Mineralogical constraints on Precambrian p_{CO_2}

Rosing and others[1] recently proposed a new model for the early Earth's atmospheric composition. They suggest, on the basis of mineral assemblages in sedimentary rocks, that atmospheric CO_2 and CH_4 concentrations have been consistently overestimated. This proposal is intriguing, given that high concentrations of these gases are traditionally considered to be the solution to the 'faint young Sun paradox' of why the Earth did not freeze over in our Sun's youth when solar luminosity was greatly decreased. Rosing and others[1] instead invoke a decreased planetary albedo during the Earth's early history. New insights into this problem, which has long captivated those interested in the Earth's early climate and biological history, are welcome. However, we believe that the arguments presented by Rosing and others[1] for roughly modern values of the partial pressure of CO_2 (p_{CO_2}) are not robust.

A fundamental assumption in the model of Rosing and others[1] is that the coexistence of the mineral phases siderite ($FeCO_3$) and magnetite (Fe_3O_4) in banded iron formations (BIFs) represents an assemblage that is nearly in thermodynamic equilibrium with the atmosphere, placing stringent constraints on the partial pressures of both CO_2 and H_2. The mineralogy of some BIFs is dominated by $FeCO_3$ (ref. 2), whereas others have mineralogies dominated by ferric oxide phases[3]. However, in well-studied BIFs with mixed Fe_3O_4–$FeCO_3$ phases (such as the Kuruman, Hamersley and Old Wanderer iron formations), carbon and iron isotope work[4,5] indicates that these minerals did not precipitate in isotopic equilibrium with the ocean. Therefore, diagenetic conditions controlled mineral formation; there is evidence for an initial rain of ferric oxides and secondary formation of reduced and mixed-valence iron minerals during early or later-stage diagenesis[4,5]. This is important given that dissimilatory iron-reducing bacteria generate Fe_3O_4 even at very high aqueous carbon dioxide concentrations and headspace values of $[\sum CO_2] \approx 50\,mM$ (ref. 6) and $p_{CO_2} \approx 0.2\,atm$ (ref. 7). Mixed Fe_3O_4–$FeCO_3$ assemblages develop as a result of an imbalance between rates of non-reductive ferric oxide dissolution, Fe^{2+} transport, and rates of Fe^{3+}–Fe^{2+} conversion[6–8]. Therefore, p_{CO_2} values very much above the modern value do not preclude the formation of magnetite.

In addition, the authors assume that both the atmospheric partial pressure and aqueous concentration of H_2 will be controlled by hydrogenotrophic methanogenesis. However, the preservation of ferric oxides, together with a paucity of organic carbon in most BIFs, strongly suggests that H_2 pressures or concentrations would instead be buffered most often by dissimilatory iron-reducing bacteria in BIF diagenetic environments. This would decrease the aqueous concentration of H_2 significantly[9], changing the relevant stability boundary to Fe_2O_3–$FeCO_3$. For instance, a threshold $[H_2]$ of about 0.1 nM would yield p_{CO_2} estimates between about 30–100 PAL (present atmospheric level) at 25 °C–35 °C (Fig. 1a of ref. 1). We view this as a non-trivial difference given the attendant implications for climatologically plausible CH_4/CO_2 ratios and atmospheric CH_4 concentrations[10].

Finally, even if we were to assume a simple thermodynamic control regulated by p_{H_2} (via methanogenesis) and p_{CO_2}, it is unlikely that the coexistence of Fe_3O_4 and $FeCO_3$ in BIFs provides any direct evidence regarding the chemistry of a surface ocean that is nearly in equilibrium with the overlying atmosphere. There is overwhelming petrographic evidence that the Fe_3O_4 observed in many BIFs is metamorphic or late-stage alteration product[11–13]. Indeed, the coexistence of Fe_2O_3–Fe_3O_4–$FeCO_3$ assemblages and significant mineralogical variability on small spatial scales in many BIFs suggest either the formation and preservation of mineral phases out of thermodynamic equilibrium with the ambient ocean–atmosphere system or secondary/metamorphic alteration. Although we do not suggest that a single depositional model applies for all BIF occurrences throughout the Earth's history, we do contend that many of the basic processes operating during their formation (microbial Fe oxidation/reduction, organic-matter remineralization in sediments, and metamorphism) are pervasive if not ubiquitous and should be considered in any attempt to relate BIF mineralogy to atmospheric composition.

