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Local ordering of hydroxy groups in hydroxyapatite

N. H. de Leeuw

Department of Chemistry, University of Reading, Whiteknights, Reading, UK RG6 5XE. E-mail: n.h.deleeuw@reading.ac.uk

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Density functional theory calculations of hydroxyapatite identified the oxygen and hydrogen positions of the hydroxy groups in the crystal structure to be well defined, alternating in a column in the *c*-direction, and we predict that the experimentally found oxygen and hydrogen disorder is due to the presence in the crystal of differently oriented locally ordered domains, a finding which is important for studies of crystal growth and surface reactivity.

Apatites $Ca_{10}(PO_4)_6(F,Cl,OH)_2$ are a diverse class of minerals, which are becoming increasingly important as likely candidates for use as biomaterials. They are the most abundant phosphorus-bearing minerals and are found extensively in igneous, metamorphic and sedimentary rocks, mainly in the form of fluor- or chlor-apatite.[1] More recently, hydroxyapatite has increased its prominence due to its biological role as one of the main constituents of mammalian bones and teeth enamel.[2] As such, hydroxyapatite may be immensely valuable in the manufacture of artificial bones, while another possible application is to use ceramic implants as a support for the crystallisation and layer growth of hydroxyapatite, which can then bond to living bone, aiding the acceptance by the body of the implant material. It is necessary for the success of these and other applications, such as the replacement of the hydroxy groups by fluorine ions to strengthen tooth enamel and prevent caries,[3] that we obtain a detailed knowledge of the structure of hydroxyapatite. Although crystallographic studies of the mineral have elucidated the locations of the heavier atoms in the hexagonal crystal structure,[4,5] the oxygen and hydrogen ions of the hydroxy groups are found to be disordered, each partially occupying two possible sites, and little is known about the hydroxy group environment in the crystal structure, *e.g.* whether the constituent atoms are completely disordered over the positions or whether there is local ordering of the groups within domains. It is important for the investigation of hydroxyapatite surfaces, *i.e.* in studies of crystal growth, interfacial bone/ceramic behaviour and interactions between natural bone material and organic matrices, that we have a good understanding of the sites and interactions of the hydroxy groups within the apatite crystal.

Computational methods are well placed to calculate at the atomic level the geometry and relative energies of the various possible hydrogen locations in apatite, investigations which are at present inaccessible with experimental techniques. The approach we have used is to employ quantum mechanical calculations based on density functional theory (DFT) to study the hydroxy groups in hydroxyapatite. The DFT methodology, often used within the generalized gradient approximation (GGA) and employing pseudo-potentials, is well established and has been successfully applied to the study of structural and electronic properties of complex materials, *e.g.* magnesium silicates[6] and microporous aluminium phosphates.[7] The VASP program[8–10] was employed to calculate the structure and total energies of a number of hydroxyapatite structures with different configurations for the hydroxy groups. We used a cut-off for the planewave energy of 500 eV, together with a $2 \times 2 \times 2$ k-point mesh, which led to a convergence of the total energy to within 0.01%.

Although a monoclinic form of hydroxyapatite is known, biological and synthetic hydroxyapatite has a hexagonal crystal structure with space group $C6_3/m$ and $a = b = 9.432$, $c = 6.881$ Å, $\alpha = \beta = 90$, $\gamma = 120°$.[1,2] After full electronic and ionic optimisation, the structure with the lowest energy configuration of the hydroxy groups relaxed to $a = b = 9.563$, $c = 6.832$ Å, $\alpha = \beta = 90$, $\gamma = 120°$, in excellent agreement with the experiment (discrepancy $\leqslant 1.5\%$). The F^- or OH^- ions in apatite structures are located one above each other in a column parallel to the *c*-axis (into the paper in Fig. 1), where the F^- ions in fluorapatite are located at a crystallographic symmetry position (0, 0, 0.25), while the hydroxy groups in hydroxyapatite are located either above or below the symmetry position in the *c*-direction (oxygen at 0, 0, 0.2008, hydrogen at 0, 0, 0.0617). The deviation of the hydroxy group away from the symmetry position, leading to four possible locations in the unit cell, on either side of two symmetry positions, causes disorder of the oxygen and hydrogen ions. In this work, we investigated whether the occupancy of the oxygen and hydrogen sites is likely to be completely random or whether we could identify local ordering in domains. To this end, we calculated four possible configurations for the oxygen and hydrogen ions in hydroxyapatite, shown in Table 1, where for clarity the (Cartesian) symmetry positions are identified together with the hydroxy group positions above and below the symmetry position in the *c*-direction. Table 1 further shows which of the oxygen and hydrogen positions are occupied in the different calculations with their final coordinates in the *c*-direction, where the unit cell shown is periodically repeated in three dimensions. In configuration 1, both hydroxy groups are located at the two sites corresponding to one symmetry position, while configurations 2 and 3 have the hydroxy groups located at sites corresponding to both symmetry positions. In configuration 2, all hydroxy groups are lined up with the hydrogen and oxygen ions alternating along the *c*-axis, whereby each OH^- group forms one O–H bond of 0.957 Å and one rather long O···H hydrogen bond of 2.483 Å, while configuration 3 forms a column of pairs of OH^- groups, with the hydrogen ions pointing towards each other at a separation of only 0.849 Å and an O···O separation of 4.117 Å. Finally, in configuration 4 we investigated whether the oxygen and hydrogen ions of hydroxy groups were likely to be found separated in the apatite structure, by splitting up one OH^- group into its constituent atoms, whereby the hydrogen atom of the remaining hydroxy group

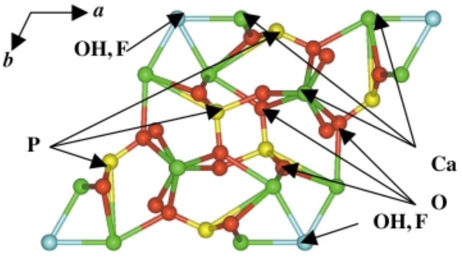

Fig. 1 Structure of the hexagonal apatite unit cell, showing the position of the fluoride or hydroxy anions in the *c*-direction into the plane of the paper [O = red, Ca = green, P = yellow, F(OH) = pale blue].

