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Computational study of cation substitutions in apatites

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Abstract

Density-functional theory plane-wave modeling of fluor- and hydroxyapatites has been performed, where one or two calcium ions per unit cell were replaced with cadmium or zinc cations. It was found that cadmium ions favor Ca(1) positions in fluorapatites and Ca(2) positions in hydroxyapatites, in agreement with experiment. A similar pattern is predicted for zinc substitutions. In the doubly substituted cases, where only hydroxyapatites were modeled, a preference for the substituting ions to be located in Ca(2) position was also observed. Displacement of the hydroxide ions from their symmetrical positions on the hexagonal axis can be used to explain the preferred configurations of substituting ions around the axis.

Keywords: Apatites; Planewave calculations; Ion migration; Absorption

1. Introduction

Apatites are a class of inorganic crystalline compounds with a general formula $Me_{10}(XO_4)_6Y_2$ where Me^{2+} is a divalent cation, $(XO_4)^{3-}$ is a trivalent anion and Y^- is a monovalent anion. The canonical examples of apatites are hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and fluorapatite $Ca_{10}(PO_4)_6F_2$. Apatites are common in the nature, including living organisms (bones, teeth). In addition, numerous synthetic apatites have been prepared.

Within the generic apatite structure various ionic substitutions are possible. Some of them can be produced only at the synthesis stage, while a limited ion exchange between a solid apatite and the surrounding solution can also occur. Due to their high chemical diversity and ion-exchange capabilities, apatites have been considered as materials for toxic waste storage and for wastewater purification [1–6]. Ion-exchange in apatitic structures in the human organism has also presented interest for medicine.

Zinc is a common bioelement. Zinc content in human bones ranges from 0.0126% to 0.0217% by weight [7,8]. Cadmium is a frequent heavy toxic element pollutant in the water. Absorption of cadmium cations in apatites is relevant both from the medical standpoint of cadmium uptake by human bones, as well as since cadmium migration in nature involves absorption and desorption equilibria with natural minerals, including apatites. Interactions between these two ions during absorption and ion-exchange processes in apatites present therefore considerable practical and theoretical interest.

A large body of experimental data on ion sorption, exchange and desorption in various apatites exists. There is, however, little evidence about the mechanisms of ion sorption and the location of absorbed ions in the structure. Even less structural evidence is available on the interactions between different ionic substitutions in apatites.

The present study aims at determining the preferred locations of absorbed zinc and cadmium cations in hydroxy- and fluorapatites, using computational modeling. Knowledge of the energetically most favorable structures helps to understand possible ion migration in the apatites and inter-ion influences.

Apatites belong to the space group $P6_3/m$ and have 42 (fluorapatite) or 44 atoms (hydroxyapatite) in the unit cell. In substituted apatites, the atom counts may vary. Due to the relatively large unit cell, they have only recently become available for study by theoretical quantum-mechanical methods. Some examples of such studies are [9–15]. Zinc substitutions in calcium hydroxyapatite have previously

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been computationally studied in [16] using a combination of atomistic simulations and density-functional theory.

2. Computational method

The calculations were performed with standard plane-wave density-functional methodology, following the model parameters chosen by de Leeuw [15] for modeling of apatites. The Perdew–Wang 91 density functional was used, together with Vanderbildt ultra-soft pseudopotentials [17]. Out-of-core *p*-orbitals were used for calcium atoms.

After checking for convergence, plane-wave cutoff was set at 500 eV and a $2 \times 2 \times 2$ Monkhorst–Pack *k*-point mesh was used. For comparison, the highest cut-off energy recommended by the software was for fluorine, 424.865 eV. Thus a safety factor of 1.18 was included in order to reduce the effects of Pulay stress on geometry optimization. A larger value (1.3) would have been desirable, but would have led to too long computation times. For hydroxyapatites, which do not contain fluorine, the highest recommended cut-off was for oxygen, 395.994 eV, corresponding to a safety factor of 1.26.

All positions of atoms in the unit cell, as well as the cell size, were relaxed simultaneously.[1] The residual external pressure (Pulay stress) at end of the relaxations was in the range of -0.91 to 0.85 kB, with typical absolute values less than 0.35 kB. This was considered to be reasonably low in order to use the results for further analysis without additional compensation for the Pulay stress.

The software package VASP, version 4.6.12 [18–21] was used for the work.

