Oxidized micrometeorites suggest either high pCO_2 or low pN_2 during the Neoarchean

Rebecca C. Payne[a,1] ![ORCID], Don Brownlee[b], and James F. Kasting[a]

[a]Department of Geosciences, Pennsylvania State University, University Park, PA 16802; and [b]Department of Astronomy, University of Washington, Seattle, WA 98195

Tomkins et al. [A. G. Tomkins et al., Nature 533, 235–238 (2016)] suggested that iron oxides contained in 2.7-Ga iron micrometeorites can be used to determine the concentration of O_2 in the Archean upper atmosphere. Specifically, they argued that the presence of magnetite in these objects implies that O_2 must have been near present-day levels (~21%) within the altitude range where the micrometeorites were melted during entry. Here, we reevaluate their data using a 1D photochemical model. We find that atomic oxygen, O, is the most abundant strong oxidant in the upper atmosphere, rather than O_2. But data from shock tube experiments suggest that CO_2 itself may also serve as the oxidant, in which case micrometeorite oxidation really constrains the CO_2/N_2 ratio, not the total oxidant abundance. For an atmosphere containing 0.8 bar of N_2, like today, the lower limit on the CO_2 mixing ratio is ~0.23. This would produce a mean surface temperature of ~300 K at 2.7 Ga, which may be too high, given evidence for glaciation at roughly this time. If pN_2 was half the present value, and warming by other greenhouse gases like methane was not a major factor, the mean surface temperature would drop to ~291 K, consistent with glaciation. This suggests that surface pressure in the Neoarchean may need to have been lower—closer to 0.6 bar—for CO_2 to have oxidized the micrometeorites. Ultimately, iron micrometeorites may be an indicator for ancient atmospheric CO_2 and surface pressure; and could help resolve discrepancies between climate models and existing CO_2 proxies such as paleosols.

micrometeorites | Archean | atmospheric CO_2 | climate

Earth's atmospheric O_2 concentration is widely believed to have been low prior to ~2.5 Ga, based on a variety of geologic evidence (1), including multiple sulfur isotopes (2–4). These constraints are relevant to the lower atmosphere but do not necessarily apply to the upper atmosphere. Tomkins et al. (5) proposed that ancient spherical micrometeorites could be used to determine past oxygen concentrations in the upper atmosphere. They extracted 59 iron-type micrometeorites from Pilbara limestone, dated at ~2.72 Ga, and used the iron oxides contained within them to estimate the amount of O_2 the micrometeorites would have encountered as they were melted during entry. These type I cosmic spheres were small Fe-Ni metal meteoroids that totally melted to form spheres during hypervelocity entry into the atmosphere. Their oxygen content was obtained in the mesopause during a brief period of frictional melting. Tomkins et al. (5) concluded that upper atmospheric O_2 concentrations must have been close to the modern value, 21% by volume, to create the largely oxidized composition of the micrometeorites. To explain the discrepancy with inferred low O_2 concentrations at the surface, they suggested that vertical atmospheric mixing in the Neoarchean could have been inhibited by the presence of a stratospheric organic haze, which would have caused a temperature inversion by absorbing incoming sunlight.

In more detail, Tomkins et al. (5) argued that the micrometeorites would have passed through the upper atmosphere, accelerated by Earth's gravitational field, and reached maximum temperature and velocity between 85 and 90 km above the surface (6). They posited that melting and quench cooling of these sand grain-size meteorites would have occurred within approximately

2 s between 75 and 90 km, so this is where oxidation should have occurred. Tomkins et al. (5) argued that the micrometeorites must have been oxidized when passing through the atmosphere and not by later alteration, based on the presence of a layer of encasing wüstite (FeO) in some of the micrometeorites, along with the preservation of delicate surface textures. They developed a mathematical model to determine the amount of O_2 that would need to have been encountered during atmospheric entry to produce the iron oxides found in the micrometeorites. This included an equilibrium chemical model coupled to a numerical model of meteorite ablation. Tomkins et al. (5) argued that CO_2 would have been an ineffective oxidant on its own because of its supposedly sluggish rate of reaction, and therefore free O_2 would have been needed to oxidize the meteorites.

These micrometeorite data have recently been reanalyzed by Rimmer et al. (7), who concluded that they require low atmospheric surface pressure (~0.3 bar) at 2.7 Ga. According to their analysis, this allows H_2O to penetrate into the upper atmosphere, where it produces O_2 from photodissociation. Zahnle and Buick (8) suggested this previously as a possible oxidation route, although they noted that it would require a much less effective tropopause cold trap than exists today. This solution would require that H_2O was a major upper atmospheric constituent in the Rimmer et al. (7) model; however, this does not seem to be the case, based on their figure 2. Instead, the O_2 in their atmosphere must be coming from photolysis of CO_2, as that is the only species that contains enough O atoms to produce it. (See our analysis below regarding conservation of O atoms with altitude.) Our own model also includes photolysis of CO_2, but this process is slower than in the Rimmer et al. (7) model, for reasons that remain to be determined. That said, while we think there may be problems with

