A theoretical and experimental study of lead substitution in calcium hydroxyapatite

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Characterization of lead substitution for calcium in hydroxyapatite (CaHA) is carried out, using experimental techniques and Density Functional theoretical (DFT) analyses. Theoretical modeling is used to obtain information of the Pb chemical environment for occupancy at either Ca(1) or Ca(II) sites of CaHA. Effects of the larger ionic radius of Pb⁺² compared to Ca⁺² are apparent in embedded cluster calculations of local chemical bonding properties. DFT periodic planewave pseudopotential studies are used to provide first-principles predictions of local structural relaxation and site preference for Pb_xCa_{10-x}HA over the composition range $x \le 6$. General characteristics of the polycrystalline material are verified by X-ray diffraction and FTIR analysis, showing the presence of a single phase of CaHA structure. A short range structure around lead is proposed in order to interpret the Pb L-edge EXAFS spectrum of the solid solution Ca_{6.6}Pb_{3.4}HA. In this concentration we observe that lead mainly occupies Ca(II) sites; the EXAFS fit slightly favors Pb clustering, while theory indicates the importance of Pb–Pb avoidance on site (II).

1. Introduction

Apatites are calcium phosphate compounds displaying a wide compositional variation within a single structural motif. Mineral apatites form an important component of the earth's crust and contain a mixture of halides and hydroxyl groups, with fluoroapatite Ca10(PO4)6F2 (FA) being a well-known highly stable synthetic compound. Calcium hydroxyapatite (CaHA), with nominal composition $Ca_{10}(PO_4)_6(OH)_2$ is known for its facile ion-exchange properties, playing a multifaceted role in medical, environmental, and chemical applications.¹⁻¹⁵ It is the classic bone-analog ceramic with wide applications in clinical practice, as in bone and dental reconstruction.²⁻⁴ Further, the pressing problem of lead poisoning in humans due to environmental contamination requires an understanding of lead uptake and retention in bone.⁶⁻⁹ CaHA has also been recognized for its potential in trapping and retention of toxic heavy metals in ground water and soil.¹⁰⁻¹³ For example, the application of apatite waste forms in the treatment of water-soluble radioactive wastes has shown an excellent capability for uptake of Cs and Sr, at relatively low (500 °C) thermal treatment temperatures.¹⁰ Metal substitution on the Ca sites involves, for example, the biologically important iron, copper, zinc, cadmium and lead. Carbonate substitution occurs at both hydroxyl and phosphate sites, and along with Ca-deficient HA, plays an important role in bone structure, in nanocrystalline form.

Metal complexes like vanadate $(VO_4)^{3-}$ and molybdate can substitute for the phosphate $(PO_4)^{3-}$, and have been synthesized and characterized as environmentally friendly catalyst materials. Nonstoichiometric calcium hydroxyapatites with composition $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$ have been shown to be catalytically active in oxidation of methane with NO.16 Modification of this active material by metal doping could be expected to provide the 'tuning' benefits of multiple active sites. Thus, lead-doped CaHA has been shown to be effective in oxidative coupling of methane to ethane at the relatively low temperature of 700 °C.¹⁷ It is believed that Pb is in this case surface-bound to the apatite particles. It is known that Pb²⁺ in solution exchanges rapidly with Ca, causing morphological changes in the surface region. It has been proposed that the adsorption of lead to form $Pb_{10-x}Ca_x$ $(PO_4)_6(OH)_2$ is rapidly followed by formation of the very stable and structurally different pyromorphite phase Pb₁₀ (PO₄)₆(OH)₂.^{13,14}

In the following we shall refer to the endpoint of 100% Pb substitution for Ca on the HA lattice as PbHA. Rietveld analysis of X-ray diffraction data on Pb-substituted stoichiometric CaHA suggests that the most stable bulk site is replacement at Ca(II) positions, see Fig. 1.^{15,18,19} A similar conclusion was reached in X-ray studies of the strontium–lead mixed compound $Sr_{10-x}Pb_xHA$ synthesized in aqueous media.²⁰

Applications of CaHA and its derivatives almost invariably involve deployment as micro- (or more recently nano-)

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Fig. 1 Structure of CaHA seen (a) in top view along *c*-axis, and (b, c) about Ca(II) and (d, e) Ca(I) sites.

particles or thin films; however, in order to understand metal uptake and surface properties we must also understand bulk properties. In the present work we report on nanoparticle syntheses, which incorporate Pb into the bulk structure as well as a probable surface phase. The resulting material is characterized by FTIR, synchrotron X-ray diffraction, and X-ray absorption (XANES and EXAFS). In addition, density functional theory (DFT) calculations using embedded cluster and periodic planewave/pseudopotential models are carried out on Pb-doped CaHA to explore physico-chemical modifications induced by substitution.