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Table 1 The experimental and calculated Cartesian coordinates (*c*-direction) of four different hydroxy group configurations in the hydroxyapatite structure, together with the calculated total energies

Symmetry position		Hydroxy sites		Configuration 1		Configuration 2		Configuration 3		Configuration 4	
F	1.720	H(1)	0.425	H(1)	—	H(1)	0.456			H(1)	0.520
		O(1)	1.382	O(1)	—	O(1)	1.453				
		O(2)	2.059	O(2)	—			O(2)	1.728	O(2)	1.518
		H(2)	3.016	H(2)	—			H(2)	2.722		
F	5.160	H(3)	3.865			H(3)	3.873	H(3)	4.146	H(3)	3.853
		O(3)	4.822			O(3)	4.871	O(3)	5.140	O(3)	4.851
		O(4)	5.499								
		H(4)	6.456								
Total energy/eV				Not converged		−311.171		−310.740		−311.175	

can form a hydrogen bond to the separated oxygen atom at 1.806 Å, while the separated hydrogen is in a position to form one short and one long hydrogen bond with the oxygen atoms at 1.634 and 2.483 Å.

After electronic and ionic relaxation, the total energies of the structures are compared (Table 1). We find that starting configuration 1, where two hydroxy groups were located either side of a single symmetry position, did not lead to a stable structure. Configuration 3 led to a stable structure, but the positions of the hydroxy groups had shifted away from the experimental locations by about 0.3 Å to the positions shown in Table 1, due to repulsion between the two neighbouring hydrogen ions, which leads to an increase in the distance between the hydroxy groups of 0.65 Å. The structure has somewhat expanded from the experimental structure in the *a* and *b* directions to $a = b = 9.551$ Å and contracted in the *c*-direction, $c = 6.868$ Å. Configurations 2 and 4 are the most stable structures, with practically identical energies ($\Delta E < 0.4$ kJ mol^{-1}). On inspection of Table 1, we see that the hydrogen and oxygen ions in configuration 2 remain virtually at their initial positions with lengthening of the O–H bond lengths from 0.957 to 0.998 Å. The *a* and *b* vectors increase to $a = b = 9.564$ Å, but contraction occurs again in the *c*-direction, $c = 6.831$ Å, which causes the apparent shift of the oxygen and hydrogen ions away from their initial position. In configuration 4 ($a = b = 9.563$, $c = 6.832$ Å), the dissociated hydroxy group in the initial structure has recombined upon geometry optimisation, and is located at the same site as in configuration 2, with a final O–H bond length of 0.998 Å, forming a series of hydrogen-bonded interactions down the *c*-axis at alternating O···H distances of 2.335 and 2.500 Å. If we compare these hydrogen bonds to configuration 2 (Fig. 2), where we find all O···H interactions down the *c*-axis at 2.42 Å, it is clear that configuration 2 is a more regular structure even though energetically identical. Contour plots of the electron density in the plane of the hydroxy groups (Fig. 2) show that the O–H bond has covalent character, but bonding of its oxygen atom to neighbouring calcium ions is fully ionic, as is the interaction between calcium ions and the oxygen atoms of the phosphate groups. Bonding within the phosphate groups is found to be covalent in character, in agreement with quantum chemical calculations of aluminium phosphates.[11]

Our calculations of different possible configurations of hydroxy groups within the hydroxyapatite structure have shown that there is a preferred arrangement of the hydroxy groups, where the energetically most favourable configurations (2 and 4) have all OH^- groups lined up with oxygen and hydrogen ions alternating in a column parallel to the *c*-axis (Fig. 2). These columns of aligned OH^- groups can of course be found in two directions, either up or down the *c*-axis, and hence we predict that the hydroxyapatite structure will consist of local domains of these well-ordered OH^- columns. When the OH^- groups have neighbouring oxygen ions (configuration 1) the structure is not stable, while introducing a pair of hydroxy groups with hydrogen ions in neighbouring positions (configuration 3) costs approximately 42 kJ mol^{-1} (0.436 eV/OH pair). A change in the ordering of the hydroxy groups within columns is therefore not energetically impossible, and may be promoted by the presence of anionic impurities such as F^-.

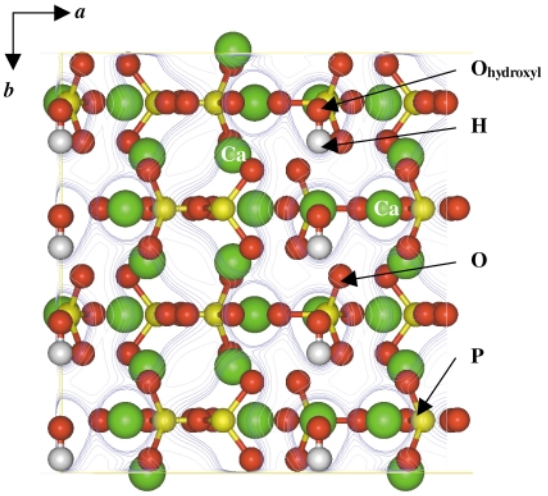

Fig. 2 Relaxed apatite crystal with OH^- configuration 2, showing electron density contour plots in blue (O = red, Ca = green, P = yellow, H = white, contour levels from 0.05 to 0.30 e Å^{-3} at 0.05 e Å^{-3} intervals).

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