Significance

Paleosols (ancient soils) have been used to estimate CO_2 concentrations during the Archean Eon, 4.0 to 2.5 Ga. However, different paleosol studies disagree with each other and with climate model estimates for ancient CO_2 levels. Oxidized iron micrometeorites dated at 2.7 Ga represent a new CO_2 proxy with which to compare. These meteorites suggest that CO_2 constituted 25 to 50% of the atmosphere at that time. This is easiest to explain if the N_2 partial pressure was lower than today so that the atmospheric greenhouse effect was modest and the climate was cool, consistent with evidence for contemporaneous glaciation.

the Rimmer et al. (7) model, or at least with their interpretations, we do agree that lower atmospheric pressure can help explain the Tomkins et al. (5) data, as it would allow for a higher ratio of $CO_2:N_2$. This is a key factor in the analysis presented here.

To test both these theories of micrometeorite oxidation, we used our own 1D photochemical model to create a suite of Archean atmosphere profiles with varying concentrations of atmospheric CO_2. Rather than focus exclusively on upper atmospheric O_2, as Tomkins et al. (5) did, we included O in our calculations as well, to assess the availability of all forms of oxygen. Furthermore, we reevaluated the efficacy of CO_2 as an oxidant and considered atmosphere–particle interactions to determine likely conditions for micrometeorite oxidation in the upper Archean atmosphere. We then simulated the effect of possible CO_2 concentrations on surface temperature and pressure, for different values of pN_2, using a 1D radiative–convective climate model.

Micrometeorite Oxidation

Entry Physics. Particles with a diameter of less than 1 mm are too small to generate a bow shock during atmospheric entry (6), meaning that micrometeorites smaller than this do not create the shock waves or gas caps that typically form around larger particles under these conditions. The interaction between the smaller micrometeorites and the atmosphere is therefore thought to be simple, as no shock-induced chemical alteration occurs to the surrounding air during entry. Instead, the micrometeorite is simply slowed by, and may react with, the gas it encounters. Deceleration is a function of momentum exchange, and frictional heating during deceleration is what causes the micrometeorite to briefly melt and quench crystallize. The speed of the micrometeorite decreases by a factor of 1/e for each particle mass column of gas that the micrometeorite impacts, assuming all of the gas momentum is transferred to the micrometeorite. A micrometeorite's speed would decrease to 0.37 and 0.135 of the initial speed after colliding with gas equal to 1 and 2 particle masses, respectively. Faster micrometeorites would encounter more air while molten because of their greater momentum.

The temperature of an entering micrometeorite depends on its velocity and on the ambient gas density, such that

$$\text{radiated power} = \frac{1}{4} \cdot \left(\frac{1}{2}\rho_{air}\right) \cdot v^3. \quad [1]$$

Here, ρ_{air} is the ambient air density and v is the micrometeorite's entry velocity. The melting temperature of Fe and its oxides is ~1,500 °C, so the micrometeorite's speed must be above 6 km/s at 80 km and above 9 km/s at 85 km (in the modern Earth's atmosphere) to reach the melting point. To take up oxygen and form the mix of magnetite, wüstite, and metal observed in the Tomkins et al. (5) spherules, the micrometeorites need to be molten.

Depending on size and particle speed, most micrometeorites should contact 1 to 2 equivalent masses of air in the time that they are traveling fast enough to be heated to their melting points. A complication is that the micrometeorites are potentially evaporating some fraction of their mass during entry, and this is strongly dependent on entry angle and initial micrometeorite size. Evaporative mass loss during entry would likely decrease the number of Fe atoms that would need to be reacting with oxidants for the micrometeorite to be fully oxidized. But newly acquired oxygen may be lost as well, and so the uncertainties associated with mass loss make it difficult to constrain in our calculations without knowing more about entry angle and initial size. For this study, we assume that the micrometeorite retains most or all of the oxygen it encounters, along with its own initial mass, so oxidizing the micrometeorites is therefore a function of how much oxygen the meteorite encounters in the upper atmosphere while molten.

Tomkins et al. (5) assumed that the altitude region within which the micrometeorites were molten would be the same in the Archean as it is in the modern atmosphere (between ~75 and 90 km, as ref. 6 specified). But the deceleration—and frictional heating—of a micrometeorite depends on the number of particles it encounters during entry. Thus, the window in which oxidation occurs is not located at a fixed altitude range, but rather at a fixed pressure range. Pressure in our model Archean atmosphere falls off more rapidly than in the modern atmosphere (*SI Appendix*, Fig. S1B) because of the cooler, ozone-poor stratosphere, along with the higher mean molecular weight caused by increased CO_2. Thus, the "oxidation altitude range" of 75 to 90 km for the modern atmosphere should really be redefined as an "oxidation pressure range" from ~2.3×10^{-5} bar to ~1.6×10^{-7} bar. The corresponding altitude of oxidation therefore varies with the CO_2 concentration and is generally lower than assumed by Tomkins et al. (5) (Table 1).