2. Theoretical methodology

Periodic DFT calculations

First principles structure optimization of selected bulk and solid solution structures of the CaHA/PbHA system were carried out using the planewave–pseudopotential DFT approach as implemented by the VASP code.^{21–24} The relevant calculation details are as follows: The generalized-gradient approximation (GGA)^{25,26} to density functional theory is used. The planewave basis set is cut off at 450 eV and coreelectrons are represented using Vanderbilt ultrasoft pseudopotentials.^{27,28} Numerical integrations over the Brillouin zone were performed using a 2 × 2 × 2 Monkhorst–Pack grid.²⁹ In the calculations, all structural parameters (internal and cell dimensions) of the respective unit cell were relaxed. All optimizations were recursively repeated at least once in order to reduce the dependence of final structure and energy on the initial cell volume. The stability of the results with respect to both plane wave cutoff and *k*-point grid size was ascertained by trial calculations with larger cutoffs (up to 500 eV) and *k*-point grids (up to 4 × 4 × 4) on pure and Pb-doped CaHA. From these trials, we estimate the error in the total unit cell energy to be approximately 0.05 eV, which is ~0.02% of the total; more relevant for our purposes is the estimated error in the Pb preference energy for sites Ca(I) and Ca(II), which is converged to better than 0.01 eV.

Embedded cluster DFT calculations

Clusters containing 48-105 atoms in the variational space were treated by the DF embedded cluster approach.³⁰⁻³² Nearminimal numerical atomic orbital basis sets, partially optimized in the cluster, were used for variational expansion of the DF wavefunctions. Both nonrelativistic and fully relativistic versions of the Discrete Variational method^{33,34} were used in order to identify any important relativistic effects on the Pb valence levels. The Coulomb potential was represented to varying degrees of precision within the Self-Consistent-Charge model (based upon output Mulliken populations) and the Self-Consistent-Multipolar model (least squares expansion of charge density in auxiliary functions³⁵) in order to investigate sensitivity of Pb-ligand interactions to details of the local environment. The exchange-correlation potential made use of the parametrization of Vosko, Wilk, and Nusair.³⁶ The number of electrons assigned to an embedded cluster was chosen initially by reference to the formal valency of the constituents, and refined during self-consistent iterations. Clusters with a variable number of atoms were used to explore consequences of interatomic interactions approximated in the embedding, number of integration points, number of angular and radial degrees of freedom in potential and wavefunction expansions, etc.

Input geometries were variously selected for the unrelaxed CaHA lattice, for atomistic simulation results, and for the relaxed band structure results. Since lead is found to be not far from its nominal divalent state, small variations in near-neighbor distances produced correspondingly small changes in electronic distributions. Self-consistent charge distributions, Mulliken atomic orbital populations, bond order matrices, spectroscopic Densities of States, and charge-density maps were generated to permit analysis of chemical bonding features. Discussion of general features of HA bonding and results expected for cation substitution can be found in our previous work on Zn:HA³⁷ and Fe²⁺/Fe³⁺:HA.³⁸

3. Materials and experimental methods

Hydroxyapatite was synthesized from dropwise addition of a $(NH_4)_2HPO_4$ aqueous solution to $Ca(NO_3)_2$ solution at 80 °C, pH = 11. After the addition, the solution was stirred for 2.5 h at the same temperature. The precipitate was separated by

filtration, repeatedly washed with deionized boiling water and dried at 100 °C for 24 h. Polycrystalline and nanocrystalline materials with a controlled range of composition and particulate size have been prepared. In the following we focus upon a single typical intermediate Pb-substitution composition. The synthesis of CaHA doped with 30 mol% Pb (referred to hereafter as Pb30HA) followed the same procedure as just described but solutions of Pb(NO₃)₂ and Ca(NO₃)₂ were used. Calcium, phosphorus and lead contents were estimated by inductively coupled plasma optical emission spectrometry (ICP-OES). X-Ray diffraction (XRD), X-ray absorption (XANES and EXAFS) and Fourier Transform Infrared Reflectance (FTIR) spectroscopy were used to characterize sample mineral composition, crystallinity and lattice parameters.

Synchrotron XRD data were collected on polycrystalline samples at two energies 55.57 keV and at 88.23 keV, using an image plate detector. These diffraction experiments were carried out at the high-energy beamline (ID 15B) of the European Synchrotron Radiation Facility (ESRF). Rietveld analysis was performed on the XRD data using the program FullProf. The infrared analysis was performed with a Perkin-Elmer FTIR-System 2000 spectrometer. The elemental concentrations were determined by ICP-OES (Ca and P) and flame atomic absorption spectrometry (Pb) using a Perkin Elmer ICP-OES Plasma 1000 and a Perkin Elmer-1100 B AA spectrometer, respectively. EXAFS and XANES measurements at the Pb L3 edge were performed at the beam line BM29 of the ESRF storage ring.

4. Results and discussion

Periodic DFT calculations

Using the periodic DFT model, we consider various solid solutions of CaHA and PbHA in order to understand structure, energetics and possible ordering of Ca and Pb on the cation sublattice. The cell dimensions for bulk CaHA are computed to be a = b = 9.560 Å, c = 6.863 Å, which compares favorably with the experimental values of a = b = 9.43 Å, c = 6.88 Å^{39,40} as well as the previous theoretical result of deLeeuw *et al.* (a = b = 9.56 Å, c = 6.83 Å)^{41,42} using an almost identical model. The bulk cell dimensions of the other end-member PbHA, in which all Ca atoms are replaced by Pb, are computed to be a = b = 10.063 Å and c = 7.455 Å, also in good agreement with estimated experimental values of a = b = 9.86 Å and c = 7.42 Å.^{18,19,43} The theoretical trend appears to be a less than 2% overestimation in the *a* and *b* axes, and tiny (<0.2%) underestimation in the *c*-axis.

