

# ***In silico* studies of calcium carbonate phases emerging from aqueous solution**

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A great deal of debate has surrounded the nucleation and growth of calcium carbonate from solution over the past decade, with a number of pathways to crystallisation proposed. Thermodynamically stable pre-nucleation clusters have been suggested to precede the formation of any solid precipitate [1]; later work suggested these could be dynamically (dis)ordered liquid aggregates of hydrated ions [2]. Liquid-liquid phase separation has also been identified to take place in supersaturated aqueous solution [3], and presents a possible precursor dense liquid phase to crystal growth. Furthermore, the possibility for classical growth of crystalline phases from constituent ions and ion pairs has not been ruled out [4].

Here we present *in silico* investigations of calcium carbonate species which emerge in aqueous solution. Classical simulations were performed using an accurate force field [2] to model the chemical interactions between species. We present data which show that ion binding in the pre-nucleation regime and at modest supersaturation can be explained in terms of ion-pairs:  $\text{CaCO}_3^0$  and  $\text{CaHCO}_3^+$ . At high supersaturation continuous dense liquids emerge in equilibrium with a lean solution of mainly ion-pairs and free ions. For concentrations between these two limits, dynamical aggregates of highly hydrated ions are seen, which might be thermodynamically distinct from the dense liquid phase, but evidence for this is not conclusive. The dense liquids are highly hydrated and TEM simulations confirm that the transmission properties are consistent with dense liquid phases which are observed in experiment.

Free energy calculations have been performed to study possible transformations of dense liquid phases. A combination of adiabatic biased molecular dynamics with umbrella sampling allows us to understand relative stabilities between dense liquid and solid amorphous phases as a function of concentration and system size.

Combined, these results allow us to conjecture phase transitions involved in the early stages of mineral growth from solution.

[1] D. Gebauer *et al.* (2008), *Science* **322**, 1819. [2] R. Demichelis *et al.* (2011), *Nat. Comms.* **2**, 590. [3] M. A. Bewernitz *et al.* (2012), *Fard. Discuss.* **159**, 291. [4] Q. Hu *et al.* (2012), *Fard. Discuss.* **159**, 509.