Rosing *et al.*[1] rightly point out that some previous work (see references in ref. 1) based on mineral stability in palaeosol profiles has also suggested low p_{CO_2} values. However, this work contrasts with experimental studies[14], indicating that mineral stability as a function of p_{CO_2} during the formation of ancient soil profiles is not fully understood. Nonetheless, the numerical model proposed by Rosing *et al.*[1] has a number of important implications. For example, by implicitly linking the Earth's planetary albedo to the oxidation state of the atmosphere, the model may provide a new mechanism for explaining the inception of widespread glaciation following changes in Proterozoic atmospheric oxygen content. Such considerations are novel and will be fruitful to examine, and it is likely that any explanation for the clement early Earth will involve a complex interplay of forcings and feedbacks. However, we conclude that early Precambrian atmospheric p_{CO_2} levels remain poorly constrained and that increased levels of atmospheric gases (CO_2, CH_4, C_2H_2) remain a compelling solution to the 'faint young Sun paradox'.

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Low p_{CO_2} in the pore water, not in the Archean air

The solar luminosity during the Archean (3.8 to 2.5 billion years ago) was 20–25% lower than at present, and was probably compensated, at least in part, by a stronger greenhouse effect[1–3]. Rosing *et al.*[4] estimate the Archean partial pressure of carbon dioxide to have been about $p_{CO_2} \approx 10^{-3}$ bar, on the basis of the simultaneous occurrence of magnetite (Fe_3O_4) and siderite ($FeCO_3$) in banded iron formations (BIFs, a type of chemical sediment). Here, we question a central assumption by Rosing *et al.*[4] that the mineralogy of BIFs reflects near-thermodynamic equilibrium with the atmosphere–ocean system; just as the presence of authigenic pyrite in modern sediments does not imply that the modern atmosphere is anoxic, the mineralogy of BIFs cannot be used to argue for a low-p_{CO_2} Archean atmosphere. Carbon dioxide is therefore still a viable greenhouse gas candidate with which to explain the warm Archean climate.

The original iron precipitate in the BIFs was probably ferrihydrite, $Fe_2O_3 \cdot xH_2O$. The ferrihydrite was precipitated out of equilibrium with the atmosphere by oxidation of upwelled ferrous iron, either by O_2 produced by cyanobacteria within the water column or by phototrophic, anoxygenic, iron-oxidizing bacteria. Once in the sediment, ferrihydrite was subsequently converted to a stable iron oxide, either magnetite or haematite, or to the reduced mineral siderite. The constraint on p_{H_2}–p_{CO_2} derives from applying the following equilibrium reaction between magnetite and siderite: $Fe_3O_4 + H_2 + 3CO_2 \leftrightarrow 3FeCO_3 + H_2O$. As discussed below, p_{H_2} is a measure of the redox potential of the system, but organic matter (CH_2O) was the reducing agent in this reaction.

In the model of Rosing *et al.*[4], p_{H_2} was controlled by methanogens. Anaerobic ecosystems of this nature have been studied by ref. 5. The downward flux of H_2 through the atmosphere–ocean interface is limited by its piston velocity to $(1–6) \times 10^{11}$ molecules $cm^{-2} s^{-1}$ (Table 2 in ref. 5). The average deposition rate of Fe_3O_4 in BIFs is estimated to be 0.1–1 mm yr^{-1}, or $(40–400) \times 10^{11}$ molecules $cm^{-2} s^{-1}$, assuming that each microband represents one year of deposition[6]. Suggestions that the deposition rate was much slower than this[7,8] are probably biased by hiatuses in the geologic record. Reducing this iron to siderite would require an equal flux of H_2, which is 7–400 times the downward H_2 flux into the ocean estimated above. Some H_2 could have been produced within the sediment via fermentation, but this requires that organic matter be available. Formation of siderite without a reducing agent—that is, by disproportionation ($Fe_3O_4 + CO_2 \rightarrow Fe_2O_3 + FeCO_3$)—would require an effective p_{H_2} of 3×10^{-6} (the value at the magnetite–haematite boundary), which is ten times smaller than the value that Rosing *et al.*[4] propose and is probably impossible to achieve.