3. Results and discussion

Calcium ions in the apatite structure occur in two different locations, Ca(1) and Ca(2). The Ca(1), four per unit cell, are located away from the fluoride/hydroxide containing hexagonal axis and are surrounded by six oxygen atoms. The Ca(2), six per unit cell, are placed around the fluoride/hydroxide channels in sets of three at different heights. If the Ca(1) ions are considered to be approximately at relative heights 0 and $\frac{1}{2}$ in the unit cell, the Ca(2) ions are located approximately at $\frac{1}{4}$ and $\frac{3}{4}$ of the total height of the cell.

A uniform numbering scheme for the calcium ion positions was used for the calculations. The numbering is illustrated in Fig. 1, the corresponding atomic coordinates are listed in Table 1. A unit cell is outlined in the figure, with surrounding atoms. All calcium ions inside the marked cell, as well as several neighboring ones are bearing the corresponding position numbers. Calcium ions 1 and 3 are not visible—they are located below ions 4 and 2, respectively. The ions 1–4 belong to the Ca(1) type, and the rest, from 5 to 10, are Ca(2).

The relative heights of ions in the unit cell are not evident from the projection and are therefore described here. Starting from the top, ion 2 is barely below the top cut-off surface of the crystal fragment depicted. Another ion 1 would be very slightly above the cut-off, and is therefore not seen in the figure. If present, it would be above ion 4. Ions 5, 8, and 9 form a triangle at $\frac{1}{4}$ unit cell height below the top surface. This triangle is surrounding the channel (hexagonal axis) which contains the F^- ions (OH^- in hydroxyapatite). At $\frac{1}{2}$ unit cell height there are ions 3 (below ion 2) and 4. At approximately $\frac{3}{4}$ depth there is another triangle: ions 6, 7, and 10. Finally, at the bottom of the unit cell there is ion 1 and, slightly below it, already in the next unit cell, ion 2 repeated again (not visible on the image).

3.1. Single substitutions

Experimental evidence [22,23] suggests that in fluorapatites, Cd^{2+} substitutes preferentially at Ca(1) sites, while in hydroxyapatites, the Ca(2) sites are preferred. The preference is not strong, however, and part of the sites of the other type are also occupied by cadmium ions. We are not aware of any experimental determinations of locations of Zn^{2+} ions in either kind of apatite structures. There also seems to be no experimental data available for the energetic differences between the structures with different locations of the substituting ions. Earlier computational studies [16], using a different computational model, indicate that the Ca(2) sites are preferred for zinc substitution in hydroxyapatite.

In a first series of calculations performed in this study, a single Ca^{2+} ion was replaced either with a Zn^{2+} or Cd^{2+} ion. During geometry relaxations, the unit cells lost their hexagonal shape, since the ions in the crystal were no longer symmetry equivalent. The cell parameters of the calculated unsubstituted and singly substituted apatites and some available experimental data are presented in Table 2. For the cadmium substitutions, the experimentally observed trend towards a reduction of cell volume is qualitatively correctly reproduced. For zinc substitutions, where no experimental data is available, an even larger effect is predicted.

Because of the lack of a unique state of reference, it is not possible to estimate the energetic effect of such ion exchange directly. It is, however, possible to compare crystals of the same stoichiometry with respect to the different location of the substituted ions. Calculations of the substituted crystal structures suggest that the substitution pattern is in qualitative agreement with the relative energies of the ions in the two binding sites. For Cd^{2+} and Zn^{2+} in fluorapatite, the structures with the substitution at Ca(1) have lower energies: by 12 kJ/mol when the substituting ion is Cd^{2+} and by 28 kJ/mol for the case of Zn^{2+}.

In hydroxyapatites, the Ca(2) site is preferred for substitution according to the calculated energy differences. For the Cd^{2+} substitution at Ca(2) the preference is 8 kJ/mol, while for Zn^{2+}, the energetic difference is 12 kJ/mol.

The energy differences between the two substituted structures in some cases are small enough to allow for

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[1] Optimized coordinates of the calculated systems reported here, as well as the corresponding calculated energies, are available from the authors upon request.