Micrometeorite Oxidation Chemistry. In a Neoarchean atmosphere with a primarily N_2-CO_2 composition, upper atmospheric chemistry would be dominated by the reaction

$$CO_2 + hv \rightarrow CO + O. \quad [2]$$

Direct recombination of CO with O is spin forbidden, and therefore slow, so O primarily recombines with itself to form O_2:

$$O + O + M \rightarrow O_2 + M. \quad [3]$$

In terms of micrometeorite oxidation, it should not matter much whether oxygen was present as O or O_2, as the high temperature of the molten iron micrometeorites should allow all of the gaseous species interacting with them to equilibrate with each other on short timescales.

Tomkins et al. (5) considered O_2 only as a potential oxidant, assuming that the concentration of other forms of oxygen would be negligible. Their figure 4 shows calculations by Zahnle et al. (9) that appear to support this assumption. But our own photochemical model of the 2.7-Ga atmosphere indicates that both O_2 and O would be present in the stratosphere (*Photochemical Calculations*). The Zahnle et al. model (9, 10), which is a derivative of our model, would almost certainly yield the same result. However, those authors were focused on the lower atmosphere and simply did not include O in their figure.

It is also possible—even likely—that CO_2 itself was an oxidant for the micrometeorites. Tomkins et al. (5) argued that Fe oxidation by CO_2 would be slow, based on studies of Fe metallurgy at temperatures below 1,470 K (11, 12). But iron micrometeorites (and iron oxide) need to reach at least ~1,770 K during entry to melt (6). Shock tube experiments above the Fe melting temperature indicate that oxidation rates of Fe to FeO by O_2 (13) and CO_2 (14) are roughly equal and are up to 3 orders of magnitude faster than reduction of FeO by CO (15). Other possible oxidation reactions include O_2 oxidation of Fe to FeO_2 (16) and CO_2 oxidation of FeO to $FeCO_3$ (17) at similar reaction rates. But it is worth noting that O can also reduce FeO to form O_2 in the upper mesosphere (18), albeit at much lower temperatures than the micrometeorites would experience during entry. Until experimental chemical reaction rate data are obtained for the appropriate temperature and pressure range, we cannot definitively state which oxidation and reduction reactions are likely to dominate. Nonetheless, the CO_2 oxidation pathway indicates the value such experiments would have for micrometeorite analysis—and, for now, existing data point to its potential significance for the Tomkins micrometeorites. In short, it suggests that at least one O atom from each CO_2 molecule may contribute to micrometeorite oxidation during entry. It also suggests that reduction of the newly formed Fe oxides by CO is unlikely to occur during the short time

Table 1. Approximate altitude of lower and upper bounds of oxidation pressure range for atmospheres with various CO$_2$ mixing ratios

CO$_2$, %	Modern	1%	10%	20%	25%	30%	35%	50%
Lower	75	59	55	54	52	51	50	46
Upper	90	72	70	67	65	64	62	58

Altitude is in kilometers.

that the micrometeorite is molten and that accumulating an adequate amount of oxidant in the oxidation pressure range is more important than the ratio of oxidants to reductants.

If so, then one should consider the oxidation potential from O, O$_2$, and CO$_2$ within the oxidation pressure window. And this, in turn, makes the calculation quite simple, as nearly all O and O$_2$ in the upper atmosphere is derived from CO$_2$. O atoms are neither created nor destroyed in the atmosphere above the altitude at which they are removed by rainout of H$_2$O. Thus, from mass balance, it is easy to demonstrate (*SI Appendix*) that if O$_2$ concentrations are low near the surface, and if H$_2$O concentrations are low at the tropopause, then

$$f(O) + 2fO_2 + fCO_2 = const. = fCO_2^0. \qquad [4]$$

Here, f_i is the volume mixing ratio of species i and fCO_2^0 is the mixing ratio of CO$_2$ at the surface. More precisely, fCO_2^0 is the mixing ratio of CO$_2$ at the base of the stratosphere; however, the difference between this value and the surface CO$_2$ mixing ratio is negligible. Thus, in our analysis, the key parameter is the CO$_2$:N$_2$ ratio at the surface. CO$_2$ oxidizes the micrometeorites, whereas both CO$_2$ and N$_2$ decelerate the meteorites. The CO$_2$:N$_2$ ratio determines whether or not they are oxidized, independent of particle size.

To make this analysis more concrete, consider the modern atmosphere, within which we know that incoming metal micrometeorites are partly to fully oxidized to form a mix of Fe$_{(1-x)}$O (wüstite), Fe$_3$O$_4$, and sometimes iron metal during entry (6). For total oxidation, this requires the addition of 1 to 1.3 O atoms per iron atom. In the modern atmosphere, this oxidation is accomplished almost exclusively by O$_2$. Assume for now that the particle remains molten, and hence reactive, only during its encounter