Before we discuss Pb substitution in this lattice, we must briefly consider the placement and orientation of hydroxyanions (OH⁻) in the apatite lattice. Slightly displaced along the [001] direction out of the triangular plane of Ca(II) sites, a number of positional combinations arise depending on (1) whether the displacement takes the OH group above or below the Ca(II) plane, (2) whether the O–H bond direction is parallel or antiparallel to this displacement, and (3) the orientation/ displacement of neighboring OH groups in the *c*-axis channel. Using first-principles computer models, these combinations have been considered in some detail by deLeeuw⁴⁴ who reports a preference for OH groups ordered into hydrogen-bonded \cdots O-H \cdots O-H \cdots O-H \cdots chains along the channel. While on the larger sample length-scales relevant to our diffraction experiments the OH group placement may well be considered as disordered, on the atomic length-scale of our defect calculations the local ordering of OH-groups matters. This is because the alignment of OH groups into chains along the c-axis breaks the mirrorplane-symmetry going through the Ca(II) triangle plane of the apatite unit cell which leads to a local reduction of the spacegroup from $P6_3/m$ (#176) to $P6_3$ (#173). Under the reduced symmetry, the six Ca(II) sites in the CaHA unit cell remain equivalent, while the four Ca(I) sites split into two subgroups of two sites each. These two subgroups will be referred to in the following as Ca(1a) and Ca(1b) and they differ slightly in their local coordination environment as will be discussed below.

A single Pb²⁺ cation can substitute for Ca(1a), Ca(1b) or Ca(II) in the CaHA lattice which leads to distinct geometries, referred to in the following as Pb(1a), Pb(1b) and Pb(II), respectively. We stress that our calculations are performed using a single HA unit cell; thus, we simulate in actuality a 10 at.% solid solution of Pb in CaHA. In this model, the energy difference between Pb(I) and Pb(II) computes to 0.035 eV [Pb(Ia)] and 0.102 eV [Pb(Ib)] in favor of Pb(II) substitution. The calculated preference for Pb(II) substitution is in qualitative agreement with the substitution model deduced from diffraction [15,18-20, vide infra]. Another interesting aspect of this result is the rather large energy difference between Pb substitution at Ca(Ia) and Ca(Ib) sites. While both sites share very similar coordination environments, the local energetic response to Pb substitution is very different. Note how the energy difference between Pb(Ia) and Pb(Ib) is substantially larger than that between Pb(Ia) and Pb(II).

Because the separation between the Pb substituent and its nearest periodic image is rather small (~ 6.9 Å) in our single unit cell model, we conducted additional calculations using a $1 \times 1 \times 2$ supercell (equivalent to a 5 at.% Pb solid solution) in order to ascertain that the computed preference is representative for a more dilute limit. In this supercell model the nearest Pb–Pb separation is 9.6 Å, and the Pb(II) site preference is found to be increased to 0.054 eV.

Since the ionic radius of Pb^{2+} is 0.2 Å greater than that of Ca^{2+} , a rigid ion model would suggest a corresponding expansion of Pb–O ligand distances. The periodic cell calculations for 5 and 10 at.% Pb permit a check on this assumption. For pure CaHA the calculated Ca(1)–O distances are 2.42, 2.48, and 2.81 Å [for Ca(1a)] and 2.39, 2.44, and 2.89 [for Ca (1b)], compared to experimental values of 2.41, 2.45, and 2.81 Å. The Ca(1b) site is thus distinguished from the Ca(1a) site by reduced distances to the six 1st and 2nd neighbor atoms (at 2.39 and 2.44 Å) and increased distance to the three 3rd neighbor atoms (at 2.89 Å). This is consistent with our finding that substitution of the larger Pb cation at Ca(1a) is energetically preferable over substitution Ca(1b).

For the Pb₁Ca₉ composition in the $1 \times 1 \times 1$ cell, the corresponding Pb(1a)–O distances are 2.56, 2.68, and 2.78 Å; for Pb₁Ca₁₉ in the $1 \times 1 \times 2$ cell the Pb(1a)–O distances are 2.56, 2.68, and 2.79 Å. The $1 \times 1 \times 1$ cell distances for Pb(1b)-O are 2.54, 2.64 and 2.85 Å. From these data we see that the

lattice reacts to Pb(1) substitution in an *anisotropic* manner, with nearest neighbor distance increasing by 0.14 Å, 2nd neighbor by 0.20 Å, and 3rd neighbor actually decreasing slightly (-0.02 Å) for the Pb(1a) site and similar trends for Pb(1b) site. The Pb(1a)–O distances calculated for the more dilute $1 \times 1 \times 2$ cell show hardly any differences compared to $1 \times 1 \times 1$ results, suggesting that the single unit cell model provides an adequate representation of the Pb(1) defect.

