The effect of chemical potential on the thermodynamic stability of carbonate ions in hydroxyapatite

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ABSTRACT

First-principles calculations were performed for CO_3^{2-} ions in hydroxyapatite in order to investigate the atomic structures and thermodynamic stability of CO_3^{2-} and its related defects. Two different chemical equilibrium conditions in high-temperature and aqueous-solution environments were considered, and atomic and ionic chemical potentials for the individual chemical equilibrium conditions were evaluated to calculate defect formation energies. It was found that A-type CO_3^{2-} (substituting OH^-) is energetically more favorable than B-type CO_3^{2-} (substituting PO_4^{3-}) in the high-temperature environment, whereas B-type is preferred to A-type in the aqueous solution environment. This result successfully reproduces experimentally observed trends. In the formation of A-type and B-type CO_3^{2-}, OH^- vacancies or protons (interstitial or substitutional) act as charge-compensating defects.

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1. Introduction

Human bones are composed of organic collagen fibers and inorganic hydroxyapatite ($Ca_5(PO_4)_3OH$, HAp) crystals. The inorganic component of biological HAp contains a variety of trace ions in the crystal lattice, which have a close relationship with the biological properties of HAp such as solubility and biocompatibility. Of the trace ions in HAp, carbonate ions (CO_3^{2-}) are most abundant, and it is thus important to understand the physical and chemical properties originating from the CO_3^{2-} present in HAp.

According to previous experiments, it was reported that there are two possible locations of CO_3^{2-} in HAp, the hydroxyl-group (OH^-) site and the phosphate-ion (PO_4^{3-}) site. Conventionally, the former case (OH^- substitution) is termed A-type substitution, while the latter is B-type substitution. Which of these two types of CO_3^{2-} substitution is preferred is dependent on the synthesis processes used. For instance, when HAp is produced by high-temperature processes such as solid-state reactions and subsequent sintering, CO_3^{2-} tends to be situated at OH^- sites (A-type substitution). On the other hand, low-temperature synthesis processes involving solution reactions result in CO_3^{2-} ions at PO_4^{3-} sites (B-type substitution). Biological HAp mainly contains B-type substituted CO_3^{2-}.

Since CO_3^{2-} has a planar triangular shape and substitutes OH^- ions or tetrahedral PO_4^{3-} ions, the two different types of CO_3^{2-} substitution may strongly affect the crystallinity of HAp and its resultant solubility. Therefore, it is necessary to understand the detailed atomic structure around CO_3^{2-} in HAp. For this purpose, experimental structural analyses of carbonated Hap have been performed by using X-ray and neutron diffraction with Rietveld analysis and Fourier transform infrared (FTIR) spectroscopy [1–7]. In the case of A-type substitution, X-ray diffraction and FTIR spectroscopy revealed that the triangular plane of CO_3^{2-} is almost parallel to the c axis and its apical direction is parallel or perpendicular to the c axis [1,2]. For B-type CO_3^{2-}, it was reported that the positions of the CO_3^{2-} plane correspond to one of the side planes of an original PO_4^{3-} tetrahedron and/or normal to the c axis [3]. Carbonated HAp with a mixture of A- and B-type substitution was also investigated, and was proposed to have a different orientation of CO_3^{2-} [4–6].

In addition to CO_3^{2-} atomic configurations, CO_3^{2-} has a different ionic charge from OH^- and PO_4^{3-} and thus the presence of charge-compensating defects has to be taken into account. In order to address this issue, first-principles calculations are a powerful tool, and have already been applied for CO_3^{2-} in HAp [8–11]. However, most of the previous calculations focused on CO_3^{2-} configurations in individual A- or B-type substitution cases. Astala and Stott studied A- and B-type CO_3^{2-} substitutions using first-principles density functional theory (DFT) calculations [10]. The authors evaluated the defect formation energies for various charge-compensating mechanisms, and showed that CO_3^{2-} at the PO_4^{3-} site (B-type) with

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a charge-compensating proton at a Ca^{2+} site is energetically the most stable. However, the chemical potentials used there were described by a combination of chemical potentials for several stable intermediate compounds. In order to investigate the dependence of CO_3^{2-} stability in HAp on processing conditions, it is straightforward to evaluate the defect formation energies by using atomic and ionic chemical potentials reflecting chemical equilibrium conditions in high-temperature and aqueous-solution environments.

In this study, systematic first-principles DFT calculations were performed for CO_3^{2-} defects in HAp, and the defect formation energies under high-temperature and aqueous-solution environments were evaluated. In order to investigate the effects of temperature and solution pH on the defect formation energies explicitly, standard and temperature-activity dependent terms of atomic and ionic chemical potentials for constituent elements were evaluated with first-principles total energies and experimental thermodynamic data. Our methodology to evaluate atomic and ionic chemical potentials described by functions of temperature and solution pH is intuitive and advantageous for revealing how the A- or B-type preference of CO_3^{2-} in HAp depends on the chemical environment. Based on the results, the physical and chemical origins of A- and B-type CO_3^{2-} substitution preference are discussed.

2. Computational procedure

2.1. Electronic structure calculations and supercell

All calculations in the present study were performed by the projector augmented wave method implemented in the VASP code [12–15]. For the exchange–correlation potentials, the generalized gradient approximation parameterized by Perdew, Burke and Ernzerhof was used [16], and $3p^6 4s^2$ for Ca, $3s^2 3p^3$ for P, $2s^2 2p^4$ for O, $1s^1$ for H, and $2s^2 2p^2$ for C were treated as valence electrons.

