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Fe(II) carbonate precipitation kinetics: Implications for palaeoenvironmental reconstruction.

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Because Fe(II) carbonate (including siderite) precipitation is subject to the availability of both dissolved iron (Fe^{2+}) and CO_2, the presence or absence of siderite in the sedimentary records (e.g., palaeosols, iron formations) has been used as a direct constraint on CO_2 levels of Earth's early atmosphere[1]. In addition, recent analyses of ancient fluvio-lacustrine rocks on Mars indicate the presence of authigenic Fe-minerals, but the absence of siderite has been used to infer very low atmospheric CO_2[2]. These studies all assume that siderite precipitates at equilibrium saturation[3] ($\log \Omega = 0$), which results in the thermodynamically calculated CO_2 levels that are insufficient on their own to mitigate the effects of a faint young sun[1,2]. Hence, other greenhouse gases have been invoked to reconcile climate evolution with geochemical records.

Here, we investigate the pseudo-homogeneous nucleation and growth of Fe(II)-carbonate from anoxic solutions as a function of pH, $[Fe^{2+}]$, and pCO_2. We observe that in freshwater solutions at relatively dilute $[Fe^{2+}]$, Fe(II)-carbonate nucleation requires significant supersaturation with respect to siderite; up to $\log \Omega \approx 2.6$. These results are consistent with solubility control through amorphous Fe carbonate (AFC). Additionally, Fe(II)-carbonate nucleation requires even higher levels of supersaturation in seawater solutions, which we hypothesise results from Mg^{2+} inhibition at high Mg/Fe ratios.

These results leave open the possibility that atmospheric CO_2 levels on early Earth and Mars were much higher than previously estimated, based on our current understanding of mineral stability in sedimentary rocks. Moreover, These new constraints, combined with the updated reaction kinetics of greenalite (Fe-silicate)[4], prompt a reconsideration on the anoxygenic mineralisation pathways of Fe^{2+} that might have contributed to the deposition of many Precambrian iron formations, and, more broadly, influenced chemical sedimentation in the ferruginous Precambrian oceans.

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