

Fe(II)-carbonate precipitation kinetics and Precambrian seawater chemistry

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In comparison with modern oceans, Precambrian seawater featured elevated concentrations of iron, dissolved inorganic carbon, and silica, but much lower dissolved oxygen and sulphate^{1,2}. The kinetic and thermodynamic controls on the chemistry of Fe(II), DIC and SiO₂(aq)-rich seawater are not well known, but nonsulphidic seawater chemistry is likely to have been governed by the competing nucleation and growth kinetics of marine precipitates such as siderite, greenalite, and other Fe(II)-bearing phases²⁻⁴.

A recent experimental study on the reaction kinetics of greenalite (Fe(II)-silicate) showed that greenalite precipitation is kinetically important across a specific pH range and Fe(II), and SiO₂(aq) concentrations⁴. Although this study investigated Fe(II)-silicate interactions in isolation from Fe(II)-carbonate, the results prompted a reconsideration of the competition for Fe(II) between siderite (Fe(II)-carbonate) and greenalite, and the controls on Fe(II) concentrations in ferruginous seawater. Indeed, surprisingly little is known about the reaction kinetics of siderite precipitation, or the corresponding effects on other carbonates (e.g., calcite; aragonite) in the presence of Fe(II) other than an apparent kinetic inhibition on CaCO₃ nucleation⁵.

The focus of this project is on constraining the nucleation kinetics of siderite as a function of pH, CO₂(aq) and Fe(II) concentrations. Siderite has been synthesised under strictly anoxic conditions, at solution composition close to the ancient marine condition. We observe the rapid generation of siderite across a finite range of pH and DIC. The chemistry, trace element content and isotopic composition are being compared to early diagenetic siderite and greenalite occurrences to better understand the conditions of crystallisation. Our results provide key information on the reactions controlling Precambrian seawater chemistry and new insights on multiple biogeochemical cycles.

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