Carbonated Apatite-(CaF)-Organic-Nanocomposites – Biominerals and Biomimetic Synthesis

E.V. Rosseeva[1], O.V. Frank-Kamenetskaya[2], R. Kniep[1]

[1]*Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany*
[2]*Saint Petersburg State University, Russia*
E-mail: rosseev@mail.ru

Apatite-organic nanocomposites play a decisive role in living organisms as functional material in the form of bone and teeth [1]. The growth of model systems such as inorganic-organic hybrid materials under controlled mineralization conditions is important for a deeper understanding of the mechanisms of biomineralization. Our previous investigations demonstrated, that the biomimetic system apatite-(CaF)-gelatine is perfectly suited for the study of biomimetic steps closely related to steps in biomineralization [2]. The present work is a further step towards mimicking natural composite systems by focusing on the biomimetic synthesis of carbonated fluorapatite-gelatine-nanocomposites. This system is more complex and significantly closer related to the respective bio-system, which plays a decisive role in process of biological mineralization of hard tissues. Carbonated apatite-(CaF)-gelatine nanocomposites were grown by the double-diffusion technique within a gelatine gel. The carbonate content was varied whereas all the others experimental parameters (Ca^{2+}, $[PO_4]^{3-}$, F^- - concentrations, gel-concentration, pH, temperature and growth time) were kept constant [3]. The composite aggregates grown within so-called Liesegang bands were characterized by XRD, chemical analysis, FT-IR-spectroscopy, Raman-spectroscopy, TG/DTA/MS, SEM and TEM.

In order to find out the relationships between biomimetic and biogenic systems we investigated the hard tissues of conodont elements composed of apatite-(CaF)-organic composites. Samples of Polygnathus conodont elements were obtained from Late Devonian deposits at the south coast of the Ilmen Lake (Novgorod region) [4]. The color-alternation index (CAI) of the investigated conodont elements ranged from 1 to 2 indicating the mild fossilization conditions favoring better preservation of the organic component [5]. By means of single-crystal XRD, EDX, Raman-spectroscopy, SEM and TEM it was demonstrated that morphology, inner structure and composition (trace element and organic content) of albid and hyaline hard tissues are different. By means X-ray and electron diffraction it was shown that the albid crown conodont hard tissue is most ordered and even exhibits scattering properties representative for a single crystal. In addition, albid crown tissue contain minor amount of trace elements. Furthermore it was demonstrated that all investigated conodont hard tissues bear strong resemblance to the biomimetic apatite-(CaF)-gelatine nanocomposite [2,3]. The nano-structured collective within composite aggregate represents a highly mosaic-controlled nanocomposite superstructure.

Furthermore it was found out, that the amount of organic components, the crystalchemical features and the size of coherence scattering domains of apatite of the biomimetic nanocomposites are similar to that of enameloids of some fishes (shark and porgy-fish) [6,7]. Apart from the fact that fossilized hard tissues contain different amounts of organic components, the chemical composition of apatite of highly fossilized hard tissues is similar to that of the artificial composites [8]. In addition, the content of carbonate and sodium ions, the amount of organic components, and the crystallite size of apatite in mammal dental enamel (including human enamel) is also closest related to the synthetic aggregates [1]. Therefore, our biomimetic system is perfectly suited for obtaining informations on processes of self-organisation, and may help in gaining insight into the essentials of the formation of inorganic-organic nanocomposites with biological relevance.

References

1. Elliott J. C. Calcium Phosphate Biominerals // Reviews in Mineralogy and Geochemistry. **2002**. N 48. P. 427-452.
2. Kniep R., Simon P. Fluorapatite-Gelatine-Nanocomposites: Self-Organized Morphogenesis, Real structure and Relations to Natural Hard Materials // Top. Curr. Chem. Springer. **2007.** Vol. 270. P. 73-127.
3. Rosseeva E.V., Buder J., Simon P., Schwarz U., Frank-Kamenetskaya O.V., Kniep R. Synthesis, characterization and morphogenesis of carbonated fluorapatite-gelatine-nanocomposites: a complex biomimetic approach towards the mineralization of hard tissues // Chemistry of Materials. **2008**. N 19. P. 6003 – 6013.
4. Zhuravlev A.V. Specific features of the hard tissues of late paleozoic conodont elements. Paleontol J. **2005**. N39, 289–293.
5. Epstein, A.G., Epstein, J.B., Harris, L.D. Conodont colour alteration - an index to organic metamorphism. // U.S. Geol. Surv. Prof. Pap. 1977. N 995, P. 1-27.
6. LeGeros R.Z., Suga S. Crystallographic nature of fluoride in Enameloids of fish // Calcif. Tissue Int. **1980**. N 32. P. 169-174.
7. LeGeros R.Z., Silverstone L.M., Daculsi G., Kerebel L.M. In vitro Caries-like lesion formation in F-containing tooth enamel // J. Dent. Res. **1983**.Vol. 62. N 2. P. 138 – 144.
8. Elorza J., Astibia H., Murelaga X., Pereda-Suberbiola X. Francolite as a diagenetic mineral in dinosaur and other upper cretaceous reptile bones (Lano, Iberian Penisula): microstructural, petrological and geochemical features // Cretaceous Research. **1999**. N 20. P. 169 – 187.