphere with equal parts CO and CO₂ if the atmospheric surface pressure was low: i) A more reducing crust and plausibly more reducing upper mantle (Yang *et al.*, 2014; Nicklas *et al.*, 2018); ii) A lower outgassing pressure favouring the outgassing of CO over CO₂ (Gaillard *et al.*, 2011); and iii) the absence of acetogens to consume the CO. Case 1 is less plausible at 2.7 Ga, because acetogens will now form a major CO sink, and CO outgassing fluxes from the now more oxidised mantle will be lower (Nicklas *et al.*, 2018). Case 2 would arise from more moderate outgassing rates of CO and CO₂ of $\Phi_{\text{out}}(\text{CO}) \approx 3 \times 10^9$ cm⁻²s⁻¹, suggesting a surface steady

state mixing ratio of CO of 3×10^{-6} . The initial conditions at the surface used in our model are shown for the two cases in Table 1.

To calculate the atmospheric temperature and pressure, we use a 1D climate model developed for high-CO₂/high-CH₄ terrestrial atmospheres (Pavlov *et al.*, 2000; Kharecha *et al.*, 2005). For case 1 we model a 0.3 bar atmosphere with 66 % N₂ and 33 % CO₂. For case 2 we model a 0.3 bar atmosphere with 33 % N₂ and 66 % CO₂. For case 1, CO is not a greenhouse gas and influences the climate primarily by pressure broadening, incorporated here *via* the increased N₂ concentration. The similar temperature – pressure profiles in cases 1 and 2, despite much larger CO₂ concentrations in case 2, indicate that taking N₂ to represent the pressure broadening effects of CO is justified (Fig. 1). We use a solar evolution model for the incoming stellar radiation at 3.9 Ga for case 1 and 2.7 Ga for case 2 (Claire *et al.*, 2012). In both cases, the profile is taken to be isothermal above 10⁻⁶ bar.

Table 1 Mixing ratios for two model atmospheres.

Species	Case 1	Case 2
N ₂	0.33	0.33
CO ₂	0.33	0.66
CO	0.33	3x10 ⁻⁶
H ₂	10 ⁻³	10 ⁻³
H ₂ O	Vapour pressure	Vapour pressure

For the atmospheric chemistry, we use the ARGO photochemistry model (Rimmer and Helling, 2016), which solves the photochemistry-transport equation:

$$\frac{\partial n_i}{\partial t} = P_i - L_i - \frac{\partial \Phi_i}{\partial z}, \quad \text{Eq. 5}$$

where, n_i [cm⁻³] is the number density of species i , $i = 1, \dots, I_s$, I_s being the total number of species. P_i [cm⁻³s⁻¹] and L_i [cm⁻³s⁻¹] represent the production and loss rates calculated from the STAND2016 chemical network and $\frac{\partial \Phi_i}{\partial z}$ is a vertical flux term capturing eddy and molecular diffusion (Rimmer and Helling, 2016). We apply fixed boundary conditions discussed above.

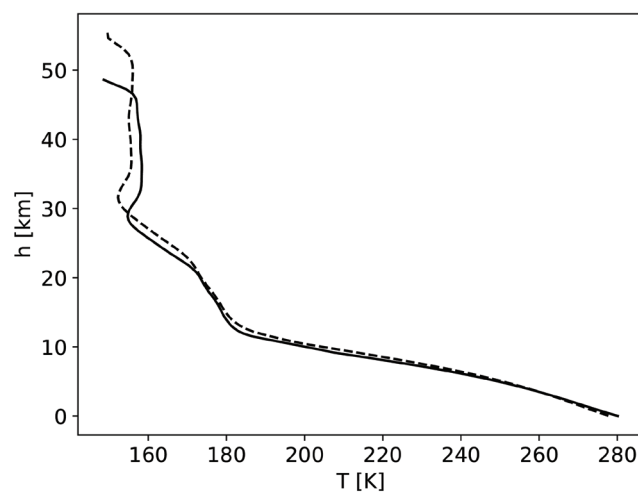


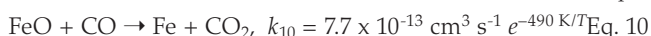
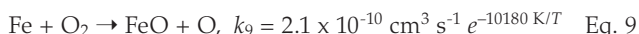
Figure 1 Temperature profile for the Earth's atmosphere with surface pressure of 0.3 bar composed of 33 % N₂, 33 % CO₂ and 33 % CO (dashed), and 33 % N₂, 66 % CO₂ (solid).