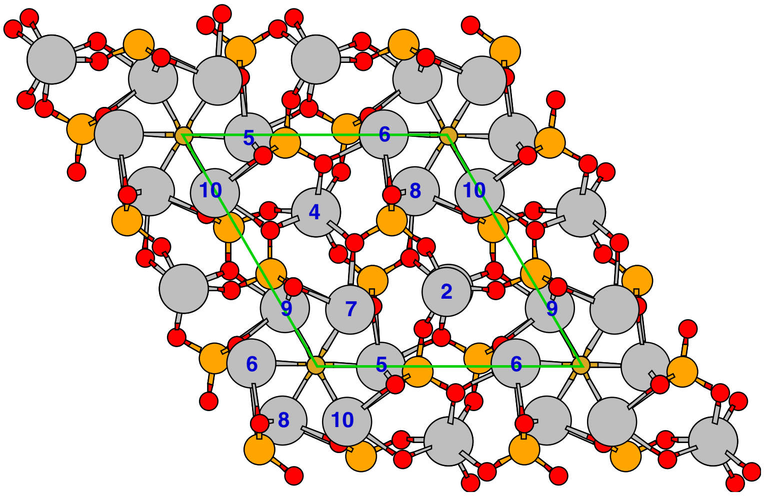

Fig. 1. A projection onto the *xy* plane of the fluorapatite structure. See text for explanation of the ion numbering scheme.

Table 1
Calculated and experimental [28] atomic coordinates of unsubstituted fluorapatite

Atom	Wyckoff letter	Multiplicity	Calculated			Experimental		
			x	*y*	*z*	*x*	*y*	*z*
O(1)	*h*	6	0.4851	0.3276	0.2500	0.4849	0.3273	0.2500
O(2)	*h*	6	0.4658	0.5880	0.2500	0.4667	0.5875	0.2500
O(3)	*i*	12	0.2559	0.3406	0.0693	0.2575	0.3421	0.0705
P	*h*	6	0.3687	0.3978	0.2500	0.3690	0.3985	0.2500
Ca(1)	*f*	4	0.6667	0.3333	0.0013	0.6667	0.3333	0.0010
Ca(2)	*h*	6	0.9978	0.2440	0.2500	0.9929	0.2423	0.2500
F	*a*	2	0.9988	0.9996	0.2500	0.0000	0.0000	0.2500

Table 2
Unit cell parameters (in picometers) of unsubstituted and singly substituted apatites

System	Calculated				Experimental			Notes
	a	*b*	*c*	*V*	*a*	*c*	*V*	
Fluorapatite:								
unsubstituted	946.4	946.4	688.6	5.3417×10^8	939.7	687.8	5.26×10^8	a
Cd at Ca(1)	947.0	947.4	686.9	5.3389×10^8	939.1	684.4	5.23×10^8	b
Cd at Ca(2)	946.5	947.1	686.5	5.3339×10^8	939.1	684.4	5.23×10^8	b
Zn at Ca(1)	943.8	944.1	680.0	5.2506×10^8				d
Zn at Ca(2)	941.4	947.9	681.0	5.2802×10^8				d
Hydroxyapatite:								
unsubstituted	955.5	955.5	690.1	5.4567×10^8	942	689	5.29×10^8	c
Cd at Ca(1)	956.1	956.1	688.1	5.4468×10^8	940	686	5.25×10^8	c
Cd at Ca(2)	951.4	956.7	688.1	5.4353×10^8	940	686	5.25×10^8	c
Zn at Ca(1)	951.0	951.0	682.3	5.3439×10^8				d
Zn at Ca(2)	940.7	956.8	689.0	5.4025×10^8				d

Notes:
(a) Ref. [28].
(b) Average values from Ref. [26], precipitated apatite. Positions of Cd ions in the structure are not known.
(c) Average values from Ref. [26], sorption experiments. Positions of Cd ions in the structure are not known.
(d) No experimental data available.
Some of the calculated cells are no longer hexagonal, therefore both *a* and *b* are presented.

certain part of both kinds of sites to be occupied at the same time. A simple statistical mechanics argument would give us relative site occupations as

$$P = \frac{\text{probability of being in Ca(1) sublattice}}{\text{probability of being in Ca(2) sublattice}} = \frac{4}{6}\exp(-E/kT),$$

where $E = E(\mathrm{Cd}^{2+}$ or Zn^{2+} on Ca(1)) $- E(\mathrm{Cd}^{2+}$ or Zn^{2+} on Ca(2)). At $T = 298\,\mathrm{K}$ this gives us $P = 54\,000$ for $E = 28\,\mathrm{kJ/mol}$ (Zn^{2+} in fluorapatite), $P = 85$ for $E = 12\,\mathrm{kJ/mol}$ (Cd^{2+} in fluorapatite, Zn^{2+} in hydroxyapatite), and $P = 17$ for $E = 8\,\mathrm{kJ/mol}$ (Cd^{2+} in hydroxyapatite). From the value of P and the fact that the sum of the two probabilities is 1, one can calculate the lower-energy site occupancies of nearly 100%, 99%, and 94%, respectively.

