

Supplemental Material for

Atomistic mechanism of cadmium incorporation into hydroxyapatite

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Supplemental material with 10 Pages, 9 Figures and 3 Tables.

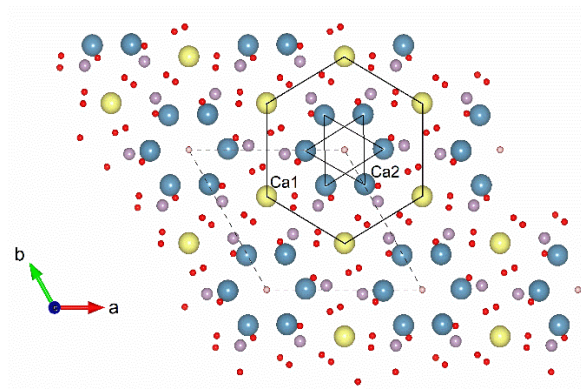


Figure OM1. Representation of the HAp structure with two nonequivalent Ca1 and Ca2 sites.

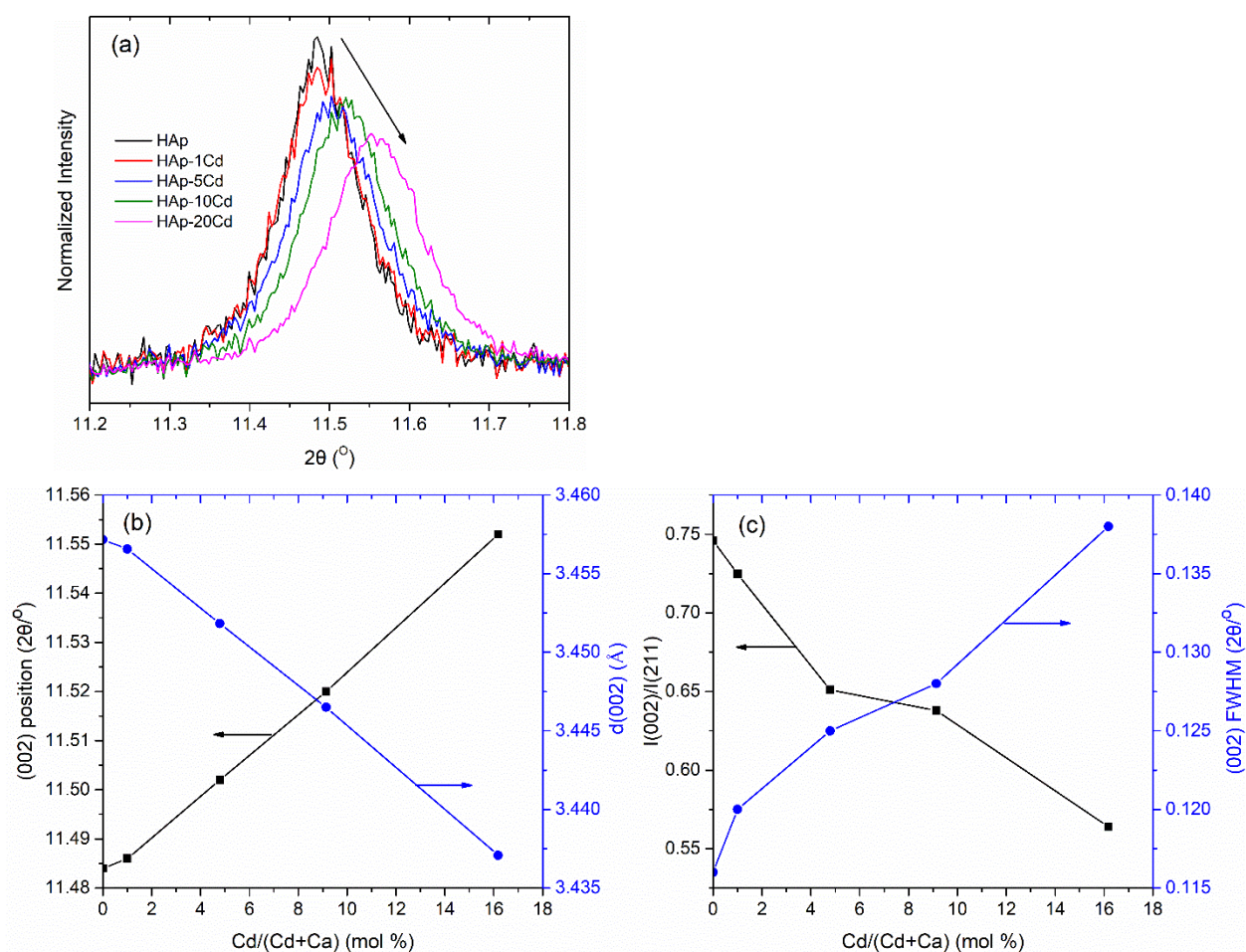


Figure OM2. The shift of (002) with Cd content in the enlarged XRD pattern (a); Variation of the peak position and d -spacing value of (002) (b); Variation of the intensity ratio of (002)/(001) and the FWHM value of (002) peak.

