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Experimental Study of the Effect of Fe on Si Adsorption by Bacillus Subtilis: Insights into Biological Precipitation of Silicate Minerals

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Although evidence from many natural systems suggests that bacteria enhance silicate mineral precipitation, the mechanisms by which bacteria do this have not been well constrained. Specifically, it is unclear what conditions are necessary for bacteria to nucleate silicates, and it is unclear whether bacteria cause precipitation in otherwise undersaturated solutions, or if the effect is simply an enhancement of the precipitation kinetics of oversaturated solutions. Most previous experiments aimed at unraveling this process have used highly oversaturated solutions in which both adsorption and precipitation reactions were occurring. In our approach, we take the first step in elucidating the mechanisms involved in bacterial precipitation of silicates by isolating and examining the adsorption behavior of Si by bacteria. This study examines and quantifies adsorption of Si onto the cell wall of *Bacillus subtilis* as a function of pH, and determines whether elements such as Fe and Al are required for Si removal by the cell walls to occur.

Batch reactor experiments were performed with *Bacillus subtilis* in undersaturated aqueous silica solutions in order to determine the extent of Si adsorption onto the bacterial cell wall. Experiments were performed under constant ionic strength conditions and conducted as a function of pH and as a function of bacterial concentration in solution. The extent of Si removal from solution was determined by sampling the aqueous phase after equilibration, and analyzing for dissolved Si using an ICP-AES technique using matrix-matched standards for calibration. Batch reactor experiments were also conducted in order to test the effects of Fe and Al oxides on Si uptake. Some experiments were conducted with Fe or Al oxides alone, and some were conducted with these oxides precipitated onto the cell walls prior to exposure to the aqueous Si.

The experimental results indicate that adsorption of aqueous Si onto *Bacillus subtilis* does occur, but that the thermodynamic stability of the surface Si-bacterial complex is extremely low. Si adsorption varies as a function of pH, with maximum adsorption occurring at low pH. Adsorption also increases with increasing concentration of bacteria in the system. Iron oxide coated bacterial surfaces caused 95 to 100% of the aqueous Si to be removed from solution. We use the experimental data to identify the important Si-bacterial (or Si-iron oxide) surface complexes, and to quantify their thermodynamic stabilities. These parameters enable quantitative models to be constructed that can be used to estimate Si removal in bacteria-bearing systems not directly studied in the laboratory. Our experimental results suggest that if Si adsorption is the first step in silicate biomineralization, then other cations such as Fe must be present on the cell wall surface in order for the bacteria to concentrate significant quantities of Si from solution. Therefore, the role of bacteria in silicate “biomineralization” may be a passive one. Bacterial cell walls may provide nucleation sites for iron oxides, but it is dominantly these oxides which promote Si removal from solution, and there is very little direct interaction between aqueous Si and the bacterial cell wall.