

## Exploring the generality of stable pre-nucleation species for alkaline earth carbonates

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Carbonate minerals are amongst the most widespread of all biominerals, as well as being significant for regulation of carbon dioxide, both naturally and as part of engineered geosequestration. Consequently there are many reasons to understand the nucleation and crystal growth mechanisms of such minerals. In the case of calcium carbonate, there has been particular interest following the observation of *stable* pre-nucleation clusters (PNCs) [1], leading to a reassessment of the conventional understanding of cluster formation via classical nucleation theory. Based on a combination of both experimental observations and computer simulation results, a new picture is emerging as to the pathway for formation of calcium carbonate. Initially, ion pairs and larger associations form that consist of Dynamically Ordered, Liquid-Like Oxyanion Polymers (DOLLOPs) [2]. As the ion activities increase the binodal region is entered and liquid-liquid separation occurs leading to the nucleation of spherical droplets of a dense liquid phase [3]. Subsequently, dehydration progressively occurs leading to further phase transitions that result in the formation of amorphous calcium carbonate.

While the above view of how CaCO<sub>3</sub> forms has begun to emerge, and PNCs are believed to exist more widely [4], it is unclear as to whether formation of dynamic supramolecular polymer species, similar to DOLLOP, is unique to calcium carbonate or a more general phenomenon. As a first step towards probing the wider applicability of this model we have considered the speciation of other alkaline earth metal carbonates, namely those containing magnesium, strontium and barium. Here molecular dynamics simulations are employed, based on force fields that have been accurately calibrated against experimental data, with a particular focus on correct reproduction of the thermodynamics, as per previous work for CaCO<sub>3</sub> [5,6]. Results will be presented regarding the validation of the computational models, plus the application to simulation of the solution speciation. Comparison of the results with those previously obtained for calcium carbonate will be made. In the case of Mg<sup>2+</sup> the issue of the slow water exchange dynamics will also be discussed.

[1] Gebauer *et al* (2008) *Science*, **322**, 1819-1822. [2] Demichelis *et al* (2011) *Nat. Commun.* **2**, 590. [3] Wallace *et al* (2013) *Science*, **341**, 885-889. [4] Gebauer *et al* (2014) *Chem. Soc. Rev.*, DOI: 10.1039/C3CS60451A. [5] Raiteri, Gale, Quigley and Rodger (2010) *J. Phys. Chem. C*, **114**, 5997-6010. [6] Raiteri and Gale (2010) *J. Am. Chem. Soc.*, **132**, 17623-17634.