The above argument assumes that the distribution is governed by statistics only, and the processes (e.g. precipitation) which lead to the particular distribution occur at the temperature used in the calculation (298 K). In real apatites these conditions may or may not be fulfilled, and the distribution may also be influenced by kinetic factors. For example, in this laboratory, most apatites are precipitated at the temperature of around 353 K (80 °C) [24], which would lead to a more uniform distribution of the ions (e.g. 91% occupation by Cd^{2+} of Ca(2) sites, where $E = 8\,\mathrm{kJ/mol}$). It is also not known whether re-distribution of the ions is possible after the precipitate has been cooled.

3.2. Double substitutions

Earlier experimental research of the authors [25,26] indicates that absorption of either Cd^{2+} or Zn^{2+} from an aqueous solution by apatites leads to approximately similar final concentrations—up to 0.082 Cd/Ca and 0.077 Zn/Ca molar ratios. This means that on the average, less than one calcium cation is replaced per unit cell: replacement of exactly one cation would lead to a 0.11 ($\frac{1}{9}$) molar ratio. However, if the solution contains both types of cations, Cd^{2+} is absorbed in a larger quantity than Zn^{2+}. Depending on the apatite used, a 1.04–1.88 Cd/Zn ratio is observed, with typical values around 1.5. The total concentration of Cd and Zn relative to calcium remains below 0.1.

In order to study the effects of inter-species interaction between Cd and Zn substitutions, a second set of calculations was performed, where one Ca^{2+} ion in the unit cell was replaced by Cd^{2+}, and another one by a Zn^{2+}. Due to the limitations of computational resources, only hydroxyapatites were considered for this part of the study. We also limited ourselves solely to Cd–Zn interactions, leaving out the Cd–Cd and Zn–Zn interactions which would have assumed a Cd or Zn concentration of more than $\frac{1}{10}$ relative to calcium. Such concentrations are not observed in absorption experiments [26].

The overall concentration of (Cd + Zn) in this model system also remains higher than that observed in sorption experiments. This is a limitation imposed by the computational model: while a supercell containing two apatite unit cells could be simulated with the current computational resources, covering of all the possible locations of ions in this case would involve a prohibitively large number of individual runs which is not computationally feasible.

In the following discussion, the calcium ion locations are again numbered as shown in Fig. 1. The notation “Cd1” in the following text means that the calcium ion at position 1 (Fig. 1) has been replaced by a cadmium ion. In a similar fashion, e.g. Zn6, means that the calcium ion at position 6 has been replaced by a zinc.

Calcium 1 was chosen as the location of the first substitution at Ca(1) site, and calcium 5 was used as a representative of a Ca(2) site. The second substitution was placed at all possible other locations, respectively. We remind the reader that positions 1–4 represent Ca(1) sites, and positions 5–10 are Ca(2) sites. Given that all Ca(1) sites are symmetry equivalent, as well as the Ca(2) sites among themselves, and the positions for the second substituting ion in each case are fully covered, this represents an exhaustive list of all possible relative locations of the ions in one single unit cell. Due to symmetry, any additional combinations are equivalent to one of those calculated here.

In a real substituted apatite the locations of substituting ions are not necessarily systematic. In neighboring unit cells the ions might be located in different positions, and there would also be unit cells without any substitutions or with more than one. Covering these situations would have again required use of supercells for the simulation, and would have therefore been computationally prohibitive.

The relative energies of the various unit cells, in kJ/mol are shown in Tables 3 and 4. The lowest energy of all those obtained, that of the Cd5 Zn7 system, −300.63860 eV, was used as the point of reference. Since all the systems have the same stoichiometry of $\mathrm{Ca_8ZnCd(PO_4)_6(OH)_2}$, the energies are directly comparable.

