Mineralogical constraints on Precambrian p_{CO_2}

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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 $[\sum CO_2] \approx 50\,\mathrm{mM}$ (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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