

## FeCO<sub>3</sub> precipitation and the chemistry of Precambrian oceans

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

We experimentally investigated 3 kinetic regimes of FeCO<sub>3</sub> precipitation: 1) homogeneous nucleation<sup>4</sup>, 2) seeded crystal growth, and 3) heterogeneous nucleation on amorphous silica. For all three kinetic regimes, we delineated saturation-dependent precipitation rates that are consistent with theoretical predictions. Solution analyses and solid characterisations revealed that the mineralisation of FeCO<sub>3</sub> involves precursor amorphous Fe carbonate and the metastable phase chukanovite. These new results permit us to specify and differentiate the chemical conditions where each of the three mechanisms was likely to operate. That, in turn, makes specific palaeo-environmental predictions for depositional and diagenetic facies associated with siderite that are testable against the geologic record.

For example, greenalite-siderite coated grains in the shallow-water chert-intraclastic carbonate facies of the ca. 2.45 Ga Griquatown formation (South Africa) indicate depositional conditions in which heterogeneous nucleation on silica and greenalite surfaces was preferred than homogenous nucleation from the water column. By assuming a [SiO<sub>2(aq)</sub>] poised at amorphous silica saturation, and a [Fe<sup>2+</sup>] controlled by greenalite solubility, we are able to place direct constraints on the shallow water pH-pCO<sub>2</sub> recorded by these Late Archaean sediments.

**1** Rye, R. *et al. Nature* 378, 603–605 (1995)

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**3** Johnson, C. M. *et al. Geochim. Cosmochim. Acta* 72, 151–169 (2008)

**4** Jiang, C. Z. and Tosca, N. J.. *Earth Planet. Sci. Lett.* 506, 231–242 (2019)