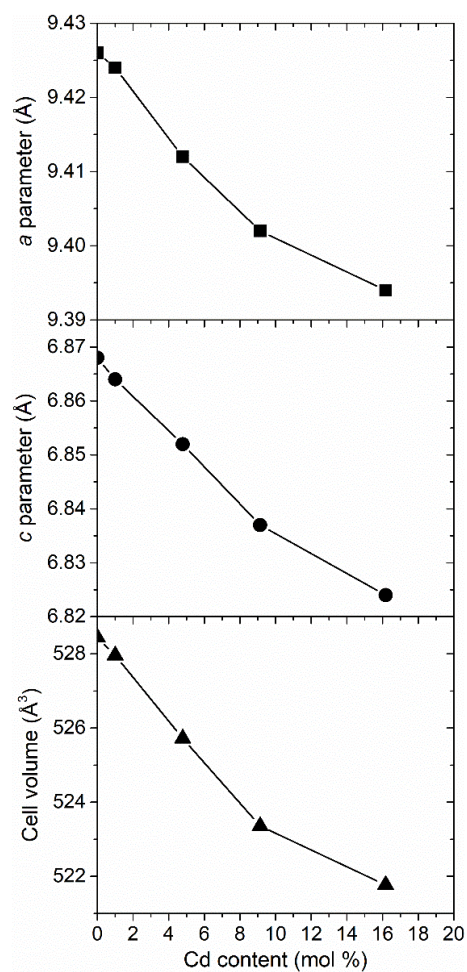


Figure OM3. Variation in lattice parameters (a , c , and V) in pure HAp and Cd-HAp samples.

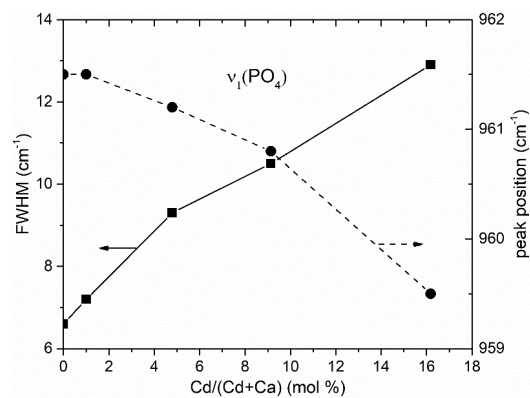


Figure OM4. The Cd concentration dependence of the $\nu_1(\text{PO}_4)$ peak positions and FWHM values in pure HAp and Cd-HAp samples.

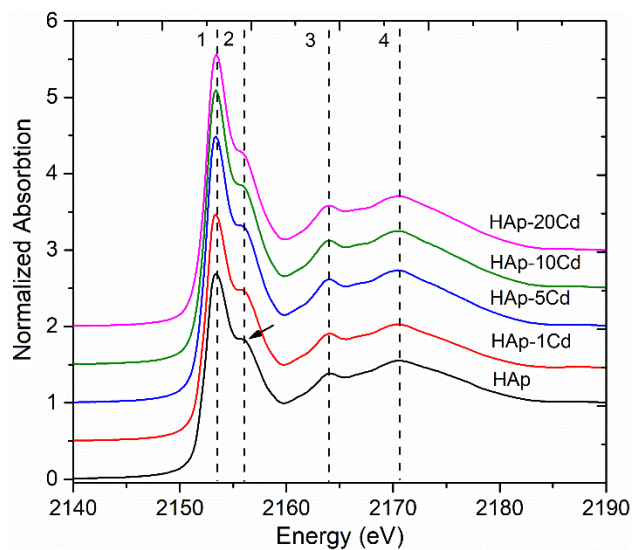


Figure OM5. XANES spectra of the P K-edge in pure HAp and Cd-HAp samples.