Wave functions were represented by plane waves up to a cut-off energy of 400 eV. For structural optimization, all atomic positions were optimized until all atomic forces became <0.02 eV $Å^{-1}$.

In the present study, two kinds of apatites, HAp and OAp (oxyapatite, $Ca_{10}(PO_4)_6O$), were treated as host crystals with CO_3^{2-}-related point defects therein. OAp is known as dehydrated HAp, and tends to form at high temperatures prior to the formation of tricalcium phosphate (TCP, $Ca_3(PO_4)_2$) [17]. As noted below, this behavior was used to investigate the stability of CO_3^{2-} defects in the high-temperature form of HAp. Fig. 1 shows the crystal structure of hexagonal HAp (space group $P6_3/m$) and OAp ($P\bar{6}$). In the case of HAp, OH^- ions are located along the c axis (OH^- column), whereas only O^{2-} ions are present in the column of the OAp crystal structure due to loss OH^- and H^+ ions (dehydration). Although there are several possibilities for the OH^- arrangement in HAp, it was found from our previous study [18] that an arrangement of –HO–HO–HO– is most stable. The calculated lattice parameters of HAp based on structural optimization were $a = 9.54$ Å and $c = 6.90$ Å, and those of OAp were $a = 9.59$ Å and $c = 6.88$ Å. In both cases, the calculated values were in good agreement with experimental data [19,20]. Based on the optimized crystal structures, supercells were constructed by doubling the hexagonal unit cells along the c axis, so that the numbers of supercells for HAp and OAp were 88 and 82 atoms, respectively. In the present supercell calculations, a $2 \times 2 \times 2$ k-point mesh was used for Brillouin zone integration. In order to check the supercell size effect, test calculations with 352-atom HAp supercells ($2 \times 2 \times 2$ extension of the hexagonal unit cell in all directions) were performed for a defect complex of an A-type substitutional carbonate ion and an OH^- vacancy. It was found that the difference in formation energy between the smaller (88 atoms) and the larger supercell is <0.02 eV per defect, which indicates that the supercell size does not affect the following discussion and conclusions. Note that the illustrations of atomic structures in this paper were performed by using VESTA [21].
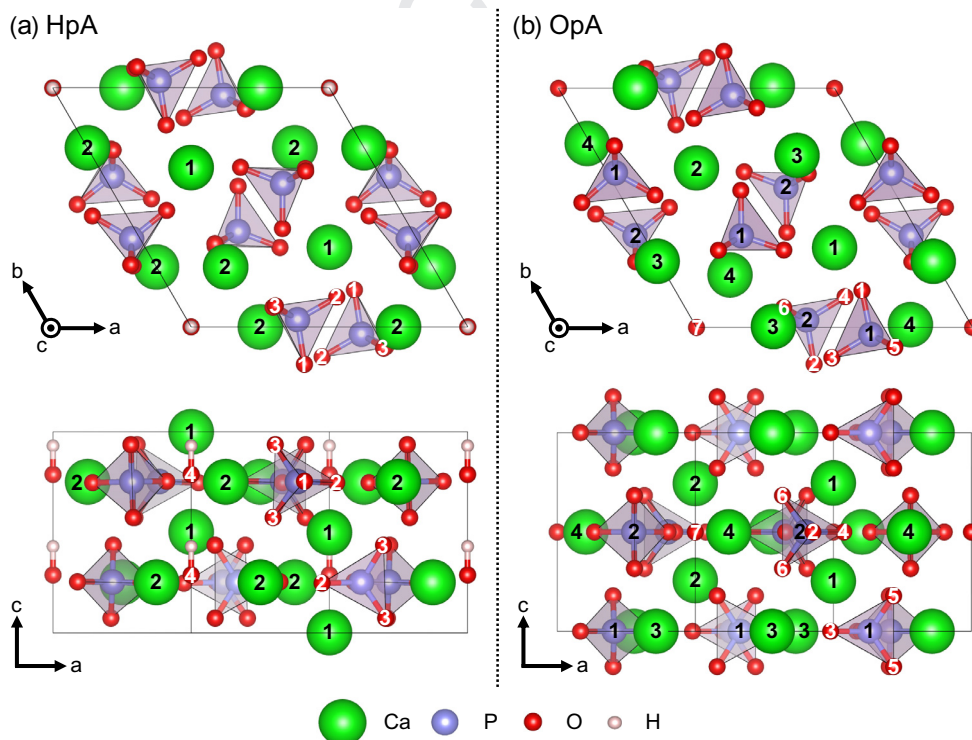
Fig. 1. Schematic illustrations showing the crystal structures of (a) HAp and (b) OAp. The numbers in the figure indicate different atomic sites. HAp in (a) has two non-equivalent Ca sites (Ca(1) and Ca(2)), one P site, four different O sites (O(1)–O(4)) and one H site, whereas OAp in (b) has four non-equivalent Ca sites (Ca(1)–Ca(4)), two different P sites (P(1) and P(2)) and seven non-equivalent O sites (O(1)–O(7)). In addition, the PO_4^{3-} groups are represented by the tetrahedra.