Probably the reducing agent was not H_2 but organic matter produced by photosynthesis in the water column. A fraction of the primary production of organic matter was exported from the photic zone to the sediment, where microbial iron respiration could produce siderite[9–12]: $2Fe_3O_4 + CH_2O + 5CO_2 \rightarrow 6FeCO_3 + H_2O$. Light carbon isotope ratios

are found in siderite, but not in associated Ca/Mg carbonates[11–13], indicating that a portion of the carbon in siderite was indeed derived from a pool of isotopically light organic matter. In BIFs, magnetite was initially in disequilibrium with the overlying CO_2-rich atmosphere and was converted to siderite. However, the above reaction was only allowed to proceed as long as a reductant (organic matter) was available. The rain of organic carbon into the sediment was not sufficient to keep pace with that of Fe^{3+}-bearing oxide, and its exhaustion led to a mineral assemblage (coexisting magnetite and siderite) that did not reflect equilibrium conditions with the atmosphere–ocean system. The transition from siderite to iron oxides in BIFs from the Campbellrand–Kuruman complex could have been caused by the decreased supply of organic material in offshore regions[10].

To summarize, microbial cycling and diagenesis of organic matter and ferric iron controlled the effective p_{H_2} and p_{CO_2} in the sediment. The mineralogy of BIFs reflects these conditions, with no simple relationship to atmospheric CO_2. Thus, p_{CO_2} in the atmosphere may have been high enough (about 0.1 bar) to explain the warm Archean climate, without the need for additional warming mechanisms.

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Faint young Sun paradox remains

ARISING FROM M. T. Rosing, D. K. Bird, N. H. Sleep & C. J. Bjerrum, *Nature* **464,** 744–747 (2010)

The Sun was fainter when the Earth was young, but the climate was generally at least as warm as today; this is known as the 'faint young Sun paradox'. Rosing *et al.*[1] claim that the paradox can be resolved by making the early Earth's clouds and surface less reflective. We show that, even with the strongest plausible assumptions, reducing cloud and surface albedos falls short by a factor of two of resolving the paradox. A temperate Archean climate cannot be reconciled with the low level of CO_2 suggested by Rosing *et al.*[1]; a stronger greenhouse effect is needed.

During the Archean eon, the Earth received 76% to 83% of the energy from the Sun that it does today. If the Earth's greenhouse effect and albedo were the same as now, the Earth would have been in continual deep freeze until one billion years ago, with glaciers reaching the Equator. However, Archean glacial sediments are rare and geological evidence indicates that the Archean was typically warmer than today (we are in a glacial period now). With the amount of energy reaching the Earth given by $F = \frac{1}{4}S_0(1 - \alpha) = 239\,\mathrm{W\,m}^{-2}$ (using the present-day solar constant $S_0 = 1{,}368$ and albedo $\alpha = 0.3$), the radiative deficit in the Archean would have been $(1 - 0.79)F \approx 50\,\mathrm{W\,m}^{-2}$. Resolution of the 'faint young Sun paradox' requires a positive radiative forcing—from reducing the albedo or increasing the greenhouse effect—of more than $50\,\mathrm{W\,m}^{-2}$.

