Discrepancies between the nanostructure of bone apatite and hydroxylapatite. An HRTEM study.

Kovacs Kis, V.[1], Dallos, Z.[2,1], Czigány, Z.[1], Nagy, D.[2], Kristály, F.[3] and Dódony, I.[2]

[1] Centre for Energy Research, Hungarian Academy of Sciences, Hungary, [2] Department of Mineralogy, Eötvös Loránd University, Hungary, [3] Institute of Mineralogy and Geology, University of Miskolc, Hungary

Bone is an organic-inorganic composite material composed by biopolymer collagen and biomineral nanocrystals. Due to the compositional and X-ray diffraction similarities between the bone mineral and geological apatite, bone mineral is historically considered (bio)apatite [1]. Later, using Raman spectroscopy, it has been shown that, in contrast to most geological apatites and enamel materials, bone apatite lacks of OH and contains significant amount of carbonate [2]. It has also been subject of measurements that the measurable physicochemical properties of bone apatite change with crystal age [3]. However, due to the extremely small size of the individual nanocrystals (60x90x2 nm [4]) and the tight nature of their intergrowth with the biopolymer, the way of CO_3 incorporation, and the crystal chemistry of bone apatite is still unknown.

In this presentation we report - to our knowledge - the first HRTEM results on the crystal structure of individual bone apatite nanocrystals down to 2Å resolution. The studied bone is a paleontological sample, a 85 Ma old turtle plate. According to TEM, the size of the crystallites doesn't exceed 70 nm along c axis and is 10-20 nm in the perpendicular direction. Rietveld analysis of X-ray diffraction data based on P63/m symmetry, provided crystallite size of ca. 20 nm. The chemical composition measured by TEM-EDS proves high degree of fluoridization, which is in agreement with the geological age of the bone sample. The Ca/P ratio values vary between 1.8-2. Crystallographic analysis has been performed on HRTEM images of individual nanocrystals taken from different orientations. Amplitude and phase relations in [001] and [010] projections imply trigonal symmetry and the lack of 6_3 screw axis, respectively which indicates polarity along [010] (Figure 1).

The discrepancies between crystal chemistry of hydroxylapatite and bone apatite are discussed and crystal chemical interpretation is given using the HRTEM structural data. Based on the observed polarity, the formation of large Ca-rich and P-rich (010) surfaces is concluded. Such a nanostructure influences solubility properties of the nanocrystals and may provide a deeper understanding in the mechanism of bone remodeling.

References:

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Acknowledgements:

This work is financially supported by the National Research, Development and Innovation Office of Hungary, grant number K-125100. VKK has been supported by the János Bolyai Postdoctoral Fellowship of the Hungarian Academy of Sciences.

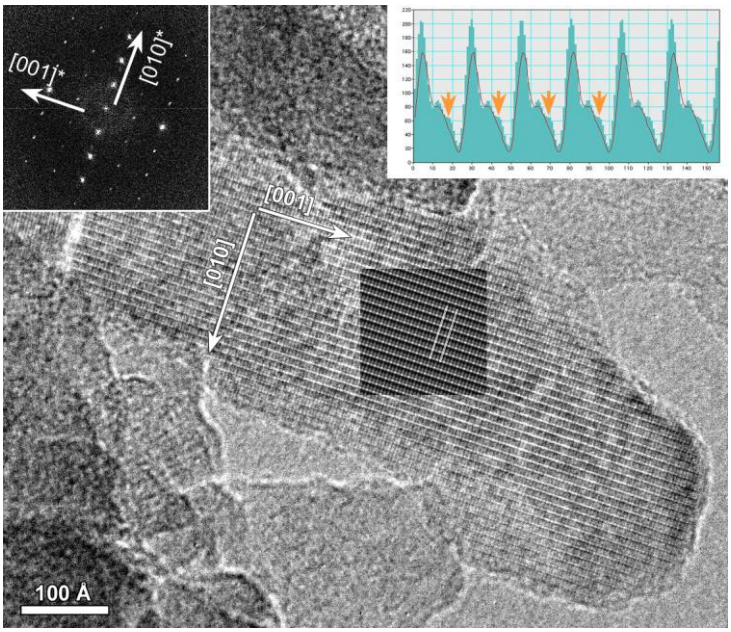

Figure 1: [100] HRTEM image of a bone apatite nanocrystal with its Fourier transform (upper left), symmetry imposed image (centre adjusted) and line profile illustrating polarity along [010] (upper right).