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Visualizing the role of pH on the transformation from amorphous calcium phosphate (ACP) to stable crystalline hydroxyapatite (HAP) by in-situ Raman spectroscopy

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The formation of stable crystalline hydroxyapatite ($Ca_5(PO_4)_3(OH)$) in various geological and biological systems usually occurs via one or more precursor phases, such as amorphous calcium phosphate (ACP, $Ca_3(PO_4)_2$ * nH_2O; n = 3-4.5). In aqueous solutions, this transformation process elapses within short time (seconds to minutes) and depends on the ambient physicochemical conditions, most likely on the saturation and availability of Ca and PO_4, temperature and pH, and how these parameters evolve with time.

In this study, we therefore performed a series of Ca phosphate precipitation experiments at room temperature over 24 hours, for which we investigated crystallization pathways as a function of different NaOH concentrations (between 0 and 1 M NaOH). These resulted in initial pH values of the reactive solutions of 9.0 and 11.3 to 11.9, respectively. Applying in-situ Raman spectroscopy, we were able to monitor the temporal transformation process of ACP to crystalline HAP. Its formation was indicated by clear Raman peak shifts, as well as a sharpening of the symmetric stretching band ($v1$) of PO_4. Distinct sampling of solids and liquids and subsequent analyses (XRD, ATR-FTIR, ICP-OES, SEM) furthermore revealed that brushite ($Ca(HPO_4)$ * 2 H_2O) and possibly octocalcium phosphate ($Ca_8(PO_4)_4$ $(HPO_4)_2$) were also involved in the transformation process. Whilst we found brushite as platy, 10-20 μm-sized, almost idiomorphic crystals, HAP occurred as nanocrystalline accumulations, almost indistinguishable from ACP in samples containing both phases. We think that the fundamental findings of this study might help to gain a better understanding of the depositional processes leading to the World's first phosphate giants around the Precambrian-Cambrian boundary.