



The kinetics of Dissolution of Biologically Formed Calcific Deposits.

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The calcification of aortic valves results in the formation of non stoichiometric apatitic deposits which may have serious health implications because of the fact that these minerals adhere tenaciously on tissues like heart valves and arteries causing permanent damage which is partly due to their low solubility.

In the present work, calcium phosphate biominerals were extracted from clinically removed tissues and were characterized with respect to their mineralogical constituents and other properties including morphology, specific surface area analyses and thermogravimetric analysis. In all cases, the biominerals may be described as non stoichiometric apatitic materials, although traces of the precursor phase of octacalcium phosphate ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, OCP) were identified on the basis of their morphological examination.

The kinetics of dissolution of the biomineral deposits was investigated in solutions undersaturated with respect to hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$, HAP) at conditions of constant undersaturation at pH 7.40, 37°C, 0.15M NaCl. Synthetic stoichiometric HAP was used as the control mineral. The experiments in the present work used solutions prepared from calcium chloride and sodium hydrogen phosphate and the relative undersaturation, σ , was in the range 0.38-0.74 with respect to HAP and 0.49-0.85 with respect to OCP ($\sigma=1$ in water). The dissolution process started immediately upon the introduction of an accurately weighted amount of powdered biomineral in the undersaturated solutions homogenized by magnetic stirring. Inert atmosphere was ensured with the bubbling of water vapor saturated nitrogen through the demineralizing solutions. A glass/Ag/AgCl combination electrode was used as a probe to monitor the process and to control the addition of diluent solutions with the stoichiometry of the dissolving mineral. The measurements of the rates of crystal dissolution, showed a parabolic dependence on the relative solution undersaturation for HAP and higher order (ca.3) for the biominerals. This mode of dependence for both minerals studied, suggested surface diffusion controlled mechanism for their dissolution. The apparent rates of dissolution of the calcific deposits were higher in comparison to the corresponding value of the stoichiometric HAP. This finding is due to the higher apparent solubility of the carbonate and other metals containing biominerals. It should be noted that the dissolution affected the morphology of the prismatic crystallites which became thinner and shorter suggesting that the dissolution was rather uniform in the a, b and c axes of the prismatic crystallites.

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