In-Situ XANES Spectroscopy at the Ca K edge of Calcium phosphate compounds

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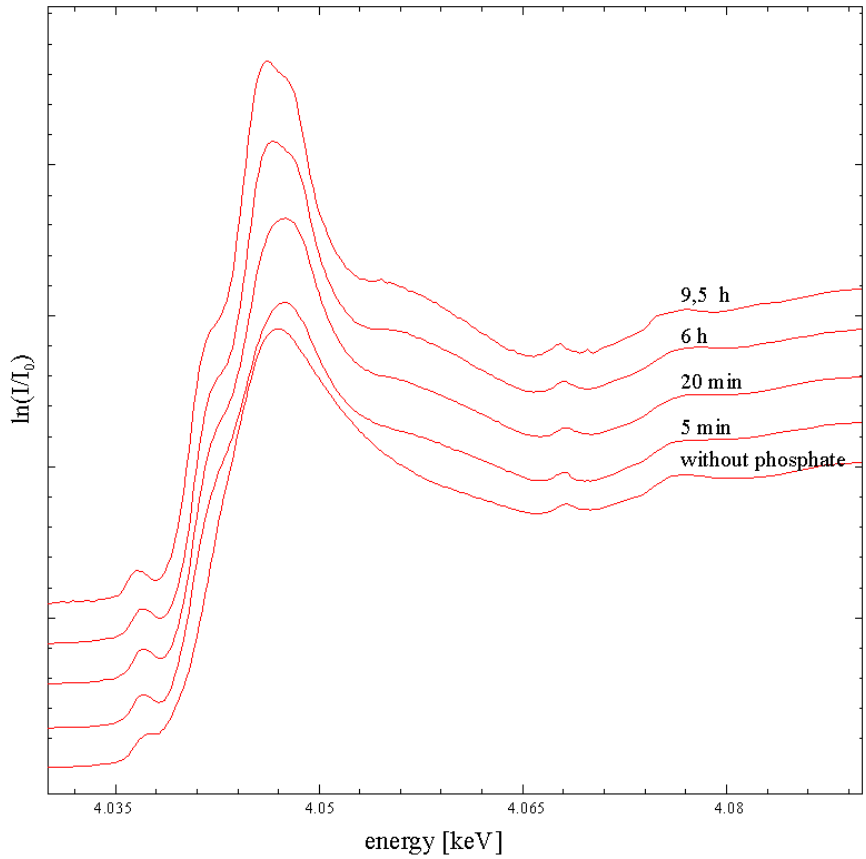
Biomimetic synthesis and characterization of biominerals like apatite is gaining increasing attention in the last years [1]. The major goal is to understand the specific interactions between the biomolecules and inorganic constituants. In our model system we study the crystallization of apatite in a collageneous matrix in a double diffusion experiment. XANES spectroscopy was used to obtain information on changes in the calcium ion environment during the crystallization prozess with due to possible intermediates like octacalcium phosphate [2,3]. Here we compare XANES spectra of calcium ions in gelatine reacting with sodium phosphate solution which diffuse in the gel in a time space from 5 min until 9 hours with spectra of synthetic apatite, octacalcium phosphate (OCP) and bone.

The measurements were performed at EXAFS II beamline with a Si 111 double-monochromator at a current of 4.44 GeV of Doris III.

Fig. 1 shows the Ca K edge spectra of the calcium phosphate compounds after different reaction times. The XANES exhibits a pre-edge peak. This effect is due to 1s → 3d (Ca) +2p (O) transition which is only



allowed to non- Figure1: Ca K XANES Spectra of the formation of apatite in gelatine (10 wt%)

centrosymmetical sites [4]. A distinct and charateristic structure of the edge itself is observed in the compounds formed after 20 minutes. Two peaks are present. The first is simply explained by dissymmetric neighbours [5]. In the gelatine without phosphate the calcium is probably symmetrically surrounded by water molecules. The result is only one smeared out peak. In the spectrum of calcium phosphate compound after 5 minutes of reaction time a shoulder appears in the smeared out peak. This shoulder becomes wider

with increasing reaction time. This is an indication that the crystallinity of the compounds increases and along with the asymmetry of the oxygen neighbours. The spectrum after 20 min reaction time reveals the same feature as the spectrum of bone in Fig.2. Since bone is composed of poorly crystalline apatite, it is possible that the apatite of the bone is similar to that formed after 20 minutes. The spectrum after 9,5 hours resembles the spectrum of crystalline apatite. By comparison with the reference spectra the absence of a spectrum resembling that of OCP can be used as a proof that an intermediate octacalcium phosphate phase does not form in the system apatite/gelatine.

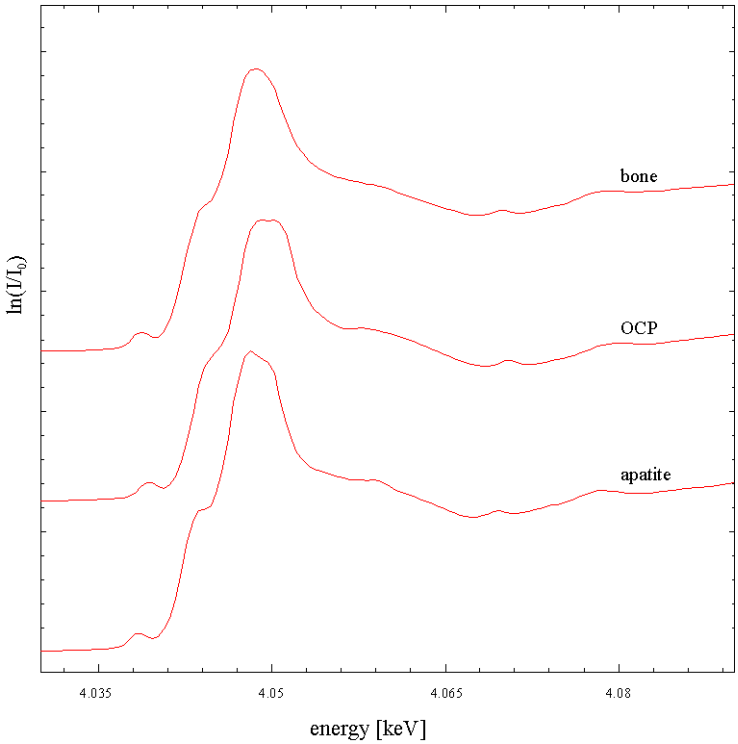


Figure 2: Ca K XANES spectra of synthetic apatite, OCP and bone

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