The accuracy of the comparisons appears to be better than 1 kJ/mol range, judging by the differences in energies of systems which are equivalent by symmetry. For example, the four systems Cd5 Zn7, Cd5 Zn10, Zn5 Cd7, Zn5 Cd10 are all within 0.1 kJ/mol of each other.

The results suggest that the lowest energy conformations, and thus the more likely ones to occur in real substituted apatites, are those where both substitutions are in Ca(2) sites, clustered around the fluoride ion channel. There is a slight preference for the ions to be located near each other: the symmetry-equivalent configurations of one ion at site 5 and the other at site 7 or 10 have lower energies than those where the other ion is located at other Ca(2) sites. The sites 5, and 7 or 10, are neighbors, although located at alternating crystallographic planes.

A set of interatomic distances for some of the systems studied are tabulated in Table 5. In the lowest-energy configurations, the OH^- ions move away from the crystallographic axis towards a Zn^{2+} ion in the channel wall. In unsubstituted hydroxyapatite the oxygen–calcium distance in the ion channels is 241 pm, while, for example in the case of

Table 3
Relative energies of doubly substituted fluorapatites with Cd^{2+} at a fixed position

Cd^{2+} at	Zn^{2+} at	Relative energy (kJ/mol)	Notes
1	2	+27.7	
1	3	+21.4	
1	4	+53.0	Highest energy
1	5	+16.0	
1	6	+8.4	
1	7	+8.3	
1	8	+16.4	
1	9	+15.7	
1	10	+8.3	
5	1	+8.2	
5	2	+19.9	
5	3	+10.5	
5	4	+20.1	
5	6	+8.4	
5	7	+0.0	Lowest energy (reference)
5	8	+7.4	
5	9	+11.8	
5	10	+0.0	Slightly higher than Cd5 Zn7

The energies are relative to that of the "Cd5 Zn7" configuration.

Table 4
Relative energies of doubly substituted fluorapatites with Zn^{2+} at a fixed position

Cd^{2+} at	Zn^{2+} at	Relative energy (kJ/mol)	Notes
2	1	+20.9	
3	1	+21.2	
4	1	+43.7	Second-highest energy
5	1	+8.2	Equivalent to Cd5 Zn1 in Table 1
6	1	+9.4	
7	1	+10.1	
8	1	+7.9	
9	1	+7.8	
10	1	+10.7	
1	5	+16.0	Equivalent to Cd1 Zn5 in Table 1
2	5	+22.2	
3	5	+8.3	
4	5	+10.7	
6	5	+8.7	
7	5	+0.0	Slightly higher than Cd5 Zn7
8	5	+13.2	
9	5	+7.8	
10	5	+0.1	One of the lowest energies

The energies are relative to that of the "Cd5 Zn7" configuration.

Cd5 Zn7 substitution, the OH^- ions alternate between being attracted towards a Cd^{2+} ion, at the distance of 232 pm, and towards a Zn^{2+} ion, with 205 pm distance. The displacement may be related to the smaller ionic radius of Zn^{2+} and Cd^{2+} relative to Ca^{2+}, as well as possibly higher attractive forces between the OH^- and the substituting ions, or both.

This seems to partially explain why the lowest energy configurations have the substituent ions at one side of the channel wall (e.g. positions 5 and 7)—this allows for the whole array of OH^- ions to be slightly shifted in this direction, without breaking the chain of hydrogen bonds between them. If the hydroxide-attracting substituents are placed further apart, e.g. in positions 5 and 6 (opposite sides of the axis), the attraction comes at the cost of weakening of the OH–OH hydrogen bonds. The situation is illustrated in Fig. 2, which shows cut-outs of the crystal structure, two unit cells high, of the ions inside and around the ion channel.

In the case where the substitutions occur among ions on the same crystallographic plane, e.g. positions 5 and 8, the two substituents both attract a single hydroxide, partially balancing the attraction. At the same time, the second hydroxide in the unit cell is in nearly symmetrical field of the Ca^{2+} ions and can not contribute to the stabilization energy.

Another part of the preference for the ions to be in one side of the wall may be related to the ionic sizes. With both the Zn^{2+} and Cd^{2+} being smaller than the Ca^{2+}, placing them close together may allow for additional relaxation in their close vicinity. The effect is not necessarily unidirectional, however. As the data in Table 5 indicates, the Ca–Ca distance is increased in the Cd5 Zn6 (opposite sides of the channel) case, but there is no significant increase in the other case.

