

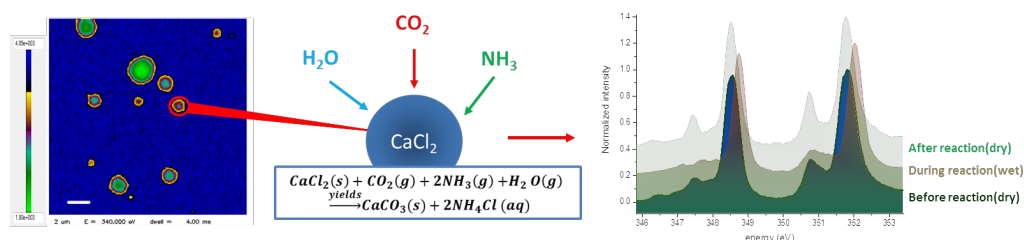
In-situ studies on the early stages of calcium carbonate nucleation from supersaturated micro droplets.

J. Xto^{1,2}, K. Henzler¹, C. Borca¹, J. A. van Bokhoven^{2,1*}, T. Huthwelker^{1*}

¹Paul Scherrer Institute, ²ETH Zurich

Calcium carbonate is one of the largest reservoirs of the earth's CO₂ which forms in nature through the reaction of calcium ions and carbon dioxide. Although biominerals have mastered the art of utilizing calcium carbonate to form functional materials ranging from eye lenses to protective shells through the careful control of the early stages of nucleation, a full understanding of these processes still pose a challenge to scientists despite years of research. Recent studies have shown that the nucleation process of calcium carbonate follows a multistep process involving formation of amorphous calcium carbonate (ACC) as intermediate[1][2]. However, stability of ACC and their subsequent transformation to more stable crystalline phases is still an open question. In particular the pathway of ACC dehydration, which is the critical route of transformation from ACC to crystalline materials is not well understood.

By utilizing a well-designed *in-situ* cell for probing microdroplets, the early stages of nucleation of calcium carbonate and subsequent dehydration of ACC were studied through the diffusion controlled reaction of calcium chloride with gas phase water, carbon dioxide and ammonia[3]. The structural changes occurring during the reaction were monitored *in-situ* using synchrotron based STXM (scanning transmission X-ray microscopy) and infrared spectroscopy. The results obtained confirmed the formation of ACC[4] as an intermediate step and further structural changes were observed in the formed ACC during dehydration under different relative humidity conditions.



[1] M. H. Nielsen, S. Aloni, and J. J. De Yoreo, "In situ TEM imaging of CaCO₃ nucleation reveals coexistence of direct and indirect pathways," *science*, vol. 218, no. April, pp. 213–218, 2014.

[2] D. Gebauer and H. Cölfen, "Prenucleation Clusters and Non-classical Nucleation," *Nano Today*, vol. 6, no. 564–584, pp. 2–59, 2011.

[3] J. Ihli, P. Bots, A. Kulak, L. G. Benning, and F. C. Meldrum, "Elucidating Mechanisms of Diffusion-Based Calcium Carbonate Synthesis Leads to Controlled Mesocrystal Formation," *Adv. Funct. Mater.*, pp. 1–9, 2012.

[4] J. Ihli *et al.*, "Dehydration and crystallization of amorphous calcium carbonate in solution and in air.," *Nat. Commun.*, vol. 5, p. 3169, 2014.