

Metal Substitution in Apatite: Zinc Incorporation into Hydroxylapatite

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Hydroxylapatite (HAP, $[\text{Ca}_5(\text{PO}_4)_3\text{OH}]$) has been the subject of interest in geochemical and biological processes because of its high reactivity. Metal partitioning to HAP has been shown to be a key factor in controlling the fate and transport of metals as well as their bioavailability. The most effective mechanism for metal partitioning and sequestration may be via coprecipitation.

Zinc (Zn) substitution in apatite-like materials has been the focus of many studies because of its presence in all biological tissues and diverse roles in biological functions, including calcification. The uptake and release of Zn in the body is strongly mediated by the bone reservoir, even though it only contains a small portion of the total body Zn. The presence of Zn in teeth has been used as an indicator of environmental exposure. Yet, the mode of Zn incorporation into hydroxylapatite, specifically the binding site and its local structure, is still not clearly understood.

Results of theoretical modelling and X-ray absorption spectroscopy (XAS) have been used to evaluate the local coordination structure of Zn substitution in hydroxylapatite. The theoretical modelling using density function theory (DFT) calculation shows that Zn favors the Ca2 site over the Ca1 site, with a preference for tetrahedral coordination. X-ray absorption near edge structure (XANES) suggests one dominant coordination environment for Zn, and no evidence was observed for other Zn-containing phases. Extended X-ray absorption fine structure (EXAFS) confirms that Zn occurs in tetrahedral coordination at the Ca2 site, with two P shells at $\sim 2.85\text{--}3.07 \text{ \AA}$, and two Ca shells at $\sim 3.71\text{--}4.02 \text{ \AA}$. These fit results are consistent with the most favored DFT model for Zn substitution in the Ca2 site. The results provide the structural basis for future models of Zn uptake and exchange in apatite-like biomaterials.