

Computational insight on the existence of CaCO_3 prenucleation clusters

P. RAITERI^{1*}, A. SCHUITEMAKER¹, R. DEMICHELIS¹ AND J.D. GALE¹

¹Curtin Institute for Computation and Department of Chemistry, Curtin University, Perth, Western Australia, Australia (correspondence: p.raiteri@curtin.edu.au)

The formation of carbonate minerals is responsible for some of the most spectacular natural sceneries on Earth. Coral reefs, the Dolomites and the Nullabor in Australia (limestone) are just a few examples of incredible landscapes which are primarily composed of calcium and magnesium carbonate minerals. For many decades scientists have tried to gain a molecular understanding of the processes underpinning the formation of these minerals at various conditions and in different environments. These conditions range from “simple” homogeneous nucleation to supercritical conditions (geosequestration) and biological systems (biomineralisation).

In recent years a new picture of the early stages of the nucleation process, which contrasts with the classical nucleation theory, has started to emerge. In the case of calcium carbonate, the existence of stable pre-nucleation clusters [1] and of a liquid-liquid separation [2] have been proposed to explain experimental results obtained with Analytical Ultra-Centrifugation and TEM. However, direct imaging of these phases is below the resolution of current experimental techniques. In parallel to these studies, computer simulations [2,3] have been used to provide supporting evidence for the existence and stability of pre-nucleation clusters.

In this work we present new results obtained by employing a recently improved model to describe calcium carbonate in water [4]. In particular, we focus on the early stages of molecular aggregation, from ion-pairs to small clusters and we attempt to unravel the thermodynamics of formation of such clusters.

[1] Gebauer *et al.* (2008) *Science* **322**, 1819.

[2] Wallace *et al.*, (2013) *Science* **341**, 885.

[3] Demichelis *et al.* (2011) *Nature Commun.* **2**, 590.

[4] Raiteri *et al.* (2015) *J. Chem. Phys. C* **119**, 24447.