

## Utilizing *In Situ* Techniques to Examine Structural Impacts of the Initial Ion Ratios on Calcium Phosphate Precursors

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During mineral precipitation, a series of precursors can form, prior to appearance of the thermodynamically stable crystalline end member. Precursors include amorphous or nano sized particles, which can be difficult to characterize due to their metastable state. This has created a need for novel experiment designs. Evaluating the short-range order in these precursors and how chemistry impacts order, requires time-resolved structural investigations, of materials still in suspension. We have adapted a mixed-flow reactor (MFR) for *in situ* synchrotron pair distribution function analysis of the calcium phosphate precursors that precede hydroxylapatite formation.

Initial calcium and phosphate solutions flow into the MFR and combine, precipitating a calcium phosphate phase in suspension, which flows out of the MFR and into an x-ray scattering cell for analysis. The pumping speed of the solutions into the MFR and the volume of the reactor constrain the residence time between initial mixing and data collection. This set-up results in a highly controlled chemical environment. With careful data processing, we can extract structural information for our *in situ* sample as a function of chemistry. We collected structural data for samples with systematically varied Ca/P ratios, but similar levels of supersaturation.

Results show structural differences in the short range order of amorphous calcium phosphate (ACP). At an initial Ca/P ratio of 0.2, ACP has a predominantly monodentate bonding geometry between calcium and phosphorus. At an initial Ca/P ratio of 5.0, the bonding geometry is predominantly bidentate.

The MFR set-up allows us to readily and systematically examine structural impacts of system conditions on solution based crystallization. This technique is easily adaptable for different crystal systems and can be applied to a multitude of questions that surround crystal growth mechanisms.