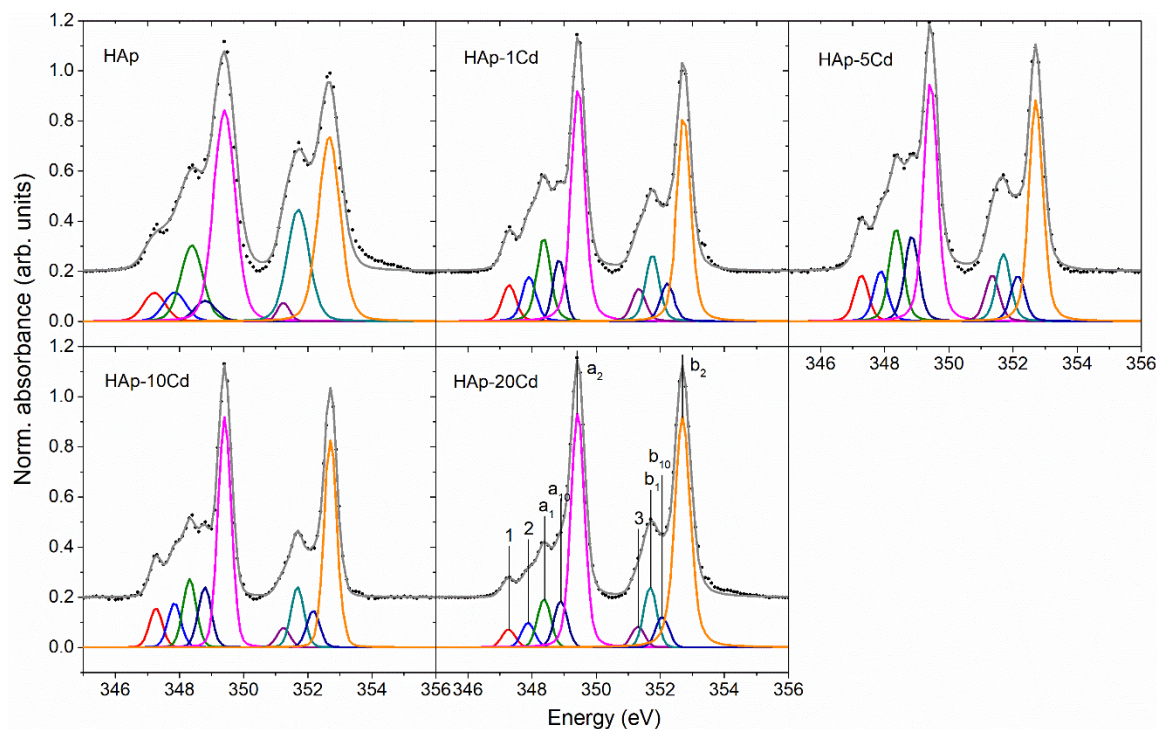


Figure OM6. Ca $L_{2,3}$ -edge TEY spectra and corresponding fitting in pure HAp and Cd-HAp samples. (Fitting of the peaks were referred to Zougrou et al. (2016))

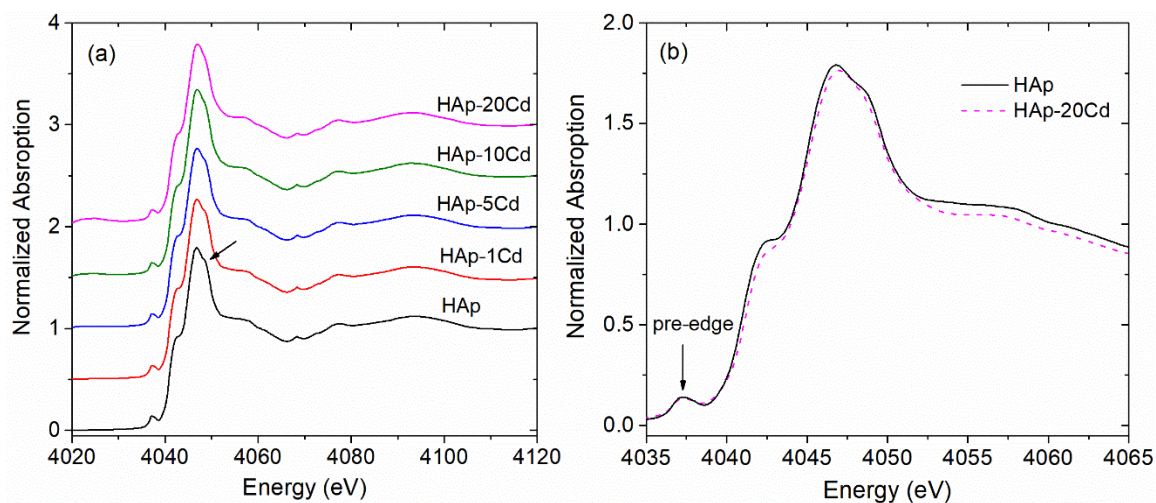


Figure OM7. XANES spectra of the Ca K-edge in pure HAp and Cd-HAp samples. The black arrow in (a) point to the shoulder peak of pure HAp.

