

## **In-situ observation of the transformation of amorphous calcium phosphate to crystalline hydroxyapatite**

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Amorphous calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ ; ACP) is often a precursor phase of the mineral (hydroxy-) apatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) that can be formed in natural settings during both authigenic and biogenic mineral formation. Particularly, in the biomineralization process of fish tissue, ACP has shown to be an important transient phase.

In solution ACP rapidly transforms into the crystalline phase. The transformation rate highly depends on the physico-chemical conditions of the solution: Ca & P availability, pH and temperature. In natural settings Ca can be provided by different sources: from (1) seawater, (2) porewater, or (3) diagenetically-altered carbonates, whereas local supersaturation of P can be induced by microbial activity.

In this study, we performed phosphate precipitation experiments in order to monitor the transformation process of the ACP to crystalline hydroxyapatite (HAP) using in-situ Raman spectroscopy. During the experiments the temperature was kept constant at  $20.0 \pm 0.01$  °C and pH at  $9 \pm 0.1$ . 50 ml of 0.3 CaCl  $2\text{H}_2\text{O}$  was titrated at a rate of 5 ml/min to an equal volume of 0.2 M  $\text{Na}_2\text{HPO}_4$ . The pH was kept constant by titration of 1 M NaOH. During the experiment samples were taken from the solution and instantly filtered. The obtained solid samples were lyophilized and analyzed with XRD, ATR and SEM. The respective solution samples were analyzed using ion chromatography and ICP OES, coupling the spectroscopic data with detailed solution chemistry data.

We observed transformation of ACP to HAP to occur within 14 hours, illustrated in a clear peak shift in Raman spectra from  $950 \text{ cm}^{-1}$  to  $960 \text{ cm}^{-1}$ . The obtained results are discussed in the aspects of distribution of major elements during the formation of phosphates and/or the diagenetic alteration of carbonates to phosphates in geologic settings.

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