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Cell surface reactivity during silicification

S. Lalonde and K. Konhauser

Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta, Canada

Experimental studies of bacterial biomineralization processes have traditionally emphasized the role of the bacterial surface as an effective sorbent. Indeed, the bacterial surface has been implicated in nucleation and/or precipitation processes by the propensity with which it absorbs and complexes cationic aqueous species. In the past, geomicrobiological experiment design has relied on batch culture techniques optimizing biologically relevant factors such as pH, temperature, and nutrient availability with the singular goal of generating sufficient quantities of suitable (i.e., live) biomass on which biomineralization studies may then focus. The reality of the situation, however, is much more complicated for natural bacterial consortia because the various species are continuously in competition for a limited suite of nutrients, and they experience a life of continual biological stresses imposed on them by the external environment.

Recent advances in our understanding of the acid-base properties of the bacterial surface have warranted increased study of potential microbiological responses to these stressors. We have previously shown that bacteria may vary the concentration and pK_a distribution of organic ligands on their surface in response to changes in nutrient availability or concentration. These studies have implied that the conditions of growth may lead to alterations in cell wall composition, and ultimately act as a determinant of microbial surface reactivity. In this study, we evaluate whether or not the growth of a bacterium in a mineralizing environment has a direct impact on the bulk organic chemistry of its own surface. We assess, by potentiometric titration, the concentrations and pKa distributions of proton-exchangeable bacterial surface ligands as a function of silica concentration, using the sheathless cyanobacterium *Anabaena* sp. PCC 7120 grown in a variety of media compositions. Liquid media was in some cases adjusted to supersaturation immediately prior to inoculation such that silica precipitated directly onto cell walls, and all cells were vigorously washed to remove any bound silica prior

to titration. We find that regardless of liquid media employed, total surface ligand concentrations decreased with increasing silica concentration. Furthermore, acidic ligands (pK_a <7) universally decreased with increasing silica concentration while basic ligands (pK_a >7) increased in concentration. These results indicate a biological, surficial chemical response to the silicification process that is manifest during growth in a mineralizing solution and is retained as an artifact in cell wall composition upon removal from mineralizing conditions.

These results indicate that the sorptive properties of the bacterial cell wall may be influenced by the temporary presence of geochemical stressors, and that future experimental studies aiming to elucidate bacterial biomineralization processes should consider the effects of the geochemical species of interest on the organism of study in addition to the vice-versa.