If one of the ions is forced into a Ca(1) site, the other ion clearly prefers a Ca(2) site, with little difference between the various particular locations among the available ones. The typical relative energies of such pairings are in the $8-11\,\mathrm{kJ/mol}$ range on our energy scale. Some of the pairs, however, such as Cd5–Zn2 or Zn5–Cd2, are at a higher energy of approximately $16-22\,\mathrm{kJ/mol}$. This is related to the location of the respective ions on different planes in the unit cell.

Placing both of the ions into the Ca(1) sites is the least favored situation, with the highest energy configuration corresponding to both of the substitutions being on the same axis—the Cd1 Zn4 and Zn1 Cd4 configurations in our nomenclature.

Analysis of some of the geometries of the higher energy configurations, where only one substituting ion is located at a Ca(2) site, reveals that this single ion can also displace one of the OH^- ions from the straight line of the former hexagonal axis. The other OH^- ion, as expected, remains centered on the axis at the center of the triangle formed by the Ca^{2+} ions. Therefore, the OH-ion chain forms a zigzag configuration, and the stabilization due to the shift of the whole ion chain does not occur.

In the cases where both substituting ions are at the Ca(1) locations, the OH^- ions remain perfectly aligned on the crystallographic axis and no energetic effects related to any potential change in their position occur.

We conclude from this analysis that the Cd^{2+} and Zn^{2+} ions in doubly substituted apatites prefer to cluster around the hydroxide ion channel (Ca(2) positions), and we speculate that probably the absorption involves some ion migration in the structure along this channel.

Table 5
Distances between various ions within and around the ion channel of selected unsubstituted and disubstituted hydroxyapatites

Distance, pm	Unsubst.	Cd5 Zn7 (same side)	Cd5 Zn6 (opposite)	Notes
Ca–Ca, same layer	414.48	412.82	421.09	Zn-containing layer
		414.37	418.07	Cd-containing layer
O–O, different layers	345.06	363.57	352.16	Zn-containing layer
		329.34	338.13	Cd-containing layer
O–O, unit cell *z*	690.11	687.08	683.68	
O–O–O, between unit cells	690.11	692.91	690.29	
O–H, intra-ion	97.94	97.98	97.72	Zn-containing layer
		97.91	97.80	Cd-containing layer
O–H, inter-ion	247.12	271.09	255.41	Zn-containing layer
		231.77	240.68	Cd-containing layer
O–H–O–H–O along H-bonds	690.12	698.75	691.61	
O–Ca	240.59			
O–Ca, Zn layer		257.29	257.08	In increasing order
		262.22	258.67	
O–Ca, Cd layer		240.22	244.49	In increasing order
		248.94	248.42	
O–Zn		204.63	205.27	
O–Cd		232.36	227.93	
Relat. energy		0.0 kJ/mol	+8.4 kJ/mol	

