БИОМИМЕТИЧЕСКИЙ ПОДХОД К ПОНИМАНИЮ СТРУКТУРНОГО И МОРФОЛОГИЧЕСКОГО РАЗНООБРАЗИЯ ТВЕРДЫХ БИОЛОГИЧЕСКИХ ТКАНЕЙ: КОМПОЗИТЫ 'КАРБОНАТИЗИРОВАННЫЙ АПАТИТ-(CaF) - БЕЛОК'

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A BIOMIMETIC APPROACH FOR GETTING CLOSE RELATIONS TO THE STRUCTURAL AND MORPHOLOGICAL COMPLEXITY OF BIOLOGICAL HARD TISSUES: CARBONATED APATITE-(CaF)-PROTEIN NANOCOMPOSITES

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The growth of model systems such as inorganic-organic hybrid materials under controlled mineralization conditions is important for deeper understanding of the mechanisms of biomineralization. Our previous investigations were devoted to the biomimetic growth of apatite-(CaF)-gelatine-nanocomposites (Kniep, Simon, 2007). The present work is a further step towards mimicking natural composite systems by focusing on the biomimetic synthesis of carbonated apatite-(CaF)-gelatine-nanocomposites. This more complex system is more closly related to the respective bio-system, which plays a decisive role in the process of biological mineralization of hard tissues.

The carbonated fluorapatite-gelatine composites with variable carbonate content at the phosphate-position in the fluorapatite crystal structure (so-called B-type substitution) were synthesized by the double diffusion technique within a gelatine gel. The carbonate content was varied whereas all the other experimental parameters (Ca^{2+}, $[PO_4]^{3-}$, F^- – concentrations, gel-concentration, pH, temperature and growth time) were kept constant (Rosseeva et. al., 2008). The composite aggregates grown within so-called Liesegang bands were characterized by XRD, chemical analysis, FTIR-spectroscopy, Raman-spectroscopy, TG/DTA/MS, SEM, TEM, HR-TEM and electron diffraction (ED). The morphogenesis and inner structure of the carbonated composites was investigated as a function of the carbonate concentration in the solutions (also reflected in the carbonate content of the composites).

The carbonate content in the apatite component of the biomimetic composites (obtained from the M-Liesegang bands) varies from 0.3 to 7.5 wt.%. The gelatine content in the biomimetic composite corresponds to about 2-3 wt.%. The morphogenesis of carbonated fluorapatite-gelatine-nanocomposites on the micrometer scale starts with an elongated (rounded) seed and develops via dumbbell states to just-closed notched spherical aggregates. Two kinds of morphogeneses are observed: the so-called fan-like and the fractal series (Kniep, Simon, 2007). The shapes of carbonated composite aggregates become significantly rounded and compressed with increasing carbonate content. The changes in morphology as well as in the slitting mechanism of the carbonated aggregates may be due to the less anisotropic growth and smaller size of the subunits leading to the nanomosaic organization of nanocomposites. Taking into account the experimental evidence for the inner structure and features of morphogenesis of the fractal and fan-like composite aggregates it can be assumed that in case of the fractal growth series the process of formation of aggregates can be described in terms of the so-called “non-classical” crystallization model (Cölfen, Antonietti, 2008) (growth control by the organic component and aggregates growing by “brick-by-brick” self-assembly processes), while for fan-like aggregate the shape development is mostly base on the “classical” crystal growth and splitting mechanisms (control by the growth of apatite component, and aggregates growing by ion-by-ion or molecule attachment to a primary particle). However, in our biomimetic system also aggregates with intermediated morphology were observed. This indicates that so-called “classical” and “non-classical” crystallization process can occur in the same system. Probably, this crystallization passway gives the additional flexibility and freedom to generate complex morphology of organic-inorganic nanocomposites aggregates which is very important especially in biosystems.

It was demonstrated, that the content of the organic component, the crystalchemical features and the size of the coherence scattering domains of apatite of the biomimetic nanocomposites are similar to that of enameloids of some fishes (shark and porgy-fish) (LeGeros, Suga, 1980). In addition, the content of carbonate and sodium ions in the apatite and the amount of organic components in mammal dental enamel (including human enamel) are also close related to our synthetic aggregates. Furthermore, our investigations shown, that inner structure and even the composition (carbonated *fluor*apatite-organic composite) of our biomimetic nanocomposites are closely related to the hard tissues of one of the first and most primitive chordates - conodonts (495-199.6 Ma) (which like biomimetic system characterized by low level of complexity) (Rosseeva, 2010). Thus our biomimetic system is perfectly suited for obtain information on process of self-organization of organic-inorganic nanocomposites and may be also helps to deeper understand the process of mineralization of biological hard tissues.

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