Turning now to the Ca(II) site, the calculated Ca(II)-O distances are 2.34, 2.35, 2.37, 2.41, 2.48, and 2.52 Å compared to experimental values of 4×2.36 , 2.39, and 2.51 Å. For the Pb_1Ca_9 composition in the 1 \times 1 \times 1 cell, Pb(II)–O distances were calculated as 2.45, 2.47, 2.51, 2.61, and 2.62 Å; for Pb_1Ca_{19} in the 1 \times 1 \times 2 cell the Pb(II)–O distances are 2.48, 2.50, 2.50, 2.56, 2.60, and 2.62 Å. Expansion around the Pb(II) site is more uniform than that of Pb(1), ranging from 0.11 to 0.17 Å, but again less than predicted by a rigid ion model. The more dilute $1 \times 1 \times 2$ cell shows an increase of first and 2nd neighbor distances by 0.03 Å, doubtless reflecting the more open structure around site (II). More distant neighbor distances are hardly altered. Taken all together, these neighbor-distance data demonstrate that Pb substitution for Ca is not simply that of rigid divalent ions, and that Pb is somewhat 'softer', which is indicative of significant covalent interactions.

We now consider solid solutions with a higher Pb content in order to address the question whether higher Pb-content in the lattice would lead to some sort of local or global ordering. To this end it is useful to define the excess energy E_x of a solid solution $Pb_xCa_{1-x}HA$ structure relative to those of the two end-members CaHA and PbHA,

$$E_x = E(Pb_xCa_{1-x}HA) - x E(PbHA) - (1 - x) E(CaHA)$$
(1)

where x ranges between 0 and 1, and lattice energies are normalized per cation site.

Computed excess energies for a number of distributions of 0 to 6 Pb atoms over the 10 cation sites of a single HA unit cell are reported in Table 1. For present purposes, an initial set of sublattice-segregated configurations was generated under the assumption that the Ca(II) sublattice is occupied first with Pb, and that the Ca(I) sublattice is occupied only above 60 mol.% when all type-(II) sites are filled. Within this constraint, all positional configurational combinations (i.e., distribution of Pb and Ca cations over available sites) in a single HA unit cell up to 60 mol.% Pb were considered in our calculations. The notation [p + q] is used to identify p-atom occupancy on one Ca(II) triangle and q-atom occupancy on an adjacent triangle. The modifiers -trans, -cis, -mer, and -fac serve to identify orientation of Pb(II) sites on one triangle relative to the other. The notation and corresponding structures are illustrated in Fig. 2. In addition, we constructed a number of *mixed* configurations, with Pb atoms distributed over both Ca(I) and Ca(II) sublattices. Due to the much larger number of combinations, we have not comprehensively surveyed all possible structural variations of mixed Pb(I)/Pb(II) configurations. The mixed configurations considered here were designed to be particularly stable, augmenting favorable Pb(II) configurations from the segregated set with additional Pb atoms in the Pb(Ia)

sublattice. With the mixed set of configurations we intend to probe whether Pb(I) occupation becomes energetically favourable prior to the complete occupation of the Ca(II)-sublattice by Pb. This has been proposed previously as an explanation for an observed break in the experimental *c*-axis versus Pb concentration curve at ~45 mol%.¹⁸

HA solid-solution system for x up to 60% is summarized in Table 1 and shown graphically in Fig. 3. Insights into the energetics of the solid solution and preferences in the distribution of cations over sites can be gained by looking at the most stable configuration for a given composition. We note that our configurations are generated within a single unit cell, which means there may exist other, more stable configurations with a larger cell repeat. Thus, the configurations shown here represent energetic upper bounds; however, we believe they broadly outline the phase field of the Pb_xCa_{1-x}HA system. Excess energies are positive across compositions across the 0-60 at.% range considered here, which suggests that these compositions are unstable with respect to dissociation into the two endmembers CaHA and PbHA. Preliminary phase-field studies show that the solid solution is energetically favorable (negative excess energies) at very high Pb-content. At the CaHA end of the phase diagram, the excess energy first exhibits an almost linear increase with concentration as expected in the dilute limit which extends over the 5 and 10 at.% data points. At 20 at.% a drop in the excess energy occurs, indicating that Pbatoms are arrayed in relatively stable configurations. Designated by us as the [1 + 1]-trans (cf. Fig. 2), it is characterized by two Pb atoms occupying each one of the two type-(II) triangular faces that constitute the channel in the HA unit cell. The triangular faces are in the *a*-*b* plane of the crystal and are arranged together in the shape of an antiprism (or a distorted octahedron). The two Pb(II) atoms are placed into different triangles and on opposite ends of the antiprism. While this arrangement maximizes the distance between the Pb atoms on the Pb(II) sublattice, this does not explain the gain in excess energy relative to the 10% and 30% configurations; somehow the symmetry of the configuration appears to release the strain due to the larger Pb cation. The 40% composition with four Pb(II) arranged in the [2 + 2]-trans configuration appears to be similarly stabilized relative to its compositional neighbors at 30 and 50% (ignoring the mixed configurations for the moment). The 30% 3 Pb(II) composition is most stable in the [2 + 1]-mer configuration, and for 50% there is only a single possible configuration ([3 + 2]) involving five Pb(II) in a single HA unit cell.

When we considered mixed configurations, we combined the favorable [1 + 1]-*trans* and [2 + 2]-*trans* configurations on the Pb(II) sublattice with one or two Pb on type-(Ia) sites. While these mixed configurations were higher in energy than the Pb (II)-only configurations for Pb-content up to 40%, mixed configurations were identified as lower in energy for 50 and 60% compositions. At 50%, four Pb(II) arranged into a [2 + 2]-*trans* configuration and a single Pb(Ia) resulted in a configuration that is 0.05 eV more stable than the Pb(II)-only [3 + 2] configuration. Similarly for 60%, a [2 + 2]-*trans* configuration and two Pb(Ia) is also 0.05 eV more stable than the [3 + 3] configuration; *i.e.*, a fully occupied Pb(II)-sublattice.

