

## **The influence of amino acids on amorphous calcium carbonate structure and formation**

COLIN L. FREEMAN<sup>1\*</sup>, AARON R. FINNEY<sup>1</sup>,  
RICCARDO INNOCENTI MALINI<sup>1</sup>, P. MARK  
RODGER<sup>2</sup> AND JOHN H. HARDING<sup>1</sup>

<sup>1</sup>Department of Materials Science and  
Engineering, University of Sheffield, Mappin  
Street, Sheffield, S1 3JD, UK  
(\*correspondence: c.l.freeman@shef.ac.uk)

<sup>2</sup>Centre for Scientific Computing & Department  
of Chemistry, University of Warwick,  
Coventry, CV4 7AL, UK  
(p.m.rodger@warwick.ac.uk)

Crystalline calcium carbonate ( $\text{CaCO}_3$ ) precipitation from solution is often pre-empted by the formation of amorphous calcium carbonate (ACC). The formation, chemistry and potential conversion of ACC into crystalline polymorphs is still poorly understood. Experiments have suggested that crystallisation occurs on the ACC surface [1] but this interface remains undefined. In both the natural world and synthetic, molecular additives are used to modify the nucleation and growth process. The binding of these molecules has been extensively studied through both experiment and simulation on the crystalline surfaces of calcium carbonate but we know little about their interactions with ACC.

Proteins, peptides and similar analogues have been suggested to (de)stabilise ACC but their binding motifs and mechanisms of chemical control are not understood. We present a computational study on ACC and its precursors interacting with a variety of amino acid molecules. Our simulations explore how the different R-groups of the amino acids interact via varying mechanisms with the ACC. Additionally, we demonstrate changes in behaviour depending on the precursor or hydration level of the ACC. Using these results we discuss which amino acids may be more important and effective in stabilising ACC, influence the dehydration of ACC and that may be significant in stimulating its conversion to a crystalline phase.

[1] Nielsen, M.H.; Aloni, S.; De Yoreo, J.J. *Science* 2014, 345 (6201), 1158-1162