The effect of Sr^{2+} on the structure, stability and crystallisation of amorphous $CaCO_3$

J.D. RODRIGUEZ-BLANCO[1], D.J. TOBLER[1],
K. DIDERIKSEN[1], LIANE G. BENNING[2], K.K. SAND[3]
AND S.L.S. STIPP[1]

[1]Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark. (jblanco@nano.ku.dk)
[2]Earth and Environment. University of Leeds.LS2 9JT, UK
[3]Lawrence Berkeley National Laboratories, Berkeley, USA.

Strontium is the fifth most abundant cation in seawater and a very common element in carbonate rocks, frequently used as a proxy for palaeoenvironmental and diagenetic conditions of carbonate sediments [1]. The incorporation of Sr^{2+} in marine carbonates depends on temperature, salinity and seawater Sr/Ca ratio. However, the initial steps in the crystallisation of carbonate usually requires the formation of an amorphous $CaCO_3$ (ACC) precursor [2] but the effect of Sr^{2+} on the local structure, kinetics and crystallization pathways of ACC are still poorly understood.

In this work, we have investigated the role of Sr^{2+} on the ACC local atomic coordination, stability, and its crystallisation using a combination of synchrotron based pair distribution function (PDF) analysis, time resolved UV-Vis spectrophotometry, conventional powder X-ray diffraction, high resolution microscopy, thermogravimetric and wet chemical analysis. Our results showed that a fast-forming, poorly ordered, nanoparticulate precursor ($\phi \approx 200$ nm) formed from solution and contained variable Sr concentrations (Sr/Ca between 0 and 0.3). The stability and Sr/Ca ratio in the precipitated ACC increased with increasing Sr/Ca ratios in solution, but no pure amorphous Sr carbonate could be synthezised because of the fast crystallisation of strontianite ($SrCO_3$). PDF analyses confirmed the short-range ordering of the so formed ACC (<15 Å) and showed that the atomic distances of some of the dominent peaks bonds in the PDF spectra (2.5, 4 and 6.5 Å, corresponding to Sr-O and Sr-Ca/Sr bonds) increased proportionally with the Sr content in ACC. The so formed Sr-bearing ACC transformed to either microcrystalline vaterite or calcite via different pathways.

[1] Flügel, E (2010) Microfacies of carbonate rocks: analysis, interpretation and application. Springer. 984 pp. [2] Rodriguez-Blanco, JD *et al* (2011) *Nanoscale*, **3**, 265.