Table 1 Calculated excess energies E_x (given in meV per cation site; cf. eqn (1) in text) and relaxed $a_{avg} [= (a + b)2]$ and c/a_{avg} lattice parameters for a series of Pb_xCa_{1-x}HA solution structures. Some compositions x have several configurations listed, which arise from different distributions of Ca and Pb atoms over available cation sites in a single HA unit cell. Within each composition, configurations are ordered by stability with the most stable (lowest E_x) configuration listed first. The notation [p + q] denotes occupancy p on one Ca(II) triangle, and occupancy q on an adjacent triangle (see Fig. 2)

| Composition | Pb(ı) | Pb(II) | Configuration | $E_x/{ m meV}$ | $a_{ m avg}/{ m \AA}$ | $c/a_{\rm avg}$ |
|-------------|-------|--------|-------------------------|----------------|-----------------------|-----------------|
| 0% | 0 | 0 | CaHA | 0.0 | 9.560 | 0.718 |
| 10% | 0 | 1 | [1 + 0] | 15.7 | 9.651 | 0.714 |
| | 1 | 0 | [0 + 0], Pb(1a) | 19.2 | 9.570 | 0.727 |
| | 1 | 0 | [0 + 0], Pb(1b) | 25.9 | 9.585 | 0.725 |
| 20% | 0 | 2 | [1+1]-trans | 11.6 | 9.778 | 0.705 |
| | 0 | 2 | [1 + 1]-cis | 24.8 | 9.724 | 0.712 |
| | 2 | 0 | 2 Pb(ia) | 27.9 | 9.590 | 0.734 |
| | 0 | 2 | [2+0] | 29.8 | 9.713 | 0.715 |
| 30% | 0 | 3 | [2 + 1]-mer | 22.3 | 9.818 | 0.709 |
| | 1 | 2 | [1 + 1]-trans, Pb(1a) | 28.3 | 9.792 | 0.713 |
| | 0 | 3 | [2 + 1]-fac | 33.9 | 9.767 | 0.715 |
| | 0 | 3 | [3+0] | 43.6 | 9.762 | 0.718 |
| 40% | 0 | 4 | [2+2]-trans | 19.5 | 9.819 | 0.714 |
| | 0 | 4 | [2+2]-cis | 28.8 | 9.829 | 0.715 |
| | 0 | 4 | [3 + 1] | 31.3 | 9.820 | 0.715 |
| | 2 | 2 | [1 + 1]-trans, 2 Pb(ia) | 36.1 | 9.767 | 0.726 |
| 50% | 1 | 4 | [2 + 2]-trans, 1 Pb(ia) | 21.3 | 9.848 | 0.720 |
| | 0 | 5 | [3+2] | 25.9 | 9.885 | 0.717 |
| 60% | 2 | 4 | [2 + 2]-trans, 2 Pb(ia) | 19.3 | 9.843 | 0.732 |
| | 0 | 6 | [3+3] | 23.9 | 9.892 | 0.726 |
| 100% | 4 | 6 | РЬНА | 0.0 | 10.063 | 0.741 |

summary, our configurational survey of $Pb_xCa_{1-x}HA$ structures illustrates the exclusive occupation of the Pb(II) sublattice up to about 40 at.%, and a prevalence of mixed configurations at 50 and 60 at.%.



Fig. 2 Cation neighborhood around the Pb(II) atom for different Pb-substitution environments [p + q], see text.

Embedded cluster DFT calculations

Both nonrelativistic and fully relativistic calculations were carried out on Pb-centered clusters embedded in CaHA, representing the dilute substitution limit. In general, all cluster models show that lead is approximately divalent, as expected. However, ionic–covalent interactions with the six nearest oxygens (or nine and seven if one counts second neighbors at Ca(1) and Ca(11) sites) lead to some significant charge redistribution among the Pb 6s, 6p, 6d valence shells. This is in contrast to the highly ionic Ca⁺² configuration found at these sites, and has been proposed as responsible for the



Fig. 3 Phase diagram showing excess energy E_x versus Pb_x composition and neighbor configuration [p + q].

observed dislocation of anion lattice positions in Pb-apatite compounds.¹⁸ Table 2 reports self consistent Pb atomic configurations, Mulliken charges, volume charges, and Pb-O shared charge for several of the models considered. The relativistic models suggest a slight decrease in Pb ionicity (Mulliken charge) compared to the NR models. This shift is the result of the subtle interplay between relativistic atomic level shifts and self-consistent charge flows (contraction of core, increasing nuclear shielding, with differential valence orbital expansion) which modify the crystalline or molecular potentials.³² Within the Pb ion, relative shifts of s, p, d and f orbitals occur along with spin-orbit splittings omitted in NR models; these effects lead to a relative increase of 6s character at the expense of 6p character in the present case. This further reduces the (already small) directionality of Pb-O bonds.