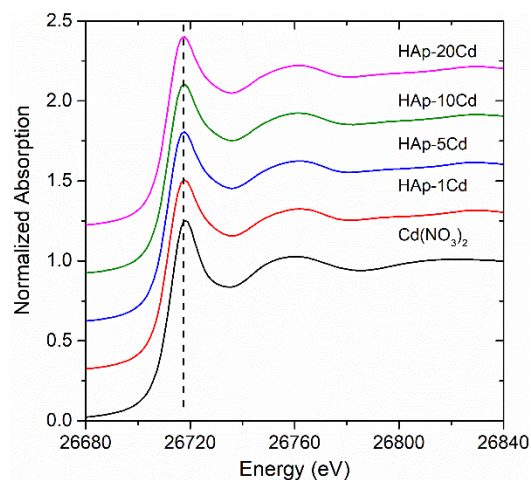


Figure OM8. XANES spectra of the Cd K-edge in Cd-HAp samples.

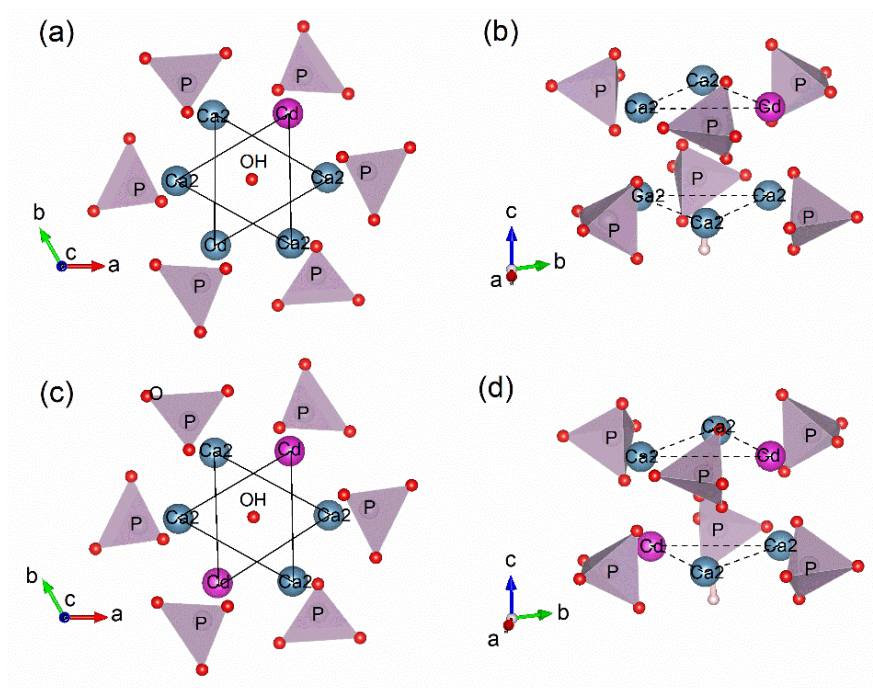


Figure OM9. Local environment of six Ca²⁺ atoms and incorporated with one Cd atom (10 mol% of total Ca) (a and b) and two Cd atoms diagonally (20 mol% of total Ca) (c and d).

Table OM1 Raman shift (cm^{-1}) and their assignments of phosphate in pure HAp and Cd-HAp samples.

Mode	HAp	HAp-1Cd	HAp-5Cd	HAp-10Cd	HAp-20Cd
$\nu_{3a} (E_{2g})^w$	1075.6	1075.7	1075.4	1075.3	1074.5
$\nu_{3b} (A_g)$	1047.1	1046.9	1046.7	1045.8	1044.1
$\nu_{3b} (E_{2g})^w$	1028.8	1028.4	--	--	--
$\nu_1 (A_g+E_{2g})^s$	961.5	961.5	961.2	960.8	959.5
$\text{FWHM}_{\nu_1} / \text{cm}^{-1}$	6.6	7.2	9.3	10.5	12.9
$\nu_{4a} (A_g)$	607.5	607.4	607.2	606.9	606.6
$\nu_{4b} (E_{2g})$	591.0	590.8	590.6	590.2	589.0
$\nu_{4c} (E_{1g})$	579.3	578.9	578.6	578.2	577.7
$\nu_{2a} (E_{2g})$	444.9	445.4	444.5	444.4	442.8
$\nu_{2b} (E_{1g})$	430.0	429.9	429.9	429.7	429.5

Notes: ^w indicated weak intensities, ^s indicated strong intensities, and -- indicated the peak intensity is too low to be identified.

