

## Atomistic mechanism of cadmium incorporation into hydroxyapatite

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### ABSTRACT

Hydroxyapatite (HAp) has been widely used to remove cadmium (Cd) in contaminated water and soils via Cd-Ca substitution. The Cd incorporation into HAp affects its structure; however, the detailed mechanism remains unclear. In this study, a series of Cd-substituted hydroxyapatites were synthesized and characterized with various techniques. Cd incorporation causes a decrease in *a*- and *c*-lattice parameters due to the radius of Cd<sup>2+</sup> being slightly smaller than that of Ca<sup>2+</sup>. As the Cd content increases, the particle sizes of the synthesized samples decrease and their specific surface areas increase. Raman bands shift linearly and the  $\nu_1(\text{PO}_4)$  peak at 961 cm<sup>-1</sup> becomes broadened with increasing Cd content. Change in X-ray absorption near edge structure (XANES) spectra of the P *K*-edge indicates distortion of phosphate with Cd incorporation. Total electron yield (TEY) spectra of the Ca *L*<sub>2,3</sub>-edge show a decrease in the octahedral symmetry, suggesting preferential occupancy of Cd over the Ca<sub>2</sub> site. Extended X-ray absorption fine structure (EXAFS) analysis of the Ca *K*-edge reveals no obvious change in the local environment of Ca induced by Cd incorporation. However, EXAFS analysis of the Cd *K*-edge indicates that the substituted Cd occupies one Ca<sub>2</sub> site in hexagonal Ca<sub>2</sub> positions at low-Cd contents [ $<10$  mol% of Cd/(Cd+Ca)], while both Ca<sub>1</sub> and Ca<sub>2</sub> sites are occupied at higher Cd contents. This study provides atomistic insight into the mechanism for Cd incorporation in HAp, which will help develop an approach for effective Cd removal using HAp for environmental remediation.

**Keywords:** Hydroxyapatite (HAp), cadmium, EXAFS, Raman, incorporation mechanism