

In-situ X-ray Absorption Spectroscopy to study the precipitation of CaCO₃

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Calcium carbonate has great scientific relevance in biomineralization and geosciences, forming enormous scales of biological (reefs and ocean sediments) and geological origin, which bind a huge amount of CO₂ and affect the chemistry of ocean water[1] and, with it, Earth's atmosphere and climate. CaCO₃ provides a model system for nucleation and crystallization analysis of mineral for classical[2] and nonclassical crystallization[3] theory and has been studied for more than a century. Despite its relevance, the precipitation mechanism of calcium carbonate is still under intense research and specified complex crystal structures challenge the classical view on nucleation considering the formation of metastable ion clusters[4]. It is known that CaCO₃ exists in at least six phases, of which three are anhydrous (calcite, aragonite and vaterite) and three are hydrated forms (monohydrate, hexahydrate and amorphous) and amorphous calcium carbonate (ACC) has been identified as a prenucleation-stage precursor in calcium carbonate mineralization[3]. There is growing evidence that different species of ACC, that is the amorphous phase shows, a specific short-range order, exists as a transient phase during calcium carbonate precipitation and this corresponds to the long-range order of the particular crystalline polymorph[3]. The life time of the transient species is temperature dependent. Micro X-ray Absorption Spectroscopy (μ -XAS) can probe the local structure around the Ca atom in both amorphous and crystalline materials, giving information on the type, number and distance of neighbouring atoms and can give important clues about the transient species that are formed during the reaction.

Using Ca-K edge μ -XAS we investigate CaCO₃ precipitation using a segmented-flow microfluidic cell[5] to study the reaction between CaCl₂ and Na₂CO₃ to form carbonate, under specific conditions. Microfluidic systems have significant advantages in terms of speed, throughput, yield, selectivity and control when compared with macroscale devices. All the mentioned characteristics are facilitated by system downscaling and related improvements in mass and thermal transfer. In addition, microfluidic systems have been shown to be crucial and highly effective when variables such as reagent concentration, temperature, and pH, have to be controlled with precision. For example, with a segmented flow microfluidic reactor picolitre-sized droplets (of variable chemical composition) at frequencies in excess of 100 Hz can be generated[5]. This allows thousands of individual reactions to be processed in very short times and the consequent transposition of the reaction time onto spatial coordinates enables the in-situ observation of the millisecond reaction. Nevertheless, manipulation and processing of samples with instantaneous volumes ranging from a few picolitres to hundreds of nanolitres provides a significant challenge for detection and identification and in many ways defines the principal limitations of current microfluidic systems. This will be overcome, in extension the already performed studies, combining a microfluidic device with synchrotron radiation. In particular at the PHOENIX beamline (SLS, Switzerland) analysis at low energy edges in diluted and micro-samples can be carried out thanks to its high photon flux, very fast detector and microfocussing beam.

[1] R.E. Zeebe et al. Science 2008, 321, 51 [2] J.J. De Yoreo et al. Rev. Mineral. Geochem. 2003, 54, 57 [3] Y. Politti et al. Adv. Funct. Mat. 2006, 16, 1289. [4] J. Rigger et al. Faraday Discuss. 2007, 136, 265. [5] A. J. DeMello Nature 2006, 442, 394.

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