Clouds have two competing radiative effects: they reflect sunlight but they also add to the greenhouse effect if they are colder than the surface. Reflection dominates in low clouds, and the greenhouse effect dominates in high clouds. Therefore the absolute upper bound on warming by decreasing cloud reflectivity would be found by removing low clouds entirely. This gives a forcing of $25\,\mathrm{W\,m}^{-2}$, half of what is needed to resolve the 'faint young Sun paradox' (our cloud model is described in the Methods). Any reduction to high clouds would cause a cooling.

Rosing *et al.*[1] justify less-reflective clouds with the incorrect statements that most cloud condensation nuclei (CCN) are from biogenic dimethyl sulphide (DMS), and that DMS is solely produced by eukaryotes. DMS is also produced microbially[2]. Products of DMS contribute only 3% of Northern Hemisphere CCN and 10% of Southern Hemisphere CCN today[3]. Other biological[4] and non-biological sources, especially sea salt, provide CCN. If CCN production were to depend only on eukaryotic DMS emissions[1], we would expect to see significant cooling when eukaryotes evolved, but no such cooling is evident.

Nevertheless, we can assume no biological CCN supply and quantify the resulting forcing. Over the modern ocean the effective radius r_e of cloud drops rarely exceeds $15\,\mu\mathrm{m}$ (ref. 5) even in remote and unproductive regions (the r_e of $17\,\mu\mathrm{m}$ to $30\,\mu\mathrm{m}$ used by Rosing *et al.*[1] is too high). For an upper bound, we increase low cloud droplet size by 50% from our standard case, from $11\,\mu\mathrm{m}$ to $16.5\,\mu\mathrm{m}$. With no change in cloud thickness, the forcing is $7\,\mathrm{W\,m}^{-2}$. Clouds with larger drops may rain out faster. Parameterizations of enhanced rain-out vary from proportional to $(r_{e,0}/r_e)^1$ to proportional to $(r_{e,0}/r_e)^{5.37}$ (refs 6 and 7); the corresponding extra forcing would be $4–15\,\mathrm{W\,m}^{-2}$ (remote sensing

data for marine stratus suggest that the low end of this range is more appropriate[8]). The sum is $11\,\mathrm{W\,m}^{-2}$ to $22\,\mathrm{W\,m}^{-2}$, with the low end being most likely.

The authoritative estimate of the global energy budget[9] gives global mean and ocean albedos of 0.125 and 0.090 respectively. The largest realistic surface darkening is from the present mean to an all-ocean world, which gives a radiative forcing of $5\,\mathrm{W\,m}^{-2}$.

Increasing the CO_2 mixing ratio to 1,000 parts per million by volume (p.p.m.v.; the upper bound according to Rosing *et al.*[1]) gives a forcing of $6\,\mathrm{W\,m}^{-2}$. Rosing *et al.*[1] rely on 1,000 p.p.m.v. CH_4 for much of their warming, ignoring relevant atmospheric chemistry. As the partial pressure of CH_4 (p_{CH_4}) approaches that of CO_2 (p_{CO_2}), hydrocarbon haze forms in the stratosphere, the cooling effect of which outweighs the greenhouse effect of CO_2 and CH_4 (refs 10 and 11). Numerical models[12] predict haze production when $p_{CH_4}/p_{CO_2} = 0.1$ and haze production has been seen in laboratory experiments[13] where $p_{CH_4}/p_{CO_2} = 0.3$. With 1,000 p.p.m.v. CO_2, the maximum CH_4 concentration that can give warming is 300 p.p.m.v., which would contribute $7\,\mathrm{W\,m}^{-2}$ of additional forcing.

Changes to clouds could in theory considerably reduce the amount of greenhouse gases required, because gaseous absorption depends on the logarithm of gas abundance. But even with the highly unlikely assumption of no biological CCN supply, cloud changes can provide only one-quarter to one-half of the required radiative forcing. Any changes to clouds would require strong justification, which Rosing *et al.*[1] do not provide. A strong greenhouse effect is required in the Archean. The alternative is an extremely cold climate with continual mid- to low-latitude glaciation, for which there is no evidence.

