Investigating the reaction pathway of crystalline orthocalciumphosphate formation via amorphous precursors in respect to different pH, Ca/P ratios and Mg presence

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The crystallization pathways of amorphous into crystalline orthocalciumphosphate phases is a widely discussed topic, with processes not yet entirely understood. Current research focuses on medical applications as well as natural sedimentary systems, for example bone-tissue-engineering, bio-mineralization and phosphogenesis, with inorganic precipitation experiments under controlled ambient conditions being the first step to improve our understanding of the fundamental formation processes. By mixing of stock solutions with CaCl$_2$/MgCl$_2$ and NaHPO$_4$ we created a supersaturated solution in respect to CaPO$_4$-phases and varied the pH by adding different amounts of NaOH. Continuous sampling was performed over the period of 24 hours, with sampling intervals after 1 min, 10 min, 60 min and 24 h. In order to record temporal changes in mineralogical and chemical composition, samples (solids and fluids) were investigated by XRD, FTIR, SEM and ICP-OES, respectively. Our experiments yield considerable differences concerning the time of amorphous calcium phosphate (ACP) transformation into hydroxyapatite (HAP), heavily depending on the pH, Ca/P ratio and Mg content of the stock solution. Main results show that a higher pH stabilizes the ACP over a period of the first 60 min, whereas at lower pH the transformation of ACP into the crystalline phase already starts at 10 min after mixing. Increasing the Ca/P ratio of the stock solution results in ACP being less stable and the transformation into HAP occurs earlier. In contrast, the presence of Mg seems to delay the formation of HAP via ACP. After 24 hours the experiments showed nano-crystalline HAP and most likely some other phases as octacalcium phosphate.