Table OM2. Fitting peak positions of the Ca $L_{2,3}$ -edge TEY spectra in pure HAp and Cd-HAp samples

Samples	Peak positions (eV)										$a_1/L_3^\#$
	1	2	a_1	a_{1o}	a_2	3	b_1	b_{1o}	b_2	a_2-	
										a_1^*	
HAp	347.23	347.86	348.39	348.81	349.42	351.26	351.72	--	352.69	1.03	0.21
HAp-1Cd	347.28	347.90	348.35	348.84	349.43	351.32	351.75	352.22	352.73	1.08	0.19
HAp-5Cd	347.27	347.87	348.35	348.84	349.43	351.34	351.69	352.14	352.70	1.08	0.18
HAp-10Cd	347.27	347.85	348.32	348.79	349.41	351.24	351.68	352.17	352.72	1.09	0.15
HAp-20Cd	347.26	347.87	348.37	348.89	349.42	351.29	351.68	352.05	352.69	1.05	0.12

*Crystallinity is defined as the difference of the $a_2 - a_1$ peak positions

$^{\#}$ indicate the peak area ratio of peak a_1 to L_3 (including 1, 2, a_1 , a_{1o} , and a_2) region.

Table OM3. Fitting parameters of the Ca K-edge EXAFS spectra in pure HAp and Cd-HAp samples

Atom/shell	HAp			HAp-1Cd			HAp-5Cd			HAp-10Cd			HAp-20Cd		
	R		$\sigma^2(10^{-2}\text{nm}^2)$	R		$\sigma^2(10^{-2}\text{nm}^2)$	R		$\sigma^2(10^{-2}\text{nm}^2)$	R		$\sigma^2(10^{-2}\text{nm}^2)$	R		$\sigma^2(10^{-2}\text{nm}^2)$
	N			N			N			N			N		
	(Å)			(Å)			(Å)			(Å)			(Å)		
O/1 st	5.4	2.39	0.011	5.4	2.40	0.012	5.4	2.39	0.011	5.4	2.39	0.011	5.4	2.39	0.011
O/2 nd	3	2.56	0.015	3	2.56	0.015	3	2.56	0.015	3	2.56	0.015	3	2.56	0.015
P/3 rd	2.4	3.18	0.013	2.4	3.18	0.013	2.4	3.18	0.013	2.4	3.18	0.012	2.4	3.18	0.012
Ca*/4 th	0.8	3.52	0.007	0.8	3.52	0.007	0.8	3.52	0.007	0.8	3.52	0.008	0.8	3.52	0.008
O/5 th	6.0	3.93	0.050	6.0	3.93	0.050	6.0	3.93	0.050	6.0	3.93	0.050	6.0	3.93	0.050
Ca*/6 th	8.4	4.09	0.024	8.4	4.09	0.025	8.4	4.09	0.025	8.4	4.08	0.024	8.4	4.08	0.027
O/7 th	4.8	4.51	0.016	4.8	4.51	0.016	4.8	4.51	0.017	4.8	4.51	0.015	4.8	4.51	0.017
O/8 th	6.6	4.72	0.067	6.6	4.72	0.028	6.6	4.72	0.035	6.6	4.72	0.028	6.6	4.72	0.027

Note: * indicated the atoms of Ca or Cd in Cd-substituted HAp samples.

Ca/4th: Corresponds to Ca(I), Ca/6th: Corresponds to 30% Ca(I) and 70% Ca(II) (Laurencin et al., 2011).

Typical errors on the bond distances and Debye-Waller factors are ± 0.02 Å in R and 20% in σ^2 , respectively.

References

- Laurencin, D., Almora-Barrios, N., de Leeuw, N.H., Gervais, C., Bonhomme, C., Mauri, F., Chrzanowski, W., Knowles, J.C., Newport, R.J., and Wong, A. (2011) Magnesium incorporation into hydroxyapatite. *Biomaterials*, 32(7), 1826-1837.
- Zougrou, I.M., Katsikini, M., Brzhezinskaya, M., Pinakidou, F., Papadopoulou, L., Tsoukala, E., and Paloura, E.C. (2016) Ca L_{2,3}-edge XANES and Sr K-edge EXAFS study of hydroxyapatite and fossil bone apatite. *The Science of Nature*, 103(7), 60.