The summed Pb-O bond orders (off-diagonal charge matrix elements Q_{ii}) give evidence of the mixed ionic-covalent nature of the metal-ligand interaction. Independent of model (relativistic/nonrelativistic) and cluster size, the Pb-O bond order is negative, and ranges from 0.4 to 1.5e in magnitude, which represents a rather small amount of covalent density distributed over six ligands. This feature was discussed previously in the context of Ca-O interactions in carbonated CaHA.45 In the classic "hemispheric" coordination of many Pb complexes, valence 6sp occupancy manifests itself as a spatially directed lone pair.⁴⁶ Considerable qualitative discussion has been given to the conditions under which a 'stereochemically active' lone pair is present, as opposed to an 'inactive', presumably pure $6s^2$, lone pair. Graphical charge density analysis of the quasioctahedral environment of lead at both Ca(I) and Ca(II) sites shows a rather spherical Pb valence distribution, with a noticeable but small polarization component along the Pb-O bond directions. Fig. 4 shows the charge distribution in a Pb–O(I)–O(II) plane for site Pb(I). The observed shift of the Pb L3 edge of ~ 1 eV toward higher energy in Pb30HA compared to PbO is compatible with an increased ionicity, compared to that compound. On the other hand, the shift to higher energy ($\sim 1.2 \text{ eV}$) of the pre-edge structure as well as the shift to lower energy of the post-edge structure tell us that a simple ionic interpretation is not possible, offering further evidence for the importance of covalent bonding components. The partial densities of states diagram of Fig. 5 shows the relative position and contributions of Pb valence and oxygen 2s, 2p states to valence and low-lying excited states for substitution at site (II). We further see that, in accordance with expectations, the Ca^{+2} and P^{+5} states show very little overlap with Pb states in the valence region 0-5 eV below $E_{\rm F}$, with strong contributions appearing in the excited state region for $E > E_{\rm F}$.

Experimental

The FTIR spectrum of Pb30HA, Fig. 6, shows the characteristic vibrational bands of a hydroxyapatite with some dislocation caused by the calcium/lead substitution. The $\nu_{\rm s}$ O–H band at 3570 cm⁻¹ is shifted to 3561. The phosphate bands at 1100– 1039 cm⁻¹ (ν_3 PO₄³⁻), 962 cm⁻¹(ν_1 PO4³⁻), 603–566 cm⁻¹ (ν_4 PO₄³⁻) and 470 cm⁻¹ (ν_2 PO₄³⁻) are shifted to 1087, 1025, 951, 599, and 558 cm⁻¹, respectively, consistent with Pbinduced shifts seen by others.^{18,47} Broad phosphate bands characterize a structure with local disorder at PO₄³⁻ sites.⁴⁸ Carbonate bands at 1400–1550 cm⁻¹ (ν_3 CO₃²⁻) were present, indicating that carbonate ions were incorporated into the HA structure as an impurity during sample precipitation. This contamination is always observed when hydroxyapatite is prepared in ambient conditions. The broad band in the 3000 cm⁻¹ region is due to water molecules that are always present in non-annealed hydroxyapatite samples.

Rietveld analysis of the Pb30HA XRD pattern, see Fig. 7, revealed that just one mineral phase is formed. It was interpreted as a calcium and lead apatite, $Ca_{6.6}Pb_{3.4}(PO4)_6(OH)_2$, with lead occupying mainly Ca(II) sites (85%). The unit cell parameters of the as-prepared material were a = b = 9.5591 and c = 6.9722 Å. Table 3 shows the atomic positions of Pb30HA compared with a natural hydroxyapatite, and a nanoparticulate CaHA prepared in the same manner as Pb30HA.

The normalized XANES spectrum of Pb30HA is shown in Fig. 8. Approximate positions of the edge and pre-edge peaks were defined from the first derivative of the spectrum; the position of the post-edge peak was determined directly from the maximum of the white line in the absorption spectrum. Curve-fitting was performed using the ifeffit package.⁴⁹ Lorentz profiles were used to fit the pre- and post-edge peaks while the edge was fitted by an arctangent function. An oscillating EXAFS function was added to increase the quality of the fitting, assuming a single coordination sphere. All components of the fitted curve are shown in Fig. 8; the difference between the experimental and fitted spectra is shown at the bottom of the graph. The main features of the XANES spectra of Pb30HA and reference compounds PbO and PbO₂ are reported in Table 4. The position of the edge, in particular, confirms the formal valency +2 of lead in Pb30HA. Additional XANES features, namely pre-edge and post-edge structures and their widths, suggest a more complex mixed ionic-covalent

Table 2 Lead Mulliken atomic orbital populations, net charges Q(Mul), volume charges Q(Vol), and shared charge (bond order, Q(Pb-O)) calculated for embedded Pb:HA clusters, in the dilute limit. Volume integrations are defined by Fermi-Dirac functions $\{1 + \exp[\zeta(R - R_0)]\}^{-1}$ centered at each atom, with roll-over at $R_0 = 1.4$ a_0 and $\zeta = 2$. NR denotes non-relativistic model, REL is relativistic, for which *j* sub-shell occupancy is indicated

| Site/Model | Pb 6s | 6p | 6d | Q(Mul) | Q(Vol) | Q(Pb-O) |
|---------------------|-------|-----------|-----------|--------|--------|---------|
| Ca(I) NR 90 atoms | 1.32 | 0.19 | 0.09 | 2.41 | 3.12 | -0.43 |
| Ca(I) REL 63 atoms | 1.83 | 0.07 0.04 | 0.01 0.01 | 2.05 | 1.80 | -1.01 |
| Ca(II) NR 48 atoms | 1.39 | 0.16 | 0.09 | 2.37 | 2.49 | -1.19 |
| Ca(II) REL 48 atoms | 1.57 | 0.07 0.06 | 0.01 0.02 | 2.28 | 2.90 | -0.72 |



Fig. 4 Charge density contour map of Pb-O(1)-O(1) plane for Pb at Ca(1) site. Top: perspective view; bottom: equal-valued contour intervals.

bond structure in lead apatite compared to PbO. It is worth noting that the presence of the pre-edge peak (Pb 6s), almost undetected in the naked-eye spectrum is clearly revealed by the curve-fitting process.

