Crystallization of citrate-stabilized amorphous calcium phosphate

T. RONCAL-HERRERO[1*], K. CHATZIPANAGIS[1], M. BILTON[1], J. M. DELGADO-LÓPEZ[2], M. IAFISCO[3] AND R. KRÖGER[1]

[1]Department of Physics, University of York, YO10 5DD, York, UK *teresa.roncal-herrero@york.ac.uk
[2]LEC, IACT (CSIC-UGR), 18100 Armilla, Granada, Spain
[3]CNR-Istituto di Scienza e Tecnologia dei Materiali Ceramici, Faenza, Italy

Bone contains 70% of mineral phase as hydroxyapatite[1] (HAp, $Ca_5(PO_4)_3OH$) and 5.5wt% of the organic matter is citrate strongly binding to HAp[2] which can form by crystallization of amorphous calcium phosphate (ACP). Such amorphous-crystalline transition is found to occur in many biological systems. Our work aims to elucidate the time dependent crystallization of citrate-functionalized ACP in the presence of water at room temperature. ACP was suspended in milliQ water at a ratio ACP/fluid of 0.5. The transformation was then followed by transmission electron microscopy (TEM) in conjunction with electron diffraction and *in situ* Raman spectroscopy. Electron diffraction (Fig.1) indicates the presence of HAp related reflections after 3 days and fully tranform to HAp after 5 days. This is in agrement with Raman data showing the transition from ACP to HAp indicated by a shift of the symmetric stretching PO_4 peak from 951 cm^{-1} up to 957.5 cm^{-1} within 5 days. These results demonstrate the fundamental impact of citrate on the crytallization of HAp.

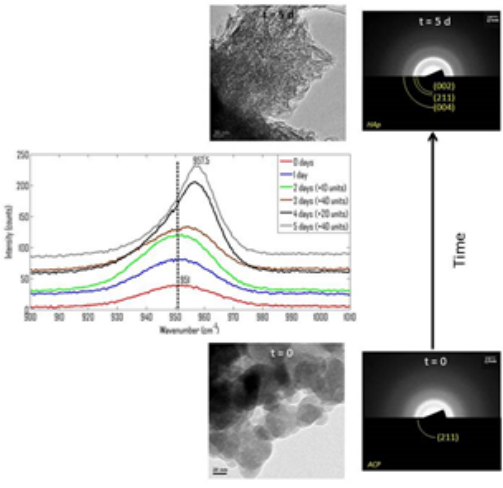

Fig.1. Raman shift of the PO_4 band as a function of time and TEM e-diffraction for ACP at time 0 days and HAp after 5 days.

[1] Yilmaz *et al*(2014) *Spectroscopy Letters* **47**, 24-29. [2] Hu *et al*(2010) *PNAS* **107**, 22425-22429.