with the first equivalent air mass. Because the atomic mass of Fe ($\sim$56 amu) is just under twice the average atmospheric mass (29.6 for N$_2$-O$_2$-^{40}Ar), the micrometeorite should encounter about twice as many air molecules as it contains Fe atoms while it is still molten. Of these, 21% are O$_2$ molecules. Therefore, the ratio of O$_2$ molecules encountered to Fe atoms within the micrometeorite is equal to $2 \times 0.21 \cong 0.4$. The ratio of O:Fe is twice that, or 0.8. This ratio is close enough to the O:Fe ratio required to form the observed oxides (as the micrometeorites contain some varying fraction of Ni instead of Fe), provided that oxidation is total and nearly 100% efficient. We can express this relationship compactly by writing

$$\left(\frac{56}{29.6}\right) \cdot 2fO_2 \cong 0.8. \qquad [5]$$

Now, let us apply this same logic to the Neoarchean atmosphere, assuming that it consists primarily of N$_2$ and CO$_2$ within the oxidation pressure window. (Fig. 1 and *SI Appendix*, Fig. S2 show that this is approximately true.) The mean molecular weight of the atmosphere is then

$$M_{at} \cong 44fCO_2 + 28(1 - fCO_2). \qquad [6]$$

Here, fCO_2 is effectively fCO_2^0, the CO$_2$ mixing ratio at the ground. We use these terms interchangeably from here on. Using the identical requirement of 0.8 O atoms per Fe atom for complete oxidation then yields
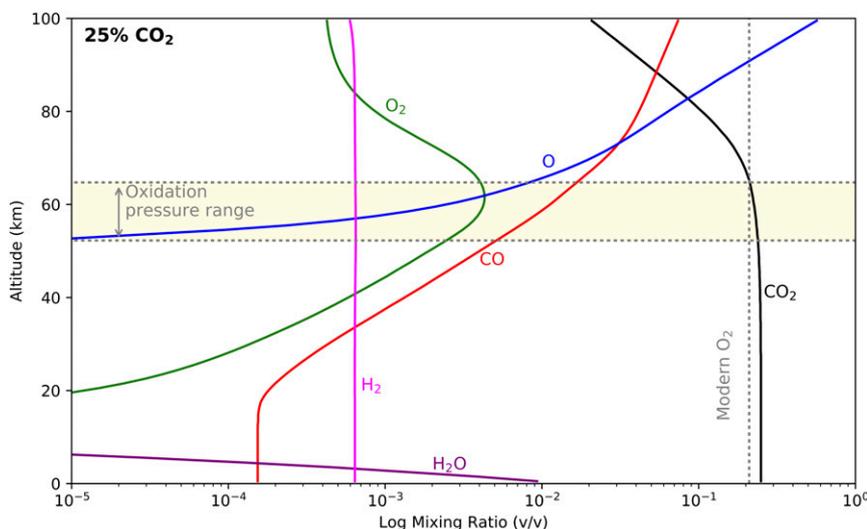
$$\left(\frac{56}{M_{at}}\right)fCO_2 = \left(\frac{56fCO_2}{44fCO_2 + 28(1 - fCO_2)}\right) \geq 0.8$$

or

$$\left(\frac{2fCO_2}{1 + \left(\frac{4}{7}\right)fCO_2}\right) \geq 0.8. \qquad [7]$$

Solving for fCO_2 gives a minimum value of 0.52 needed to oxidize a micrometeorite encountering one equivalent mass of air during entry.

Suppose now that the meteorite remains molten during its encounter with 2 equivalent air masses. The required CO$_2$

Fig. 1. Vertical profiles of major constituents mixing ratios for $fCO_2 = 25\%$, close to our minimum estimated value. The pressure range for micrometeorite oxidation is indicated by the shaded yellow region. The modern O$_2$ mixing ratio is shown by the vertical dotted line. Atmosphere also contains 0.8 bar N$_2$.

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mixing ratio is lower, but not exactly by a factor of 2. The analog to Eq. **7** is

$$\left(\frac{56}{M_{at}}\right) \cdot 2f\text{CO}_2 = \left(\frac{56f\text{CO}_2}{44f\text{CO}_2 + 28(1 - f\text{CO}_2)}\right) \geq 0.8$$

or, more simply,

$$\left(\frac{4f\text{CO}_2}{1 + \left(\frac{4}{7}\right)f\text{CO}_2}\right) \geq 0.8. \qquad [8]$$

Solving for $f\text{CO}_2$ in this case yields a value of 0.23. It is slightly less than half the value predicted from Eq. **7** because the mean molecular weight of the atmosphere is lower, causing the micrometeorite to encounter more air molecules as it decelerates.

