Heating experiments on bone apatite to observe structural alterations.

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Thermal reactions on bones have been extensively studied in the fields of mineralogy, biology and archaeology. Besides the oxidation of organic materials, structural changes are observed in the inorganic component as well. The inorganic component of bone materials is a kind of calcium-phosphate which structure is like hydroxyl-apatite ($Ca_5[PO_4]_3OH$), characterized by ionic substitutions (Mg, Na, F, CO_3) and very small crystallite sizes [1]. Earlier experiments suggest that hydroxyl-apatite s.str. and bone-apatite must be distinguished, mainly due to the differences in structural ordering [1].

In this study, a bovine femur sample was used to characterize nanostructural changes during heat treatment in the temperature range 25-1100℃, focused on the structural alterations. After each step of the thermal treatment, the sample was measured by X-ray powder diffraction (XRD, Bruker D8 Advance, Cu-KΦ#177; source with 40 kV and 40 mA, Göbel mirror, Vantec1 detector) applied to reveal the mineralogical composition and TEM (Philips CM20, 200 kV, LaB_6 cathode, and energy dispersive spectrometry, EDS) and HRTEM (JEOL 3010 UHR, 300 kV, LaB_6 cathode, C_s 0,6 mm, point resolution 1.7 Å) to determine crystallite size and nanostructural alterations. The observed structural changes of bone-apatite during heat treatment are described as recrystallization [2]. Coupled differential thermal analysis and thermogravimetry (MOM Derivatograph-C, air atmosphere, 10°C/min linear heating, tmax 1100°C) were applied to observe reactions in the bone during heating. Weight loss of the bovine femur between 100 and 800 °C represents the breakdown of organics (e.g., collagen) and their volatilization. The decomposition of structurally incorporated carbonate and its release as CO_2, and the release of apatite's lattice water in different steps are also observed in this range [3].

Based on the DTA-TG results, seven samples were selected as useful to observe critical transformations. Recrystallization begins over 300 °C, in parallel with organic component breakdown. Some pronounced exothermic reactions observed on DTA curves at 540°C and 810 °C suggest crystallization of nano size "amorphous" Ca-phosphate into apatite crystal structure. According to TEM observations, the crystallites are 3-7 *nm* sized with length between 8-25 *nm*. We studied the structural changes and tried to characterize each sample of different thermal stage. We observed transformations from nano sized polycrystalline (diffraction rings) to single crystal development by size increase, indicated by discrete reflections. Crystallite size increased up to 700 *nm* at 1100 °C which is interpreted as recrystallization by cation ordering and sintering-like adherence of nanocrystals.

References

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