

## **Biotic and Abiotic Controls on Iron Reduction and Biomineralization over Broad Geochemical Conditions**

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Microbial reduction of ferric oxide minerals is a ubiquitous biogeochemical process that occurs over a broad range of environmental conditions and is driven by a diverse array of microorganisms. Here we performed the first assessment of secondary iron mineral formation over a broad range of environmental conditions by *Orenia metallireducens*, a novel member of Firmicutes. A total of 17 distinct geochemical conditions were tested over a range of pH (6.5-8.5), temperature (22-50 °C), salinity (2-20% NaCl), anion availability (phosphate and sulfate), electron shuttle availability (anthraquinone-2,6-disulfonate), and ferric iron oxide mineralogy [2-line ferrihydrite [Fe(OH)<sub>3</sub>], lepidocrocite (γ-FeOOH), goethite (α-FeOOH), hematite (α-Fe<sub>2</sub>O<sub>3</sub>), and magnetite (Fe<sub>3</sub>O<sub>4</sub>)]. The observed rates and extents of iron reduction by *O. metallireducens* differed significantly, with  $k_{int}$  between 0.186 and 1.702 mmol•L<sup>-1</sup>•day<sup>-1</sup> and Fe(II) production between 6.3 and 83.7 % of the initial Fe(III). X-ray absorption and scattering techniques revealed the formation of siderite (FeCO<sub>3</sub>), vivianite [Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>] and green rust as the most common secondary minerals; hematite and ferrihydrite were also observed as products under specific conditions. In contrast to previous studies where iron reduction rates and/or extents are suggested as the control for biomineral composition, we propose a new conceptual model based on the extent to which Fe(II) adsorbed to the remaining Fe(III) minerals. Specifically, the bifurcation in mineralization pathways observed in our work is explained by enhanced Fe(II) adsorption leading to mixed-valent and ferric secondary minerals, whereas inhibited Fe(II) adsorption promotes the formation of ferrous secondary minerals.