Structural substitutions in uroliths: The case of carbonates in carbapatite urinary stones

P. Anastassopoulos¹, K. Bouropoulos¹, N. Ferakis¹, H. Poulias¹, <u>N. Bouropoulos²</u>

¹ Hellenic Red Cross Hospital, Department of Urology, Athens, Greece

² Department of Materials Science University of Patras, Patras Greece

Detailed knowledge of the composition of uroliths is important for their management and dissolution. The most frequently encountered compounds in calcium phosphate urinary stones are apatite and brushite. Apatite stones as occur in many biologically formed apatites, may contain substituted ions in comparison to stoichiometric apatite such as carbonate. Carbonate incorporation in biological apatites structures can reach concentrations up to 7 %. This substitution causes a decrease in particle size and simultaneously an increase in the surface area making the dissolution rate of carbonate apatites (CAP) higher to acidic solutions in comparison with stoichiometric hydroxyapatite. Although extensive research has been performed on the assignment of carbonates in biological apatites like enamel, dentin or bone, the presence of carbonate ions in carbapatite urinary stones has not been studied adequately. The objective of the present work is to assign the presence of carbonate apatite urinary stones using Fourier Transformed Infrared Spectroscopy (FTIR) spectroscopy.

Thirty five urinary stones were examined in this study. The chemical composition of the stones was assessed using FTIR spectroscopy. The samples were powdered and next 1,5 mg of powder was mixed with 150 mg of spectroscopically pure potassium bromide (KBr) using a mortar and pestle. The mixture was pressed by a hydraulic press at 9 th to form pellets in a stainless steel mould. The FTIR spectra were recorded on an Excalibur Digilab FTIR spectrophotometer in the range of 4000– 400 cm^{-1} at a resolution of 2 cm⁻¹.

A stone composed of carbonate apatite in a proportion up to 95% was characterized as carbonate apatite stone. Nine of the examined stones (26 %) were found to be composed of carbonate apatite as the dominant component. Analysis of the FTIR spectra showed the presence of characteristic phosphate and hydroxyl vibrational bands of hydroxyapatite. In addition, bands corresponding to carbonate groups appeared. Carbonate anions can be located at the hydroxyapatite structure in hydroxyl (A-type CAP) or phosphate (B-Type CAP) positions. The assignment of carbonate bands showed both A and B substitution. Analysis of the intensities of characteristic peaks at 872 and 879 cm⁻¹ corresponding to B-type and A-type, respectively implied that in all cases the majority of carbonate ions are incorporated in the phosphate positions.

It was found that carbonate apatite urinary stones are constituted by a mixed AB type carbonate apatite with a greater amount of substitution at B site. The results obtained from this study may contribute to a better understanding for the dissolution of carbapatite urinary stones.