

Synthesis of calcium phosphate and calcium carbonate phases and their characterization by Raman spectroscopy

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The crystallization of calcium phosphate in the presence of carbonate and of calcium carbonate in the presence of phosphate is relevant to biomineralization because different calcium phosphate biominerals incorporate carbonate ions and phosphate is regarded as a stabilizer of amorphous calcium carbonate (ACC), a precursor in many biomineralization processes. Although precipitated calcium phosphate is usually referred to as hydroxyapatite (HAP), other phases may also form, in order of increasing solubility, such as tricalcium phosphate (TCP), dicalcium phosphate anhydrous (DCPA), octacalcium phosphate (OCP) and dicalcium phosphate dehydrate (DCPH). Among the phases of calcium carbonate, only calcite and aragonite are extensively deposited as biominerals.

In order to obtain crystals of calcium phosphate phases containing carbonate ions and calcium carbonate containing phosphate, crystallization experiments were performed in a double diffusion system consisting of two vertical branches separated by a column of silica hydrogel. The vertical branches were filled with 0.5 M CaCl₂ and 0.5 M Na₂CO₃ solutions. Different amounts of a Na₃PO₄ solution were added to the mixture during the preparation of the gel, so that the gel column initially contained a homogeneous concentration of phosphate (50, 500 and 1000ppm). Reagent diffusion led to the development of concentration gradients and a range of phosphate/carbonate ratios within the gel column. The crystals formed in different regions of the gel were extracted two months after nucleation and studied by scanning electron microscopy, electron microprobe and X-ray diffraction. Moreover, Raman spectra of the samples were collected using a confocal Raman microscope.

In the experiments carried out with 50 ppm of phosphate in the gel medium only calcite crystals were obtained. These crystals showed a shape elongated along the c-axis. This shape is characteristic of calcite crystals grown in the presence of foreign tetrahedral anions like sulphate, chromate, etc. The incorporation of phosphate anions into the calcite structure is supported by the features of the Raman spectra, where an additional band due to the symmetric vibration of the P-O can be seen at 965 cm⁻¹. In the experiments with 500 and 1000 ppm of phosphate in the gel medium, the sequential formation of calcium phosphate spheres and calcite crystals was observed. The calcite crystals showed characteristics similar to those obtained in the experiments using gels with 50 ppm of phosphate, with a marked elongation parallel to [001]. The calcium phosphate spheres show the characteristics of amorphous calcium phosphate (ACP), which transforms into a microcrystalline aggregate of OCP after a certain induction period. These spheres show a complex internal structure consisting of three regions concentrically arranged. Moreover, each region shows a specific texture, with both the most inner region and the intermediate region well developed and the outer region showing a scarce development. Slight differences were observed in the Raman spectra depending on the phosphate concentration in the gel, illustrating the strong influence of both composition and structure on which band positions in the Raman spectra. In any case, the small thickness of the outer region in the spheres made impossible is complete characterization..

Acknowledgements: This research has been funded by projects CGL2010-20134-C02-01(DGICYT) and GR42/10-962062.