Similar calculations can be performed for the case when CO_2 is not considered to be an oxidant for Fe. We do this here because it remains unclear which assumption is actually correct. In this case, CO_2 and N_2 would still be the dominant constituents in the oxidation pressure range, so M_{at} remains unchanged, but the fraction of oxidant is $f\text{O}_{oxy} \equiv (f\text{O} + 2 f\text{O}_2)$, rather than $f\text{CO}_2$. Thus, if the particle remains molten during encounter with one equivalent air mass, we can write

$$\left(\frac{56}{M_{at}}\right)f\text{O}_{oxy} = f\text{O}_{oxy}\left(\frac{56}{44f\text{CO}_2 + 28(1 - f\text{CO}_2)}\right) \geq 0.8$$

or

$$\left(\frac{2 \cdot f\text{O}_{oxy}}{1 + \frac{4}{7}f\text{CO}_2}\right) \geq 0.8. \qquad [9]$$

The value of $f\text{O}_{oxy}$ needed to oxidize the micrometeorites still depends on the mixing ratio of CO_2, but the relationship is more complicated, as O and O_2 are both produced, directly or indirectly, from CO_2 photolysis. Thus, a photochemical model is needed to determine this relationship. We have performed such modeling (*Photochemical Calculations*) and, not surprisingly, the required atmospheric CO_2 mixing ratios for micrometeorite oxidation using only O and O_2 are much higher. For a 2-air-mass oxidation event, the required value of $f\text{O}_{oxy}$ in Eq. **9** is cut exactly in half, as the mean molecular mass does not change. But, as we shall see, attaining even this lower value of $f\text{O}_{oxy}$ is difficult to achieve in a realistic Archean atmosphere.

Photochemical Calculations

Methods. Photochemical model calculations are required if CO_2 is not included as a possible oxidant for Fe micrometeorites. For our calculations, we used a version of our 1D photochemical model developed for high-CO_2, low-O_2 atmospheres (19). Our model contains 49 chemical species involved in 221 reactions (see supporting information in ref. 20 for the full list). It extends upward from the Earth's surface to 100 km in 1-km thick layers. Vertical mixing is parameterized as a combination of eddy and molecular diffusion, using a profile appropriate for the modern atmosphere (21). Absorption and scattering of solar radiation were calculated using a 2-stream algorithm (22), assuming a fixed solar zenith angle of 50°. The time-dependent, coupled chemistry/diffusion equations were integrated to steady state using the (fully implicit) reverse Euler method. We also calculated changes to the solar UV flux using a parameterization developed by Ribas et al. (23). Properly scaling the UV flux is essential for this analysis, as the rate of free oxygen production via CO_2 photolysis depends on this parameter. At 2.7 Ga, the Sun would have been only ~81% as bright as today in the visible wavelength range (24, 25), but ~50% brighter than today at far-UV wavelengths (<1,750 Å).

Calculations were performed for a 1-bar, CO_2-N_2 atmosphere with 1 to 50% CO_2, along with low concentrations of methane (below). We should note that we are solving minor-constituent diffusion equations for major species, which introduces some error in the ratio of CO_2:CO:O at high altitudes in the model atmosphere. However, this should have little effect on our results because, as discussed earlier, it is only the sum of CO_2, O_2, and O that matters, as iron reduction by CO is slow. Furthermore, the largest errors in these ratios occur close to the top of the model atmosphere, above the altitude range at which most meteorite oxidation occurs.

We assumed a simplified temperature structure that decreases from 285 K at the surface to 175 K at 9.5 km and then remains constant above that height (*SI Appendix*, Fig. S1A). This is consistent with predictions from 1D climate models (e.g., ref. 26), which suggest that the temperature profile of an ozone-free atmosphere should follow a moist adiabat from the surface up to the tropopause and then become roughly isothermal above that altitude. We have not attempted to keep the surface temperature consistent with the assumed CO_2 concentration and solar flux in these calculations, reasoning that upper atmospheric composition should be relatively insensitive to this parameter. We examine the implications of atmospheric composition and photochemistry on surface temperature in our climate calculations (*Discussion*).

An upward CH_4 flux of 3.0×10^9 molecules·cm^{-2}·s^{-1} was assumed for our photochemical calculations. This is about 3% of the present CH_4 flux and well below the estimated CH_4 flux during the Archean (27). Unlike Tomkins et al. (5), we do not rely on a stratospheric temperature inversion to help build up upper atmospheric O_2, and so we avoid the regime in which $f\text{CH}_4/f\text{CO}_2 > 0.1$ and in which organic haze may form (28). The actual amount of CH_4 present should have little effect on micrometeorite oxidation; however, it does have implications for climate at that time, so we return to this issue in *Discussion*.

Data for both photochemical and climate model calculations are available on request from the corresponding author.

Results. Vertical profiles of major atmospheric constituents for our 25% CO_2 case are shown in Fig. 1. Key reducing and oxidizing species in the upper atmosphere at different CO_2 concentrations are shown in *SI Appendix*, Fig. S2. Both O and O_2 are present within the micrometeorite oxidation pressure range, with O dominating in the upper part of this region and O_2 in the lower part. In all these simulations, the sum of $f\text{O} + 2f\text{O}_2$ ($f\text{O}_{oxy}$) is much less than $f\text{CO}_2$. That is because virtually all of the O and O_2 is coming from CO_2 and because CO_2 itself is relatively resistant to photolysis (CO_2 photolyzes only below ~200 nm, where the solar UV flux is relatively low). Accumulating large amounts of O and O_2 in the stratosphere would require unrealistically low eddy mixing. Tomkins et al. (5) argued that such low mixing might result from a stratospheric temperature inversion caused by the presence of organic haze. But the eddy diffusion profile used here already accounts for this phenomenon, as it was derived for the modern stratosphere which has a temperature inversion caused by ozone.