The magnitude and imaginary part of the Fourier Transform of the weighted EXAFS oscillations are shown in Fig. 9 and 10, together with the respective fitting curves. The structural model used in the spectral simulations takes into account the results obtained from theoretical modeling and data available from XRD analyses, but with rounded off values. We assumed that half the sites of Ca(II) (Wyckoff site 6h) are occupied by Pb and only a small amount of sites of Ca(I) (Wyckoff site 4f) are substituted by Pb. The cation neighborhood associated to the Ca(II) site is schematized in Fig. 2 as part of a column of face-sharing trigonal antiprisms running along the 6_3 axis. Thus, the central atom (the absorber) A_0 has two nearest neighbors A1 belonging to the same triangular face, four second nearest neighbors A2 and two farthest neighbors A₃ in the two adjacent faces. Assuming a negligible occupation of site Ca(I) by lead in the solid solution, only two meaningful short range order parameters are needed to describe the solid solution; these are the substitution ratios of the first and second cation neighbors A_1 and A_2 . Site A_3 is too far



Fig. 5 Partial densities of states for Pb at Ca(II) site and nearby ions; relativistic model. In order, from bottom: Pb 6sp; P 3spd; Ca 4s; Oxygen (summed) 2sp.

from the central atom to contribute significantly to the EX-AFS spectrum. We further assume that backscattering from oxygen ligands is negligible. Initially, two independent parameters were attributed to the occupation ratios of each kind of neighbor A₁ and A₂, affecting all respective single and multiple backscattering paths. A third parameter was introduced to describe the Pb occupation ratio of site (1). The Feff8⁵⁰ calculation was based on the structural parameters given by ref. 18 in their refinement of Ca_{2.79}Pb_{2.21}(PO₄)₃(OH), where 71% of site Ca(II) is occupied by Pb. It was thus assumed that this phase best describes the neighborhood of Pb in site Ca(II).

Indeed, very poor simulations of the EXAFS spectrum were obtained when the XRD-refined data described in the preceding section were used. Subsequently, two overall Debye–Waller factors and path lengths deviation were used, one for each site (Ca(I) and Ca(II)). The multielectronic factor was used as calculated by Feff8 ($S_0^2 = 0.937$). In this case, good fits could be obtained but high uncertainties were associated to the order parameters. A single order parameter was then used and



Fig. 6 FTIR of a hydroxyapatite doped with 30% of lead.



Fig. 7 XRD pattern of hydroxyapatite doped with 30% of lead.



Fig. 8 Normalized XANES spectrum of Pb30HA at the L3 Pb edge (open circles) with the arctangent baseline, the fitted pre-edge and post-edge peaks (straight line) and the EXAFS oscillations (dotted line); the difference spectrum is plotted underneath.

two models were optimized in order to evaluate local order around the absorber. In the first one (model A), preferential agglomeration of lead atoms in the site of Ca(II) was forced by assuming only Pb occupation of the nearest sites to the absorber: $(2 - x) A_1$ sites and $(x) A_2$ sites being occupied. Including the absorber, this brings a total of three neighboring Pb atoms over any two adjacent Ca(2) triangles. In the second model (model B), the two sites A1 and A2 were constrained to have the same Pb occupation degree (x). This can be interpreted by assuming that Pb atoms first occupy the farthest site A₃ and that the remaining Pb atoms are then randomly distributed over the nearest sites A1 and A2. Model A corresponds then to a higher stabilization energy of pairs Pb-Pb while model B corresponds to a higher stabilization of pairs Pb-Ca. In both models, the fraction of Pb atoms in site (I) was kept as a free parameter.

The best fit of the experimental EXAFS data was obtained for model A and is presented in Fig. 9 and 10. Thus, we got [Pb in A₁] = 1.7(5) lead atoms in the same face as the central atom A₀ and a fraction [Pb(i)]/[Pb] = 0.2(2) of lead atoms occupying site (1) ($e_0 = -8(1)$ eV, *R*-factor = 0.05). Despite the high associated uncertainty, this value of the fraction [Pb(i)]/[Pb] is in good agreement with that given by XRD data. The value of the order parameter [Pb in A₁] is significant and suggests that the site (II) is not randomly occupied. Indeed, this value of the parameter should imply preferential substitution of Pb for Ca atoms in an entire face of the antiprism (Ca(II) triangle), without substitution in the two adjacent faces, that is: the Ca(II) triangles are alternatively occupied by three Pb atoms or three Ca atoms. However, the quality of the fit (*R*-factor) was almost equally good with model B. The main difference

