

INFRARED AND RAMAN STUDIES OF BIOAPATITE DEPOSITS IN HUMAN HEART VALVES

VALENTINA COTTIGNOLI^{1*}, SARA MANGIARDO², ELENA CAVARRETTA³, LORIS SALVADOR⁴, PAOLO POSTORINO², ADRIANA MARAS¹

¹Dept. of Earth Sciences, La Sapienza University of Rome, Rome, 00185, Italy

²Dept. of Physics, La Sapienza University of Rome, Rome, 00185, Italy

³Dept. of Experimental Medicine, La Sapienza University of Rome, Rome, 00185, Italy

⁴Div. of Cardiac Surgery, San Bortolo Hospital, Vicenza, 36100, Italy

valentina.cottignoli@hotmail.it

The carbonate group is an important constituent of bioapatite, a calcium phosphate close to hydroxyapatite, main constituent of bone and dental enamel. $[\text{CO}_3]^{2-}$ can occupy two different sites in the structure (type A and B), and seems to control the growth, evolution, morphology, and physical properties of synthetic nano-carbonated hydroxyapatite [1]. Infrared and Raman spectroscopy were used to evaluate the carbonate substitution in pathological bioapatite from patients undergoing valvular replacement caused by severe aortic and mitral stenoses [2]. FTIR spectra were collected in the 4000-400 cm^{-1} spectral range using a PerkinElmer System 2000, while Raman spectra in the range 4000-200 cm^{-1} using a Horiba Jobin-Yvon LabRam Confocal Microscope at a resolution of about 3 cm^{-1} . The 3- PO_4 IR mode appears as an intense band at 1023 cm^{-1} , a shoulder at 1059 cm^{-1} , and a third band at 1104 cm^{-1} . The asymmetric stretch vibration mode (3) of CO_3 is represented by four bands at 1418, 1450, 1471, 1503 cm^{-1} while the out-of-plane bending mode (2) of CO_3 by the band at 872 cm^{-1} . This characteristic IR signature seems to be typical of Na-bearing type A-B carbonate apatite [3]. The band at 1503 cm^{-1} could indicate the accommodation of the carbonate group in a second channel position (Type A2) usually present in carbonate apatite synthesized at high-pressure [4]. On the contrary the Raman band at 1071 cm^{-1} , observed in all spectra and due to 1- CO_3 , is specific of $[\text{CO}_3]^{2-}$ substituting $[\text{PO}_4]^{3-}$ (type B) and the band observed at 961 cm^{-1} due to 1- PO_4 mode is in agreement with the shift assigned to 1- PO_4 mode for bone and synthetic type B carbonate apatite with different carbonate contents [5]. The height and area of many of the Raman peaks are strongly correlated with weight percent carbonate. The ratio of peak area at 1071 cm^{-1} and peak area at 961 cm^{-1} was used to determine the percentage of carbonate in the analyzed samples, as described by Awonusi et al. [6]. Values obtained (4.5-7.0 %) are in good agreement with those of biological apatite from bone.

[1] Liao S. et al. (2007): Materials Letters, 61, 3624-3628;

[2] Maras A. et al. (2010): Acta Mineralogica-Petrographica, 6, 374;

[3] Fleet M.E, Liu X. (2007): Biomaterials, 28, 916-926;

[4] Fleet M.E. et al. (2004): American Mineralogist, 89, 1422-1432;

[5] Penel G. et al. (1998): Calcified Tissue international, 63, 475-481;

[6] Awonusi A. et al. (2007): Calcified Tissue international, 81, 46-52.

Keywords: bioapatite, FTIR, Raman