

## XAFS study of hydroxyapatite and fossil bone apatite

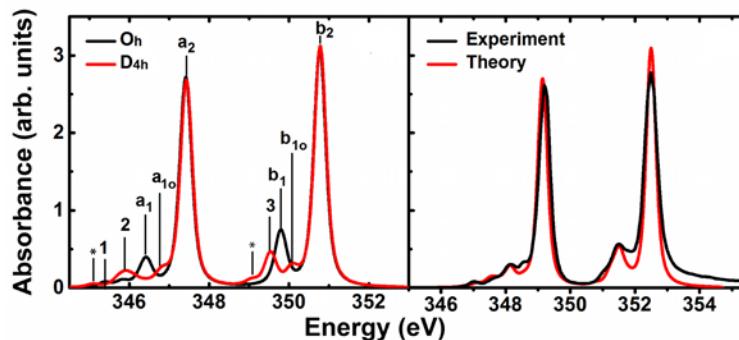
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**Abstract:** Ca  $L_{2,3}$ -edge XANES spectroscopy is applied for the study of variations in fossil bone apatite crystallinity due to heavy bacterial alteration and catastrophic mineral dissolution. The results are referred to those from well-preserved fossil apatite, fresh bone, and geologic apatite. In order to identify the origin of the peaks in the Ca  $L_{2,3}$ -edge XANES spectrum of hydroxyapatite,  $\text{Ca}^{[1]}_4\text{Ca}^{[2]}_6(\text{PO}_4)_3(\text{OH})_2$ , the spectrum was simulated using the CTM4XAS code. The atomic multiplet spectrum arising from the distorted octahedral bonding geometry of the  $\text{Ca}^{[2]}$  site was simulated using octahedral ( $O_h$ ) crystal field symmetry ( $10Dq=0.76$  eV). The simulation gives rise to the 1, 2,  $a_1$ ,  $a_2$ ,  $b_1$  and  $b_2$  peaks (Fig. 1). The  $\text{Ca}^{[1]}$  nine-fold coordinated site, that was simulated using  $D_{4h}$  symmetry ( $10Dq=-0.6$  eV,  $Dt=0.06$  eV,  $Ds=0$  eV), gives rise to the  $a_{10}$ , 3 and  $b_{10}$  peaks and also contributes to the intensity of the 2,  $a_2$  and  $b_2$  peaks. As shown in Fig. 1, the simulated spectrum, that results after summing up the contribution of the  $\text{Ca}^{[2]}$  and  $\text{Ca}^{[1]}$  sites and taking into account the site occupancy, reproduces very well the experimental spectrum. In fossil bone samples the apatite crystallinity was determined from the energy difference between the  $a_2$  and the average position of the  $a_1$  and  $a_{10}$  peaks in the Ca  $L_{2,3}$ -edge XANES spectra. The highest and lowest crystallinity values were observed for the bone with increased microbial porosity and the well preserved fossil bone respectively, indicating that bioerosion influences the crystallization process presumably *via* its by-products. The local bonding environment of Sr and the Ca site-preference with varying Sr/Ca content in fossil bone apatite was studied by Sr K-edge EXAFS spectroscopy. The analysis reveals a mixed  $\text{Ca}^{[1]}$  and  $\text{Ca}^{[2]}$  occupancy for Sr with a small preference for the  $\text{Ca}^{[2]}$  site for Sr/Ca = 0.017–0.024 gr/gr and a definite preference for the  $\text{Ca}^{[2]}$  site for Sr/Ca = 0.040 gr/gr.



**Fig. 1:** CTM4XAS simulation of the Ca  $L_{2,3}$ -edge XANES spectra of hydroxylapatite: (Left) Simulated contribution of the  $\text{Ca}^{[1]}$  and  $\text{Ca}^{[2]}$  sites with point symmetry  $D_{4h}$  and  $O_h$ , respectively; (Right) Comparison of the simulated and experimental spectra.

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