Results

The chemical profile for a 0.3 bar atmosphere dominated by N₂, CO₂ and CO is shown in Figure 2. The upper atmosphere is composed of N₂, O₂ and CO, with O₂ mixing ratios achieving modern levels (Tomkins *et al.*, 2016). It is water vapour that is responsible for the enhancement of O₂ within a low pressure atmosphere. A dominant mechanism by which water vapour produces molecular oxygen is as follows:



This is similar to the mechanism that can lead to large amounts of oxygen in exoplanets without a cold trap (Wordsworth and Pierrehumbert, 2014). When CO is present, however, neutral iron (Fe⁰), acts as a catalyst for the oxidation of CO by O₂, at the rates (Smirnov, 2008 and Akhmadov *et al.*, 1988) respectively:



The balance between Equations 9 and 10 determines the amount of oxygen needed relative to CO, in order to reproduce the observed micrometeoritic iron oxidation. The minimum ratio of O₂/CO needed to explain the data is shown

in Figure 3. Because of the large energy barrier for reaction (Eq. 9), at temperatures <1700 K, reaction (Eq. 10) is faster than (Eq. 9), and so much more O₂ than CO is needed to oxidise the iron sufficiently. At higher temperatures, however, CO can be as much as 50 times as abundant as O₂ and oxidation still occurs. Tomkins *et al.* (2016) demonstrate that, given the size of the micrometeorites, they would have oxidised while at a temperature above 1600 K. The micrometeorites could, therefore, have been oxidised within a reducing, low pressure, early Earth atmosphere like that shown in Figure 2.

Discussion and Summary

We have shown that the presence of magnetite and wüstite in 2.7 Ga micrometeorites is consistent with the surface pressure of the 2.7 Ga Earth being much less than today. This fits well with other evidence of low atmospheric surface pressures on the Archean Earth (*e.g.*, Som *et al.*, 2016).

Kopparapu *et al.* (2014) have investigated the effect on climate when atmospheres are at low pressures. At low pressures and without a cold trap, water vapour extends much further into the upper atmosphere. This by itself resolves the Faint Young Sun Paradox (Sagan and Mullen, 1972), possibly providing too much of a correction as, with water being such a strong greenhouse gas, there is the risk such atmospheres enter a runaway

