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Experimental modelling of calcium carbonate precipitation during anoxygenic phototrophic bacteria Rhodovulum sp.activity

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Microbial carbonate formation occurring for most of Earth's history was largely controlled by mineral nucleation processes driven by microbial metabolism. 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 anaerobic bacteria (APB) likely to be involved in CaCO3 formation in soda and saline lakes. These bacteria use organic substrates for non-oxygenic photosynthesis and thus may mediate CaCO3 precipitation without CO2 consumption in highly-saline, highly-alkaline, NaHCO3-rich solutions.

Electrophoretic mobility measurements and surface adsorption of Ca on living, inactivated, and heat-killed haloalkalophilic Rhodovulum steppense, A-20s, and halophilic Rhodovulum sp., S-17-65, anoxygenic phototrophic bacteria (APB) cell surfaces were performed to determine the degree to which these bacteria metabolically control their surface potential equilibria. Zeta potential of both species was measured as a function of pH and ionic strength, calcium and bicarbonate concentrations. For both live APB, the zeta potential is close to zero at pH from 2.5 to 3 and it further decreases from -30 to -40 mV with pH increase from 3 to 5, whereas it remains constant and negative at $4 \leq pH \leq 8$. However, in alkaline solutions both bacteria strains cells show an increase of zeta potential with a maximum value of -10 to -20 mV at a pH of 9 to 10.5. Moreover, we show that the increase of zeta potential in alkaline solutions is reduced by the presence of NaHCO3 (up to 10 mM) and only slightly affected by the addition of equivalent amount of Ca. Nonetheless, for inactivated (exposure to NaN3, a metabolic inhibitor) and heat-killed bacteria cells, the zeta potential was found to be stable (-30 to -60 mV, depending upon the ionic strength) between pH 5 and 11. Adsorption of Ca ions on A-20s cells surface was more significant than that on S-17-65 cells and started at more acidic pHs, consistent with zeta-potential measurements in the presence of 0.001 to 0.01 mol/L CaCl2.

To characterise the link between the rate of bacterial growth (biomass production) and the rate of CaCO3 precipitation, batch kinetic experiments were performed. Kinetic experiments were carried out with initial concentration of calcium chloride and sodium bicarbonate ranging from 1 to 10 and 5 to 20 mM, respectively. All biotic experiments were performed with initial biomass concentration between 1.6 and 3.5 gwet L-1. Precipitation experiments were carried out over a range of initial saturation index with respect to calcite varying between 20 and 56 for A-20s, and between 15 and 40 for S-17-65. There is a clear correlation between carbonate precipitation rate and the saturation index for both bacterial species ($r^2 = 0.90$). The maximal precipitation rates are observed during period of maximal bacterial growth. The values of calcium carbonate precipitation rates strongly depend on the initial solution composition ([Ca2+], [HCO3-]) and the saturation index.