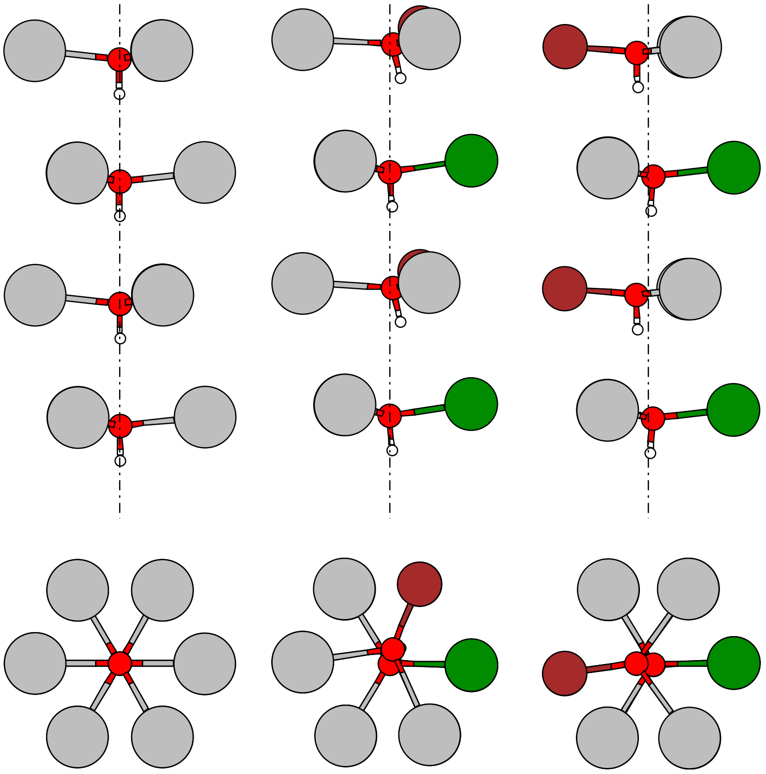

Fig. 2. Ions inside and around the ion channel in unsubstituted hydroxyapatite, and for the cases of Cd5 Zn7 and Cd5 Zn6 substitutions. The latter has 8.4 kJ/mol higher energy than the former.

If we assume that the ions always stay at the Ca(2) positions, the results do not provide a way to explain preferential absorption of Cd^{2+} relative to Zn^{2+} from binary solutions. However, as the statistical arguments presented above show, a small part of the ions, especially Cd^{2+} ions, could occupy Ca(1) positions as well. Such occupancy would be 6% for Cd^{2+} ions, and 1% for Zn^{2+} ions at room temperature, if statistics were the only factor influencing ion distribution.

Once we assume that a small portion of Ca(1) sites are occupied by Cd^{2+}, we may look at the relative energies of various doubly substituted systems. The relative energies of Zn^{2+} at Ca(1) and Cd^{2+} at Ca(2) are lower than for the opposite locations (Cd^{2+} at Ca(1), Zn^{2+} at Ca(2)). The same is true for the case where both substitutions occur at Ca(1) sites. At the same time, cadmium more easily substitutes at Ca(1) than zinc as the simulations of singly substituted systems showed. Thus, once a cadmium ion has occupied a Ca(1) site in a unit cell, it is less probable than average for a zinc ion to be placed in its vicinity. Such placement is energetically unfavorable. A single Cd^{2+} ion at Ca(1) position, a rare occurrence by itself, may influence the placement of several Zn^{2+} ions in its neighborhood and beyond, leading to the experimentally observed behavior.

A Zn^{2+} is statistically less likely to occupy a Ca(1) position. At the same time, even the small number of ions which substitute there, have a smaller influence on the cadmium ions at either Ca(1) or Ca(2), as the present results suggest. Therefore, the opposite type of hindering is less prominent, again supporting the available experimental evidence.

Even though the simulations of doubly substituted apatites did not include fluorapatite systems, we may infer by analogy with singly substituted systems that the Ca(1) sites are preferred also for the doubly substituted cases. Assuming this, their poorer sorbtion characteristics [27] can be related to more hindered mobility of the substituent ions in the tightly packed Ca(1) environment relative to the surroundings of the hydroxide ion channel. While the additional ions can possibly move into and out of the hyroxide channel relatively easily, it is much harder to envisage the actual movement of cations into and out of the Ca(1) positions.

4. Conclusions

Singly substituted hydroxy- and fluorapatites and doubly substituted hydroxyapatites were computationally modeled, where the substitutions were Cd^{2+} and Zn^{2+} ions replacing Ca^{2+} in either or both of the structurally inequivalent positions.

For singly substituted cases, a preference to occupy the Ca(1) sites in fluorapatites and Ca(2) sites in hydroxyapatites was observed. This is in agreement with experimental findings about the cadmium substitutions.

For doubly substituted hydroxyapatites, there is a preference for both substitutions to occur in the Ca(2) position. A displacement of the hydroxide ion chain from the hexagonal axis of the ion channel favors situations where both substitutions are located on alternating crystallographic planes and on the same side of the channel.

The preference of both single and double substitutions to occur around the ion channel in hydroxyapatites leads us to suggest that migration might proceed primarily via these channels. Since Ca(1) positions are preferred in fluorapatites, we also think that this preference accounts for the poorer sorbtion characteristics of fluorapatites.

A mechanism is proposed where occupation of a Ca(1) site by a cadmium ion creates an area in its vicinity where placement of Zn^{2+} is less probable than average, which would explain the relatively poor uptake of Zn^{2+} ions from binary Zn/Cd solutions.

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