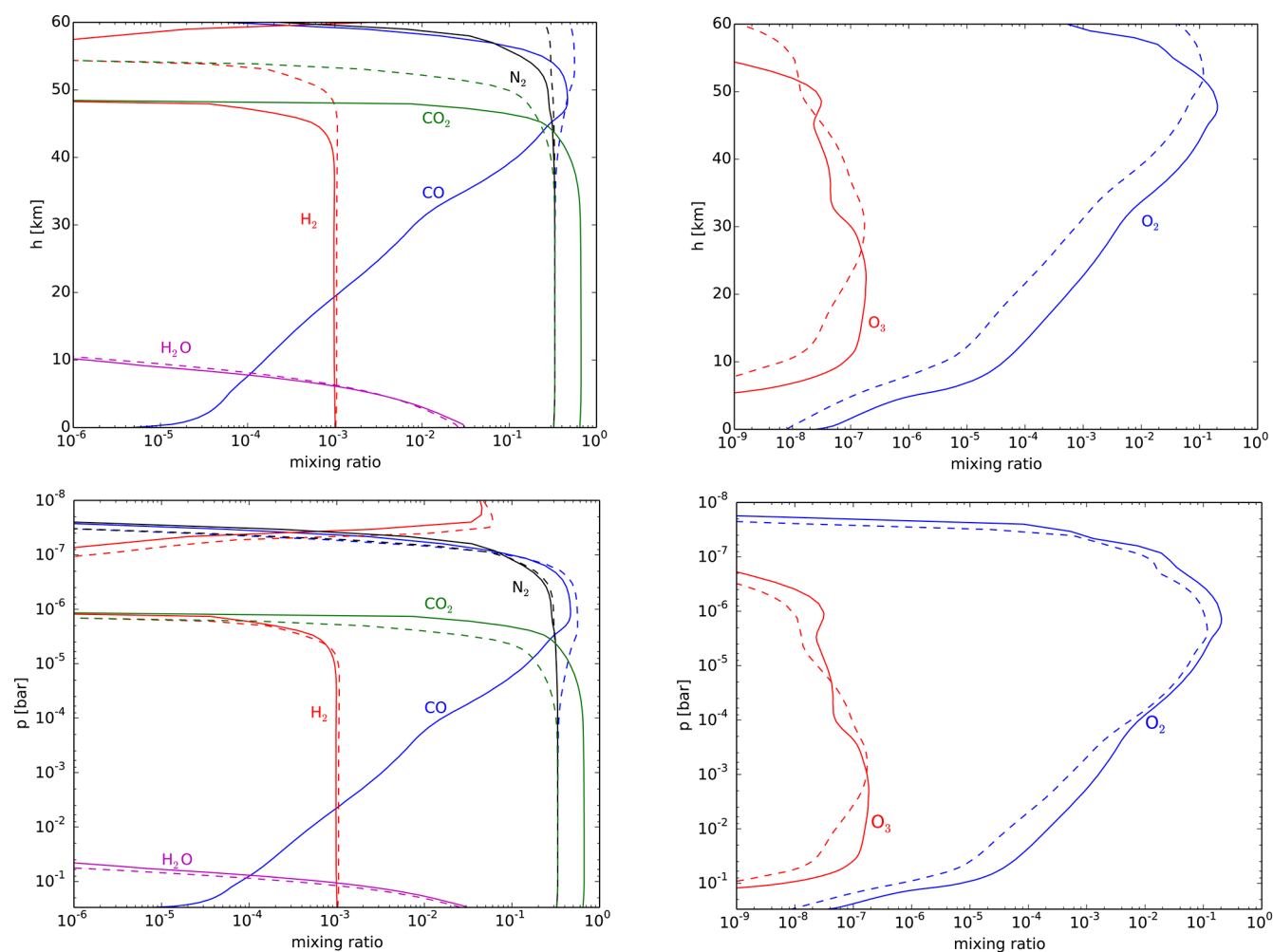


Figure 2 Two low pressure model atmospheres of the 3.5 Ga – 2.7 Ga Earth. One model includes a surface mixing ratio of CO of 0.33 (dashed), and the other a surface mixing ratio of 10⁻⁶ (solid). The surface pressure is 0.3 bar for both models. Mixing ratios are shown as a function of atmospheric height, *h* (km; top two figures) and pressure (bar; bottom two figures).



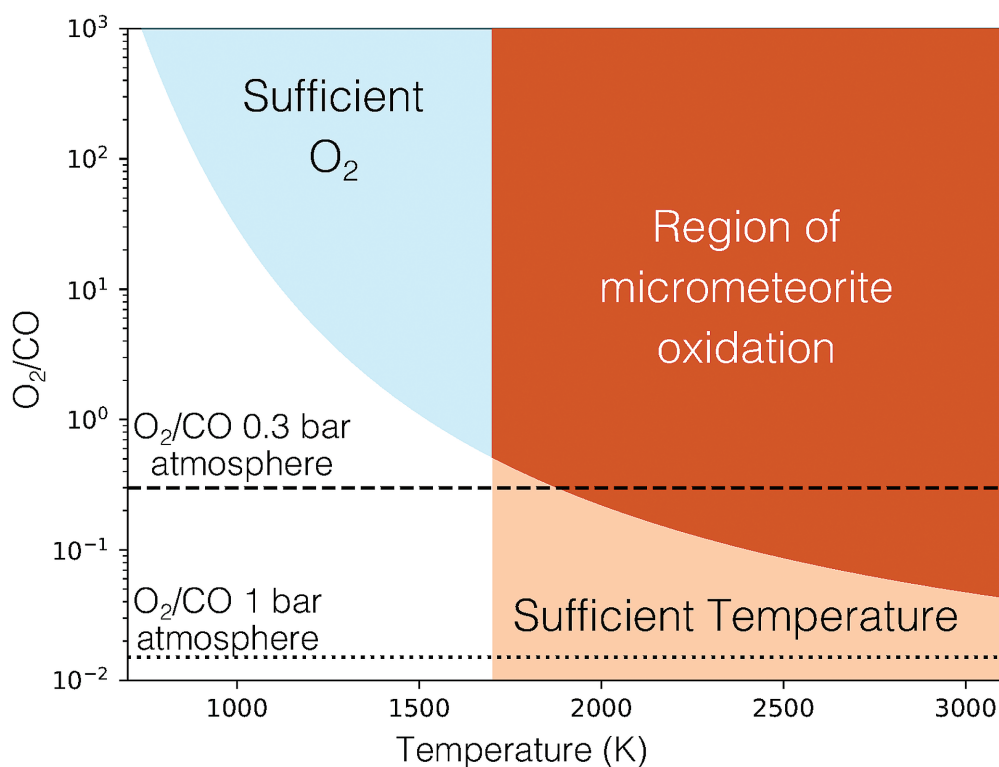


Figure 3 The minimum O_2/CO ratio suggested by the observed iron oxidation in 2.7 Ga micrometeorites (Tomkins *et al.*, 2016), as a function of the melting temperature T [K]. Shaded regions show where there is sufficient O_2 (light blue), sufficient temperature (light orange), and the overlap between these two regions (dark orange). The dotted line is the O_2/CO ratio in the upper atmosphere for an anoxic atmosphere with a 1 bar surface pressure, and the dashed line is the O_2/CO ratio in the upper atmosphere for an anoxic atmosphere with a 0.3 bar surface pressure.

greenhouse state. However, low pressure atmospheres are not necessarily unstable (Kopparapu *et al.*, 2014), and the growing evidence for low atmospheric pressures on the 2.7 Ga Earth suggest that somehow the Earth avoided this runaway scenario.

A low surface pressure on the early Earth may be explained by a reasonably fast rate of abiotic nitrogen fixation without any efficient abiotic mechanism for restoring nitrogen (Som *et al.*, 2016). Alternatively, Lammer *et al.* (2018) have speculated that the Earth's nitrogen reservoir was largely held within its interior following the lunar impactor stripping the Earth of its primordial atmosphere. The N_2 would take some time to build up because of slower N_2 outgassing under abiotic conditions (Mikhail *et al.*, 2014), and more rapid N_2 removal from fixation and escape due to heightened solar activity (Lammer *et al.*, 2018). Lammer *et al.* (2018) consider these sources and sinks and estimate that the N_2 partial pressure at 2.7 Ga was somewhere between 0.1 and 0.5 bar. The consequences of an initially low and increasing nitrogen content need to be explored, both for understanding the effects of low pressure on the evolution of climate, atmosphere, crust and upper mantle, and for identifying further tests of this low pressure hypothesis.

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Additional Information



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