## FeCO<sub>3</sub> nucleation kinetics and the Late Archaean C cycle

CLANCY ZHIJIAN JIANG<sup>1</sup>, BIRGER RASMUSSEN<sup>2</sup>, JANET MUHLING<sup>2</sup>, NICHOLAS J. TOSCA<sup>1</sup>

<sup>1</sup>Dept. of Earth Sciences, University of Oxford, Oxford, UK.
<sup>2</sup>School of Earth Sciences, University of Western Australia, Crawley, Australia.

Recent debates on palaeo-atmospheric  $CO_2$  levels, limits on seawater  $Fe^{2+}$ , and the role of microbial processes in Precambrian iron formations have all centred on siderite[1–3]. However the lack of kinetic constraint on FeCO<sub>3</sub> precipitation have prevented the use of siderite as a reliable palaeoenvironmental proxy.

We experimentally investigated the homogeneous and heterogenous precipitation of siderite from solutions that simulate Archaean seawater. For both kinetic regimes, our results show a strong exponential decrease in FeCO<sub>3</sub> nucleation rate consistent with theoretical predictions. This dependence allows us to delineate critical thresholds in FeCO<sub>3</sub> saturation that correspond to homogeneous and heterogeneous nucleation and evaluate the conditions of siderite nucleation in sedimentary systems.

We apply these thresholds to greenalite-siderite coated grains in shallow-water chert-intraclastic carbonate facies of the ca. 2.45 Ga Griguatown formation (South Africa). This early diagenetic fabric provides clear evidence that siderite nucleated on amorphous silica and greenalite surfaces (heterogeneously) during early diagenesis, but direct nucleation from solution (homogeneously) far less commonly. By assuming a [SiO<sub>2(aq)</sub>] poised at amorphous silica saturation, and a  $[Fe^{2+}]$  controlled by greenalite solubility, we solved for the inorganic C system over a limited pH range. Our results place direct constraints on the Late Archaean marine C system, and provide new estimates for DIC and  $pCO_2$ .

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