Table 3 Atomic positions of a natural apatite HA-1,¹⁸ nanocrystalline apatite as prepared HA-2, and Pb30HA, from XRD Rietveld analysis. Fractional cell coordinates *x*, *y*, *z* in space group $P6_{3/m}$ and standard deviations σ are listed. Hydroxyl group *z*-coordinate actually varies with Pb content, see text

| | HA-1 | σ | HA-2 | σ | Pb30HA | σ |
|----------|--------|---|---------|----|---------|----|
| Ca(I) x | 1/3 | | 1/3 | | 1/3 | _ |
| v | 2/3 | _ | 2/3 | _ | 2/3 | _ |
| Z | 0.0015 | 1 | -0.0001 | 12 | 0.0020 | 23 |
| Ca(II) x | 0.2468 | 2 | 0.2468 | 5 | 0.2424 | 4 |
| v | 0.9934 | 1 | -0.0086 | 6 | -0.0108 | 6 |
| Z | 1/4 | _ | 1/4 | _ | 1/4 | _ |
| O(I) x | 0.3284 | 2 | 0.3243 | 12 | 0.3617 | 37 |
| y | 0.4848 | 2 | 0.4745 | 14 | 0.4755 | 26 |
| Z | 1/4 | _ | 1/4 | _ | 1/4 | _ |
| O(II) x | 0.5873 | 2 | 0.5809 | 13 | 0.5863 | 33 |
| y | 0.4651 | 2 | 0.4568 | 13 | 0.4472 | 26 |
| Z | 1/4 | _ | 1/4 | _ | 1/4 | _ |
| O(III) x | 0.3437 | 2 | 0.3474 | 9 | 0.3438 | 16 |
| y | 0.2579 | 1 | 0.2534 | 9 | 0.2490 | 19 |
| Z | 0.0702 | 2 | 0.0759 | 8 | 0.0819 | 17 |
| OH x | 0 | _ | 0 | _ | 0 | _ |
| v | 0 | _ | 0 | _ | 0 | |
| Z | 0.1950 | 7 | 1/4 | _ | 1/4 | _ |
| P x | | | 0.3987 | 7 | 0.4018 | 18 |
| у | | | 0.3689 | 6 | 0.3837 | 17 |
| Z | 1/4 | | 1/4 | — | 1/4 | |

Table 4Main XANES features for Pb L-edge in Pb30HA andreference compounds; all values are given in eV

| | Pre-edge (width) | Edge (width) | Post-edge (width) |
|------------------|------------------|---------------|-------------------|
| PbO | 13037.5 (6.7) | 13042.4 (3.5) | 13060.1 (6.5) |
| PbO ₂ | 13036.1 (7.4) | 13045.2 (3.9) | 13065.7 (14.1) |
| Pb30HA | 13038.7 (5.9) | 13043.9 (2.6) | 13059.4 (9.1) |



Fig. 9 Magnitude of the experimental (open circles) and fitted (solid line) EXAFS spectra of Pb30HA at the L3 Pb edge.

between the two models being that uncertainties over the order parameter (x) were comparatively larger in model B than in model A. In this case, small values of (x) were obtained, indicating less than three Pb atoms per cell occupying the sites of Ca(II). We should then conclude that experimental data are insufficient to provide information concerning the distribution of Pb over site (II). On the other hand, it is worth noting that the value obtained for Pb atoms in site (I) was independent of the model and confirmed the preferential occupation of site (II) by Pb. It is apparent that model A is in contradiction with theoretical energetic arguments presented above, while model B is consistent with theory.



Fig. 10 Imaginary part of the experimental (open circles) and fitted (solid line) EXAFS spectra of Pb30HA at the L3 Pb edge.

5. Concluding remarks

In the present work we report Density Functional analyses of bulk-substitution of Ca by Pb in CaHA over the composition range $0 \le x \le 0.6$ in Pb_xCa_{1-x}HA. This investigation throws light on the local chemical environment of lead and corroborates the interpretation of experimental results as due to divalent Pb occupying Ca sites. The anisotropic nature of Pb-induced local lattice expansion, and the small energy differences found to control site preference militate against highly simplified rigid-ion atomistic models. Moreover, the present first-principles data (energetics and atomic coordinates) can be used as a 'training set' to improve semiempirical interatomic potentials, within the framework of existing pairwise interactions. In the quasi-octahedral Ca sites occupied by Pb, no evidence is found for the frequently postulated stereochemically active 6sp lone-pair structure among the occupied states. Experimental syntheses, and FTIR, XRD, and XANES/EXAFS investigations of Pb:CaHA were reported. focusing upon a typical mid-range composition Pb30HA. The EXAFS spectrum of lead in Pb30HA was interpreted with the help of results obtained by theoretical analysis and XRD data. It was found that calcium-triangle sites along the c-axis, Ca(II), are preferentially occupied for a lead concentration of about 30 mol%, as suggested in previous studies. However, these sites may not be randomly occupied; at that lead concentration the EXAFS fitting model shows a slight preference for Pb-Pb clustering on alternating triangles, while theory predicts that Pb-Pb repulsions are sufficient to distribute the ions more evenly. Qualitative arguments based upon ionic size, and the predicted correlations between calculated lattice parameters and site energies argue in favor of the hypothesis that Pb ions on site (II) will minimize clustering.

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