Even with CO_2 concentrations as high as 50%, the fraction of the atmosphere within the oxidation pressure range that is composed of O and O_2 combined is less than 2% (*SI Appendix*, Fig. S2). Oxidizing the micrometeorites with oxygen alone (Eq. **9**) requires reaching a value of $f\text{O}_{oxy}$ roughly 10 times higher than this. Doing so would thus require both an extremely high CO_2 concentration and extremely low eddy mixing. It is therefore difficult, or even impossible, to oxidize the Tomkins et al. (5) micrometeorites using just O and O_2, unless O_2 was abundant throughout the atmosphere. But this

possibility is ruled out by geologic data, including sulfur isotope studies, as mentioned earlier. It is much more likely that the micrometeorites were oxidized by CO_2, in which case the limits on fCO_2 derived in *Micrometeorite Oxidation Chemistry* remain applicable.

Discussion

Constraints on pCO_2 from Neoarchean Climate. The high atmospheric CO_2 concentrations required to oxidize the micrometeorites can be compared with CO_2 levels required to explain the climate of the Neoarchean Earth. Ojakangas et al. (29) have reported diamictites dated at 2.7 Ga in the Dharwar Supergroup, India. This is approximately the same age as the micrometeorites (2.721 ± 0.004 Ga) analyzed by Tomkins et al. (5). Even more convincing evidence for glaciation is found in 2.9-Ga rocks from the Pongola Supergroup in South Africa (30). Together, these observations suggest that the climate of the Neoarchean was not too different from that of today. In a long-term sense, Earth's climate is glacial today because ice caps exist at both poles.

Approximate constraints on global mean surface temperature, T_S, during glacial periods have been estimated by Kasting (31), and we follow the same approach here. The modern value of T_S is ~288 K. Polar ice caps were absent during the early Cenozoic and preceding Mesozoic eras. The Antarctic ice cap started to grow about 35 My ago, at which time T_S was about 5 °C warmer than today, or 293 K, based on oxygen isotopes in deep sea carbonate cores. This suggests that 293 K is a reasonable upper limit for continental-scale glaciation. The argument is not ironclad, because changes in land–sea distributions—in particular, the opening of the Drake passage at about this same time—could also have helped trigger Antarctic glaciation. But we use this as a reasonable guess at the upper limit on T_S at 2.7 Ga. At the same time, we can take 0 °C, or 273 K, as a reasonable lower limit on T_S, as climate models predict that Earth's climate would go into a Snowball state if temperatures were to drop much below this value. Climate theory (32) then predicts that silicate weathering would slow, and atmospheric CO_2 would build up if this were the case.