METHODS

We calculate the radiative forcing (change in net flux at the tropopause) on a single global annual mean atmospheric profile, with three layers of clouds that overlap randomly[14]. The radiative fluxes on eight sub-columns corresponding to each cloud combination are calculated with the RRTM model[15]. For our standard case, cloud water paths are $[W_{high}, W_{mid}, W_{low}] = [20, 25, 40]\,\mathrm{g\,m}^{-2}$, fractions are $[f_{high}, f_{mid}, f_{low}] = [0.25, 0.25, 0.40]$ and the surface albedo is 0.125. Standard low- and mid-level clouds are liquid with $r_e = 11\,\mu\mathrm{m}$ and high clouds are ice with generalized effective size of $D_{ge} = 75\,\mu\mathrm{m}$. For radiative forcings described in the text, the low cloud water path is varied but all other parameters are unchanged.

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Rosing, Bird, Sleep & Bjerrum reply

Reinhard and Planavsky[1] and Dauphas and Kasting[2] question whether the formation of Fe^{2+}/Fe^{3+}-rich sediments and the preservation of magnetite in banded iron formations (BIFs) constrains atmospheric p_{CO_2}. Goldblatt and Zahnle[3] question whether reduced albedo in combination with a slightly increased greenhouse effect could compensate for the reduced luminosity of the faint young Sun. Reinhard and Planavsky[1] and Dauphas and Kasting[2] suggest that BIF mineralogy is solely controlled by diagenetic and metamorphic processes decoupled from ocean–atmosphere chemistry. We focus on the persistent preservation of magnetite in all Archean BIFs, and of magnetite and siderite in many BIFs[4], and estimate the partial pressure of CO_2 during the Archean (p_{CO_2}) using the least number of assumptions concerning unconstrained parameters. Our conclusions[5] are not undermined by any geochemical data that support high p_{CO_2}.

Diagenesis is an open-system process driven by consumption of Gibbs energy through lowering the extent of chemical disequilibrium between the sedimentary phases and surrounding environments, whether biologically mediated or not. Magnetite forms in the presence of dissimilatory iron-reducing bacteria when the pore water is supersaturated in magnetite according to standard thermodynamic principles[6,7] and its formation is not microbially controlled[8,9]. Isotopic data for the Kuruman BIF requires extensive transport of Fe and C between the sediment and the supernatant water by infiltration of sea water and molecular diffusion through interconnected pore space[10]. In modern sapropels ocean CO_2 concentration penetrates to a depth of about 15 cm in the sediment, from which point it increases more than tenfold downwards[11]. We conclude that the CO_2 concentration in the sediment pore water would have been greater than or equal to the supernatant water. The suggestion by Dauphas and Kasting[2] and Reinhard and Planavsky[1] that diagenetic siderite formation was a closed-system process is not supported by the studies they quote, which call upon extensive communication with the supernatant water[10,12].

Formation of BIFs depends not only on mechanisms for precipitation of solid Fe compounds but also on the transport efficiency of dissolved iron. The saturation constraints on p_{CO_2} and p_{H_2} imposed by siderite and magnetite not only pertain to the BIF, but also to the water body supplying dissolved Fe to sedimentary basins, and thus couple directly to the atmosphere. We note that for our estimated range of p_{CO_2} the solubility of Fe in sea water is 1–3 µM, which is well within the range necessary for BIF formation[13], while at the increased p_{CO_2} favoured by Reinhard and Planavsky[1] and Dauphas and Kasting[2] the maximum Fe concentrations are between two and four orders of magnitude lower and within the range of modern ocean water concentrations that preclude BIF formation. (We note that the 1–3 µM range covers the bare Fe^{2+} ion corrected for activity in sea water at siderite saturation with equilibrium constant for the reaction $Fe^{2+} + CO_{2,g} + H_2O = FeCO_3 + 2H^+$ calculated in SUPCRT (see ref. 5) and total Fe calculated using EQ3-6 (ref. 14) for siderite saturation in modern sea water, corrected to anoxic conditions and assuming pH = 8.25 buffered by basalt in accordance with ref. 15. See ref. 5 for thermodynamic conventions and data sources.)

