

The Effects of Additives on the Formation of Biomimetic Calcium Carbonate

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Calcium carbonate is the most abundant biomineral, being produced by organisms for use as shells, skeletal supports and even optical lenses [1]. Biomineral formation usually occurs at temperatures and pressures close to atmospheric conditions, with crystallisation regulated by control of ionic reactants and/or additives, hence biomineralisation synthesis routes are of interest in the development of ‘green chemistry’.

Biomineralised calcite has been shown to exhibit small shifts in lattice parameter compared to the calcite crystal structure, attributed to the incorporation of organic matrix proteins within the crystal structure [2], these shifts are also observed in biomimetic calcite when amino acid additives are used (as analogies for the matrix protein side chains) [3].

In this work we explore the influence of crystallisation method (slow diffusion based vs fast mixing), amino acid additive, pH and concentration on the formation and crystal structure of calcium carbonate and in particular the role of additive during the early stages of formation. Laboratory based spectroscopy techniques were used to monitor the rate of precipitation, determine polymorph formation as well as measuring the stress, crystallinity and water content of samples. High resolution synchrotron powder diffraction measurements allowed determination of structural properties whilst SAXS allowed determination of the role of additive in controlling particle size at different stages of crystallisation. In addition novel techniques including solid state NMR and nano-XRD mapping are applied to these systems in an attempt to uncover the mechanism of additive inclusion in the crystal structure.

[1] J. Xiao and S. Yang, *Nanoscale*, 4, 54 (2012)

[2] B. Pokroy et al., *Journal of Structural Biology* 155, 96–103 (2006)

[3] Borukhin et al., *Adv. Funct. Mater.*, 22(20), 4216-4224 (2012)