We used an existing 1D climate model (33) to study the effects of high atmospheric CO_2 levels on Neoarchean climate. To do so, we needed to first establish a relationship between fCO_2 (the CO_2 mixing ratio) and surface pressure. This relationship is nonlinear because the total atmospheric
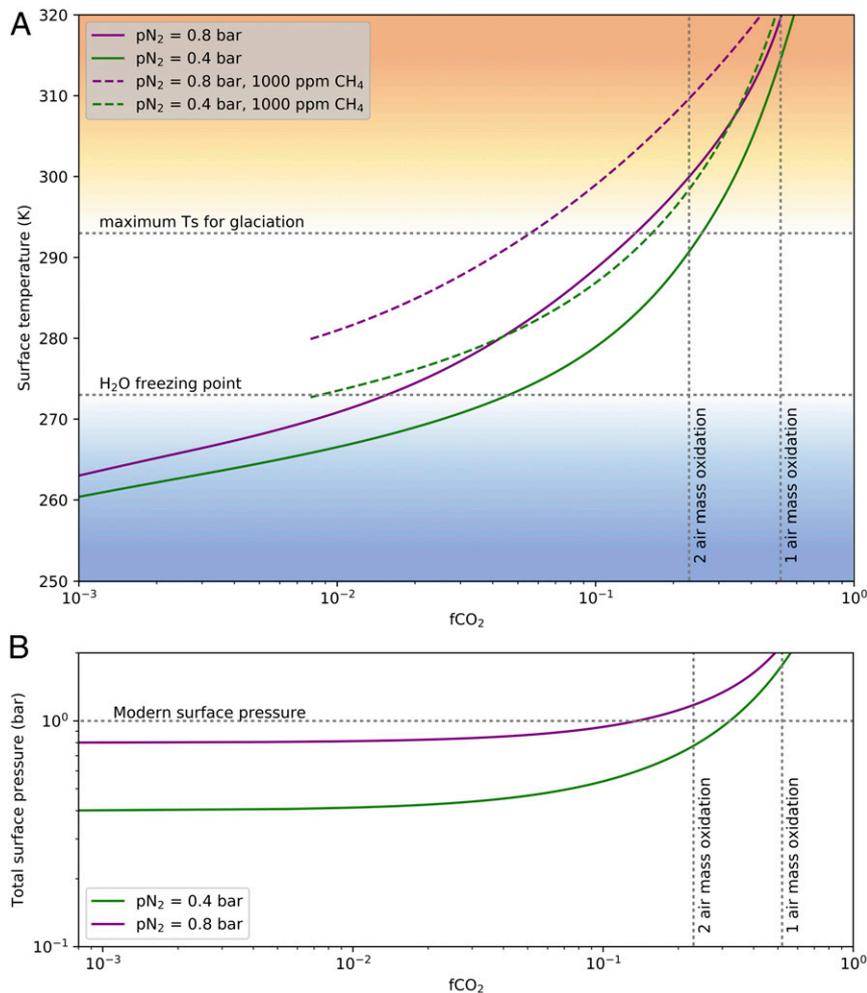
Fig. 2. Results from our 1D climate model. (*A*) Surface temperature as a function of fCO_2, for atmospheres with 0.8 bar (purple) and 0.4 bar (green) of N_2. Solid curves are for zero CH_4; dashed curves are for 1,000 ppm CH_4. Blue shaded region denotes subfreezing global mean surface temperatures; orange shaded region indicates a global mean surface temperature too high to facilitate glaciation (main text). The 1- and 2-air-mass oxidation lines represent the fCO_2 needed for oxidation to occur if the micrometeorite reacts with these amounts of air during entry. (*B*) Surface pressure versus fCO_2 for a N_2-CO_2 atmosphere with 0.8 bar N_2 (purple) and 0.4 bar N_2 (green), as calculated from Eq. **11** in the main text.
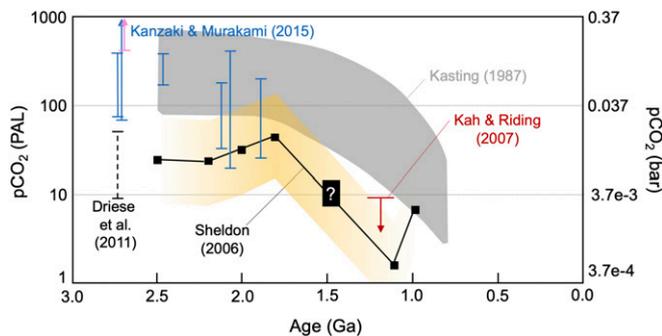
Fig. 3. pCO₂ estimates from paleosols compared to those from climate model calculations (gray shaded region) (31). Estimates from Sheldon (39) are shown by the black squares and solid black line (with error in yellow). The dashed vertical bar is the paleosol estimate at 2.7 Ga from Driese et al. (38). The downward red arrow is the upper pCO₂ limit from cyanobacterial sheath calcification at 1.2 Ga (Kah and Riding, ref. 42). The vertical bars in blue are the paleosol estimates from Kanzaki and Murakami (41). The upward pink arrow indicates the pCO₂ from our calculations at 2.7 Ga if pN₂ was 0.8 bar. Reproduced from ref. 43 with permission of Cambridge University Press through PLSclear.

pressure changes as $f\mathrm{CO}_2$ increases, given a fixed amount of N_2. The required relationship (derived in *SI Appendix*) is

$$p\mathrm{CO}_2' = p\mathrm{N}_2' \cdot \left(\frac{44}{28}\right) \cdot \left(\frac{f\mathrm{CO}_2}{1 - f\mathrm{CO}_2}\right). \qquad [10]$$

Here, $p\mathrm{CO}_2'$ and $p\mathrm{N}_2'$ are the "partial pressures" of CO_2 and N_2. The term partial pressure is used loosely here, as these are not true partial pressures. Rather, they represent the surface pressure that would be exerted by that amount of gas were it to exist by itself in Earth's atmosphere. Lighter gases cause heavier ones to diffuse away from Earth's surface, whereas heavier gases cause lighter ones to diffuse toward it; hence, the actual partial pressure of a gas can be different from its pressure in isolation, seemingly contrary to Dalton's law. The advantage of defining these terms in this way is that surface pressure, $\mathrm{P_S}$, is then given by

$$\mathrm{P_s} = p\mathrm{CO}_2' + p\mathrm{N}_2'. \qquad [11]$$

With these relationships in hand, we used the 1D climate model to calculate mean surface temperature as a function of $f\mathrm{CO}_2$. The results are shown in Fig. 2. The assumed solar luminosity was 0.81 times present, following Gough (24). Fig. 2A shows $\mathrm{T_S}$ versus $f\mathrm{CO}_2$ for different amounts of N_2 and CH_4. CH_4 is a greenhouse gas which is scarce enough to have little effect on surface pressure, but abundant enough (1,000 ppmv, or parts per million by volume, in these calculations) to raise $\mathrm{T_S}$ by 8 to 10 °C. This CH_4 concentration is an approximate upper limit derived from Archean ecosystem modeling (27). The micrometeorite oxidation constraints are on $f\mathrm{CO}_2$, not $p\mathrm{CO}_2$, and are displayed as vertical dotted lines.