Reinhard and Planavsky[1] suggest that siderite and haematite can coexist at 0.1 nM H_2 and p_{CO_2} in the range 30–100 PAL at 25 °C–35 °C, in accord with minimum $H_{2(aq)}$ metabolic constraints of dissimilatory iron-reducing bacteria and phase relations in Fig. 1 of ref. 5. This logic precludes the presence of magnetite in BIFs. Neglecting observed magnetite parageneses in BIFs and selecting a value of $H_{2(aq)}$ far below the stability field of magnetite does not provide a viable geochemical constraint. Dissimilatory iron-reducing bacteria metabolism may have occurred in BIF sediments during the Archean, but we are not aware of geochemical evidence suggesting that the metabolic activity of dissimilatory iron-reducing bacteria in BIF sediments controlled the composition of the Earth's fluid envelopes. On the contrary, the presence of magnetite and the mere formation of BIFs indicate that ambient ocean water had a molarity of H_2 considerably greater than 10^{-10} M, conditions under which haematite is the only stable Fe oxide and Fe would be practically insoluble in ocean water, precluding aqueous iron transport sufficient to sustain BIF sedimentation.

It has never been controversial that there is a large uncertainty about Archean cloud forcing. Our hypothesis reiterates this specifically for an Earth with no continents, no continental dust, no land-plant-generated secondary organic aerosols and only a few other biogenic aerosols from a low-productivity ocean (0.1 to 0.25 times the present value[16,17]). The cloud physics are affected by an aerosol optical

depth that probably showed much lower global values than today and should be evaluated using proper general circulation models. Goldblatt and Zahnle[3] miss the point when focusing on dimethyl sulphide from a sulphur-poor Archean ocean and sea-salt aerosols, which seem to contribute only a few per cent of the free troposphere cloud condensation nuclei[18].

The net cloud radiative effect of our model was $(-18\,W\,m^{-2})$ relative to $-20\,W\,m^{-2}$ from satellite estimates. Our calculations used[19] an effective radius of cloud droplets of $r_e = 17\,\mu m$ (green solid line in Fig. 2d of ref. 5) (we note that although the legend mentions $20\,\mu m$, this was erroneous, and should have stated $17\,\mu m$; also, we showed the line for $30\,\mu m$ to show no added effect at larger droplet sizes). Goldblatt and Zahnle's later published calculations[20] use more realistic clouds, which are not very different from ours. Our model values versus theirs[19] were: r_e increase to $16.5\,\mu m$, $7\,W\,m^{-2}$ versus $7\,W\,m^{-2}$; enhanced rain-out, $15\,W\,m^{-2}$ versus 4–$15\,W\,m^{-2}$; aqua planet, $6\,W\,m^{-2}$ versus $5\,W\,m^{-2}$; $1{,}000$ p.p.m.v. CO_2, $5\,W\,m^{-2}$ versus $6\,W\,m^{-2}$. Our methane contribution was a bit high ($9\,W\,m^{-2}$; ref. 17's was $7\,W\,m^{-2}$) and should probably be adjusted down to $0.3 \times p_{CO_2}$. Rain-out of low clouds (we made no change to high clouds) was calibrated to general circulation model results[21], and an estimated forcing three times the r_e forcing[18]. Our calculations showed[5], as subsequently stated by Goldblatt and Zahnle[20], that "…precipitation feedback is of first order importance and must be treated carefully in any model addressing the climatic effect of changed particle size."

We maintain that formation and preservation of magnetite-rich BIF could not take place under a high-p_{CO_2} atmosphere. Surface albedo and cloud changes would have significantly decreased the Earth's albedo and reduced the greenhouse gas concentrations needed for clement conditions on the Earth. We do not claim to have provided a final and unique solution to the 'faint young Sun paradox', but rather demonstrate that the presence of liquid water on the young Earth can be explained within uncertainty by constrainable parameters and is thus not so paradoxical.

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