# The onset of calcium carbonate nucleation: A computational study

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The formation of calcium carbonate ($CaCO_3$) from supersaturated solutions has been studied for more than a century as it represents a process of considerable importance, especially in the fields of $CO_2$ sequestration and biomineralization. It is now understood that the first step in the mineralisation of $CaCO_3$ is the homogeneous nucleation of amorphous particles [1], but the details of the onset of nucleation of the particles are still unclear. Our aim is to use a range of complementary computational methods to investigate the firts stages of the calcium carbonate nucleation process.

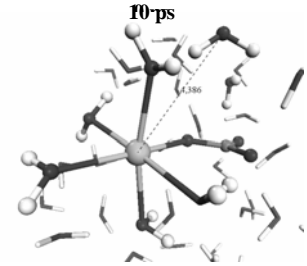


**Figure 1:** Representative snapshots from the CPMD.

Extensive Car-Parrinello molecular dynamics (CPMD) simulations of $Ca^{2+}/CO_3^{2-}$ and $Ca^{2+}/HCO_3^-$ immersed in water show that the formation of the monomer of $CaCO_3$ occurs through an associative mechanism (see Figure 1) and that the dominant building block of calcium (bi-)carbonate in aqueous solution is $Ca[\eta^1\text{-}(H)CO_3](H_2O)_5$, i.e. the preferred hydration number is five and the (bi-)carbonate is coordinated to the calcium in a monodentate mode [2]. This result agrees with static *ab initio* calculations, where a hybrid approach using a combination of explicit solvent molecules and a polarizable continuum model to treat the bulk of the aqueous environment has been applied to compute the solvation free energies of calcium bicarbonate species [2]. Based on this information, we consider the condensation reaction of calcium (bi-)carbonate particles in aqueous solution.

[1] D. Pontoni *et al*. (2003) *J. Phys. Chem. B* **107**, 5123-5125. [2] D. Di Tommaso and N. H. de Leeuw (submitted) *J. Phys. Chem B*.

# Formation of membrane vesicles on cyanobacteria surfaces

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## Membrane Vesicles of Gram-negative Bacteria

Recent research has shown that membrane vesicles (MVs) are a common particular feature of the matrix of gram-negative bacterial biofilms [1]. The ubiquitous distribution of MVs is evident from observations of biofilms from a variety of natural and artificial environments. Experiments with planktonic biofilms demonstrate that MVs bind antibiotics and increase the sorption capacity of biofilms [1]. Because MVs mimic the bacterial cell surface, they should have strong, adhesive properties, possibly with specific adhesions for attachment. It has also been shown that environmental conditions may play a role in the expression of outer membrane of *Helicobacter pyroli* [2]. However, in spite of the tremendous effort to understand the contribution of MV to biofilms properties, our knowledge of the factors responsible for their formations is still limited.

## Impact of Calcium on the MVs Formations

We have performed experiments with three different strains of cyanobacteria, i.e., *Synechococcus*-type: *Synechoccocus elongates*, *Synechococcus* Green, containing phycocyanin, and *Synechococcus* Red, containing phycoerythrin. The strains were washed two times and then exposed to CaCl2 solutions with different concentrations (0.6 mM, 1.5 mM, and 4mM) for periods ranging from 2 hours to 2 days. One set of samples were kept in the dark and the other was incubated under day-/night-light conditions. The surface properties of cyanobacteria strains were examined with vertical scanning interferometry (VSI [3]), an imaging technique that resolves sample surface features as small as 20 nm. Our results show that calcium ions impact the formation of MVs by *Synechoccocus* Green cells under day/night-light conditions at calcium concentrations between 0.6 and 4 mM. In the case of *Synechoccocus* elongates, MVs formed at [Ca] > 1.5 mM. By comparison, cell surfaces of *Synechococcus* Red were not strongly impacted by dissolved calcium. Our results suggest that MV formation is strain-specific and triggered by environmental calcium concentrations.

[1] Schooling & Beveridge (2006) *J. Bacteriol.* **188**, 5945-5957. [2] Keenan & Allardyce (2000) *J. Gastroenterol. Hepatol.* **12**, 1267-1273. [3] Davis & Luttge (2005) *Am. J. Sci.* **305**, 727–751.