The results show that if $p\mathrm{N}_2'$ were the same as today (~0.8 bar), the climate at 2.7 Ga would have been warm—300 K or more—even if $f\mathrm{CO}_2$ was equal to the minimum value, ~0.23, estimated from 2-air-mass oxidation. For $f\mathrm{CO}_2 = 0.52$, the minimum value for 1-air-mass oxidation, then $\mathrm{T_S} \geq 320$ K. Either of these mean surface temperatures would almost certainly have precluded polar glaciation.

The results are more promising for a potentially glacial climate if $p\mathrm{N}_2'$ was half its present value, or 0.4 bar. For $f\mathrm{CO}_2 = 0.23$, the predicted $\mathrm{T_S}$ for the no-methane case is ~290 K, which is within the glacial "window." The high-methane case is several degrees warmer and is outside our nominal window. However, given the uncertainties in estimating this window, along with the uncertainties in age dating of the micrometeorites and the glaciations, this result also seems plausible.

All of this suggests that if the micrometeorite oxidation story—with CO_2 facilitating Fe micrometeorite oxidation by up to 2 air masses during entry—is correct, levels of $p\mathrm{N}_2$ must have been appreciably lower than those today back at 2.7 Ga. While some theoreticians have argued just the opposite (34), more recent authors have provided empirical support for this hypothesis. For example, analysis of vesicles in 2.7-Ga basaltic lavas erupted at sea level imply $\mathrm{P_S} < 0.5$ bar (35), and measured $\mathrm{N}_2/^{36}\mathrm{Ar}$ ratios in fluid inclusions trapped in 3- to 3.5-Ga hydrothermal quartz suggest $\mathrm{P_S} < 1.1$ bar to possibly as low as 0.5 bar (36, 37). All 3 of these estimates are consistent with the low $p\mathrm{N}_2$ and $\mathrm{P_S}$ values derived here.

Constraints on $p\mathrm{CO}_2$ from Paleosols. Archean CO_2 levels have also been estimated from paleosols. Driese et al. (38) published an estimate of 10 to 50 PAL (times the Present Atmospheric Level) CO_2 at ~2.7 Ga, based on an analytical technique developed by Sheldon (39). A total of 1 PAL CO_2 corresponds to 370 ppmv, or 3.7×10^{-4} bar, in their model, so their estimate is ~0.004 to 0.02 bar. By comparison, our minimum estimates of $p\mathrm{CO}_2$ are ~0.16 bar for the 0.4-bar $p\mathrm{N}_2$ case and ~0.25 bar for the 0.8-bar $p\mathrm{N}_2$ case (these are true CO_2 partial pressures—hence, no prime on $p\mathrm{CO}_2$—obtained by multiplying $f\mathrm{CO}_2 = 0.23$ by the corresponding surface pressure in *SI Appendix*, Fig. S1B). Our $p\mathrm{CO}_2$ estimates are clearly much higher than Sheldon's (39) estimates. But Sheldon's method of analysis can be criticized on several different grounds (40). Most importantly, it implicitly assumes that every CO_2 molecule that enters the soil will react with a silicate mineral, which is probably not the case. Hence, his method should provide only a lower limit on atmospheric $p\mathrm{CO}_2$. A more recent analysis of the same paleosols by Kanzaki and Murakami (41) yields $p\mathrm{CO}_2$ values ranging from 0.03 bar to almost 0.4 bar (Fig. 3). The upper end of these estimates overlaps nicely with the CO_2 partial pressures derived here. So, ~0.2 bar might be considered a "best guess" of atmospheric $p\mathrm{CO}_2$ at the time when the Tomkins et al. (5) micrometeorites fell to Earth. At the very least, the $p\mathrm{CO}_2$ estimates from micrometeorite oxidation provide support for the higher Kanzaki and Murakami (41) $p\mathrm{CO}_2$ estimates from paleosols compared to the older estimates from Driese et al. (38) and Sheldon (39).

Conclusions

To truly solve this problem, experimental data on iron oxidation by CO_2, O, and O_2 in conditions like those a micrometeorite would experience during entry are needed. Nonetheless, existing data support the idea that the oxidation of Archean iron micrometeorites, melted during atmospheric entry, depends primarily on the amount of CO_2 available in the atmosphere. Assuming 2-air-mass oxidation and that CO_2 itself is the primary oxidant, we find that at least ~23% CO_2 would be needed to oxidize the Tomkins et al. (5) micrometeorites at 2.7 Ga. This CO_2 concentration can be reconciled with values derived from paleosols, provided that one accepts the higher estimates of Kanzaki and Murakami (41). It is most easily reconciled with climate models if levels of $p\mathrm{N}_2$ were lower than they are today, as this would facilitate a global mean surface temperature low enough for glaciation to occur. A surface pressure of about 0.6 bar, with less than 25% CO_2, would have allowed the Tomkins et al. (5) micrometeorites to be oxidized without conflicting with the evidence for glaciation at 2.7 Ga. There is thus no need to invoke unusually high atmospheric O_2 concentrations to explain the micrometeorite oxidation. Instead, these oxidized micrometeorites imply a Neoarchean atmosphere that was rich in CO_2 and somewhat poorer in N_2 than today's atmosphere.

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