

## Calcium carbonate precipitation in the presence of phototrophic anaerobic bacteria *Rhodovulum* sp.

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Haloalcaliphilic *Rhodovulum* sp. A-20s isolated from soda lake in southern Siberia and halophilic neutrophilic *Rhodovulum* sp. S-1765 isolated from hypersaline water body in Crimea steppe represent large group of phototrophic bacteria likely to be involved in CaCO<sub>3</sub> formation in soda and saline lakes. These bacteria use organic substrates for non-oxygenic photosynthesis and thus may mediate CaCO<sub>3</sub> precipitation without CO<sub>2</sub> consumption in highly-saline, highly-alkaline, NaHCO<sub>3</sub>-rich solutions.

To characterise the interfacial structure of the cells and to determine the degree to which cell surface electric potential and proton/hydroxyl adsorption affected by cellular metabolism and control the carbonates precipitation, we performed electrophoretic measurements and acid-base titrations of active, NaN<sub>3</sub>-inactivated and dead species. Similar to previous results on cyanobacteria [1] there is a net increase in zeta-potential towards more positive values at pH = 10.4 for active cells which suggests the existence of CO<sub>3</sub><sup>2-</sup> - attracting mechanisms in alkaline solutions.

The second part of the studies is aimed at establishing the relationship between the growth rate of phototrophic bacteria and associated calcium carbonate precipitation. Experiments were conducted in closed vials with initial calcium concentrations from 1 to 20 mM and 5 mM [HCO<sub>3</sub><sup>-</sup>]. Cell biomass, pH, [Ca<sup>2+</sup>], and [Alk] were measured as a function of time during the experiments. Control experiments with cell-free media or autoclaved cells were always performed. Vaterite, aragonite and amorphous calcium carbonates were detected as precipitated products and the relationships between cell number and bacteria growth rates and CaCO<sub>3</sub> precipitation rates were established.

[1] Martinez *et al.* (2008) *J. Coll. Interf. Sci.* **323**, 317-325.

## Au adsorption to *Pseudomonas putida* bacteria – An XAFS study

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The objective of this study was to determine the mechanisms of Au adsorption onto gram-negative bacteria, and determine if differences exist between gram-negative and gram-positive cell wall binding mechanisms. We investigated the adsorption of Au by *Pseudomonas putida* from Au (III)-chloride solutions as part of a larger project conducted by our group to study the sorption behavior of Au to non-metabolizing bacteria.

Batch measurements of Au adsorption onto *P. putida* showed similar adsorption behavior as a function of pH to that exhibited by the gram-positive species *Bacillus subtilis*, with the greatest extent of adsorption occurring below pH 6, and with decreasing adsorption above pH 6. In order to determine the binding mechanism, we conducted X-ray absorption fine structure (XAFS) measurements of the biomass from experiments with two different bacterial concentrations (1.0 and 7.0 g/L, wet mass) each with fixed Au (III) concentrations of 5 ppm, and with ionic strength buffered to 0.1 M with NaClO<sub>4</sub>. For each bacterial concentration, four samples were prepared at pH values that spanned the pH range in which the extent of adsorption decreases from a maximum value to nearly zero. XAFS data show that a significant proportion of adsorbed Au (III) atoms were reduced to Au (I), but that no Au (0) or Au-Au nearest neighbors were observed. For the 1.0 g/L samples below pH 7, Au atoms were bound to a mixture of amine/carboxyl and sulfhydryl functional groups on the *P. putida* cell wall. Above pH 7 for these samples, sulfhydryl groups became the dominant binding site. For the samples with a higher bacterial concentration, almost all Au atoms were bound to sulfhydryl functional groups under all pH conditions studied, with coordination numbers and bond distances consistent with bidentate binding.

The results from this study suggest similar binding mechanisms between gram-positive and gram-negative cell walls, and the results form the foundation for models of Au-bacteria adsorption reactions in bacteria-bearing geologic systems.