Phosphorus triggers $CaCO_3$ biomineralization by affecting *Synechoccocus* cells surfaces

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The extracellular polymeric substances (EPS) on the *Synechococcus* cell envelope are recognized key players in the nucleation of carbonates minerals in marine and freshwater environments. However, little is known about how environmental conditions (e.g., nutrient contents) control the molecular composition of *Synechococcus* cell envelope, and consequentely, biomineralization.

Here we show how a variation of the phophorus (P) concentration on the cyanobacterial growth media (45, 90 and 180 μM) can led to changes in the surface reactivity of marine and freshwater *Synechoccocus* cells and affect their ability to form carbonates.

An increase in the ratio of polysaccharides to proteins on the surface of cells exposed to higher P concentrations was detected by Fourier transform infrared spectroscopy (FTIR), tip-enhancement Raman spectroscopy (TERS) and X-ray photoelectron spectroscopy (XPS). TERS revealed that glycosidic ring and carboxylate molecules from polyanionic polysaccharides were more prominent in these cells. Moreover, the concentration of P-contained functional groups on the cell envelope varied significantely, as reveled by potentiometric titrations. Biomineralization experiments with cells showed that the morphology, size and the precipitation rate of carbonate minerals were strictly dependent on the surface properties of the cells. Faster calcium adsorption rates were obtained with the cells cultured in higher P concentrations and on their surface we found small minerals clusters (<2μm) representing branches of nanometer irregular filaments linked with the cell surface.

Our experimental results provide a direct evidence that phosphorus plays a significant role in the control of the EPS dynamics and synthesis by Synechococcus and, hence, phosphorus concentration should be taken into account when interpreting the role of microbes in mineral formation.