

Influence of pore-scale hydrodynamic regimes and reactant gradients on manganese biomineralization in porous media

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The mobility of manganese (Mn) in soils and sediments, both as an essential micronutrient or environmental contaminant, is largely controlled by microbially catalyzed redox reactions. Among these, the enzymatic oxidation of aqueous Mn(II) produces reactive solid-phase Mn(III, IV) oxide nanoparticles that can participate in subsequent sorption and redox reactions. While this process of Mn biomineralization has been studied extensively in well-mixed batch systems, the reaction extent in poorly mixed systems, like porous media in the subsurface, is not well understood. The Mn biomineralization reaction depends on the balance between two competing timescales – transport and reaction rate. The transport timescale (relative between advection and diffusion) determines the spatial collocation (i.e., mixing) of bacteria, aqueous Mn(II), and oxygen reactant gradients. The reaction rate timescale is determined from the kinetic limitations of oxidation in a well-mixed system.

Our research explores how pore-scale hydrodynamic regimes control reactant transport, mixing, and reaction extent in porous media. We specifically assess the spatial distribution, mass produced as a function of time, and morphology of bacteria-Mn oxide aggregates in a simulated pore network. Microfluidic “soil-on-a-chip” reactors modeled after the structure of a real soil were used to visualize the porous medium with brightfield and epifluorescence microscopy; in future experiments, oxygen optode sensors will also be integrated into these reactors to measure *in situ* dissolved oxygen gradients and correlate oxygen concentration with sites of aggregation and Mn oxidation. Time-lapse experiments in reactors inoculated with a representative Mn-oxidizing bacterium (*Pseudomonas putida* GB-1) were conducted at variable flow rates (low, medium, or high Darcy velocity) and reactant availability (nutrient-enriched growth medium or minimal salts solution with Mn(II)) to constrain the controls on mixing and resulting Mn biomineral formation in the pore space. Preliminary results show that large bacterial aggregates of variable morphologies coalesce in the reactor pore throats and attach to grain contacts. *P. putida* GB-1 subsequently produce Mn biominerals selectively at the aggregate edges exposed to pore fluid. Our findings will provide new insights into environmental controls on spatially heterogeneous biogeochemical redox reactions, which are highly relevant for major geochemical cycles.