Understanding structural changes in Amorphous Calcium Phosphates as function of composition

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Amorphous Calcium Phosphates (ACP) have long been thought as possible precursors to bone apatite. But only recently was ACP definitively found in mineralizing tissues by X-ray scattering experiments. Subsequently, electron microscopy studies of mammalian cells in tissues and culture have found ACP occurring as dense intracellular calcium phosphate containing granules. Analysis of these granules demonstrated a surprisingly low Ca/P ratio of 0.75, whereas synthetic ACP is known to have a Ca/P ratio of 1.5; leading to questions about nature of the ACP phase found in cells. Though, less recognized, studies of ACP have reported a range of Ca/P ratios (1.0-1.5) in synthetic ACP. These observations suggest unprotonated phosphates can be replaced by acidic phosphates particularly at lower pH found under physiological conditions. Early structural characterization by laboratory based X-ray scattering and synchrotron EXAFS reported that no structural variations occurred as a function of Ca/P ratio, leading to claims that the measurable structure is invariant even with large compositional changes. Here we present our work using X-ray total scattering/Pair Distribution Function analysis (PDF) of a large number of ACP samples with continuous range of Ca/P ratios between 1.0 and 1.5 obtained at APS beamline 11-ID-B. From these data we can confidently describe the changes in ACP structure as a function of Ca/P ratio.