

The CO_2^- radical in the structure of type A carbonatehydroxylapatite by computer modeling

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Abstract. *The type A carbonatehydroxylapatite (CHAp) (with CO_3 -group or CO_2^- -radical replaced two hydroxyls in channel of hexagonal hydroxylapatite (HAp)) has been investigated by computer modeling in the GULP program using GRID-techniques. The 3x3x3 supercell with overall composition $[\text{Ca}_{270-x}\square_x]_{270}[\text{PO}_4]_{162}[\text{OH}_{52-y}(\text{CO}_3)_1\square_y]_{54}$ (0.16 wt % CO_2) at x and $y = 0$ or 1 has been considered. The web-sites of uagrid.org.ua and grid.inpracom.kiev.ua were used for calculations, which were executed in the "GEOPARD" virtual organization. It is established that in the most stable structures C lies in the channel at $z \leq 0.5$, H atoms of hydroxyls in channel fragments near structural defects direct in one side. Carbonate oxygens occupy sites close to such in bioapatite, accommodation of radical oxygens is substantially differed. Hydroxyl bond orientations in unidirectional channel fragments lead to the strong hydrogen-bonded interactions between O and H of different hydroxyls. The radical atom O3 is located near the OH vacancy (\square_{OH}) unlike the axial O2, so that the approximately aligned O2–C–O3 structure is formed (the O–O axis is oriented at an angle of 5.5° with the c-axis). Radical forming results in appearance of additional structural defects (close-spaced \square_{OH} and \square_{Ca}) and considerable displacements of ions in the nearest structure. The obtained data complement and are in agreement partly with experimental and theoretical investigations of type A CHAp. The obtained structure of CO_2^- -radical corresponds partly to expected one of radicals responsible for axial peaks in EPR spectra of type A CHAp.*

Keywords

Isomorphism, type A carbonatehydroxylapatite structure, CO_2^- -radical, computer modeling, GULP.

1 Introduction

Apatites $\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{Cl},\text{OH})_2$ are known to have large characteristic isomorphous substitutions. Apatites with CO_3^{2-} substitutions are widespread in the nature. Isomorphous variations in carbonateapatites (CAp) reflect the genesis of geological rocks in postmetamorphic processes [1 – 9]. Non-stoichiometrical carbonatehydroxylapatite (CHAp) with isomorphous substitutions and admixtures of mineral phases is the basis of the high-mineralized tissues (bones, teeth enamel) of living organisms [1, 3 – 8]. Investigation of carbonate and accompanying substitutions in hydroxylapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HAp) is important for solving mineralogical problems and developing synthesis technologies of biocompatible materials and matrices of sorbents and catalysts on the HAp basis [1 – 9].

2 Related works

The CO_3^{2-} -ions in natural, biogenic and synthetic carbonateapatites were established to replace F^- (OH^-)- ions in structural channels (type A CAp) and PO_4^{3-} -ions (type B CAp), resulting in structural defects and changes of physical and chemical properties [1, 3 – 7, 10].

Electronic paramagnetic resonance (EPR) is widely used to investigate crystallochemical properties of apatites. The strongest EPR peaks in biogenic and synthetic carbonateapatites are produced by CO_2^- -radicals on crystallite surfaces

and in the structure [7 – 9]. It is established that CO_2^- -radicals responsible for axial EPR signals are located in apatite channels [8, 9]. Formation mechanisms and structural environment of these radicals require further investigation.

Computer modeling complements experimental techniques in investigation of structural properties of solids [5, 8, 10 – 12]. Results of computer simulation of apatite structures with different substitutions have been reported by several authors [5, 8, 10, 12 etc]. The MD simulation has been employed to investigate the accommodation of carbonate in monoclinic HAp of types A and B [5]. The study of the electron density distribution in type A CHAp based on density-functional theory has shown that this distribution diverged significantly in the vicinity of CO_3^{2-} -ions and CO_2^- -radicals, but the effective O charges in carbonate impurities are practically identical [8].

3 The type A CHAP structures with carbonate impurities

The aim of this research was to study specifics of type A CHAp structure with CO_3^{2-} -group (CHAp/ CO_3^{2-}) or CO_2^- -radical (CHAp/ CO_2^-) replaced two hydroxyls in the channel using computer modeling.

3.1 Methodology of computer modeling

CHAp structures with carbonate impurities in hydroxyl channel (type A) and possible accompanying defects (\square_{Ca} or/and \square_{OH}), were modeled by the semiempiric method, using interatomic potential-based simulation techniques. Interactions between ions in type A CHAp structure were approximated by interatomic potentials which are used to simulate carbonate substitutions in CAp [5]. It should be noted, that with these parameters, the effective radical charge is $q^{\text{eff}}(\text{CO}_2^-) = -0.955e$.

The 3x3x3 supercells with composition $[\text{Ca}_{270-x}\square_x]_{270}[\text{PO}_4]_{162}[\text{OH}_{52-y}(\text{CO}_3)_1\square_y]_{54}$ (0.16 wt % CO_2) were considered with x and $y = 0$ or 1 (about 1100 atoms). As an initial approximation, crystallography coordinates of ions in the hexagonal HAp structure ($a = 9.4166 \text{ \AA}$, $c = 6.8745 \text{ \AA}$) [2] and the $(\text{CO}_3)_A$ -group in CHAp [3, 4] were used. For potential parameters used in the simulation, effective radical charge is close to the formula value ($-1e$). Therefore, the coordinates of a CO_3^{2-} -group with an O vacancy or presumed coordinates of radical ions [8] were used to model the CO_2^- radical incorporated into the channel. In total, 5 possible structures of O–H-orientations in the channel on the both sides of a structural defect were considered, 4 \square_{OH} in the channel and 12 \square_{Ca} in sites of Ca1 and Ca2.

Optimization of structure variants with different coordinates of defects had been carried out and the Helmholtz free energies (F) of optimized structures have been calculated using GULP in order to determine the structures of CHAp/ CO_3^{2-} and CHAp/ CO_2^- [10, 11]. The structures with the $\min(F)$ are the most stable.

3.2 Using of GRID -techniques for modeling

The GULP module must be compiled as the library added to ChemShell. ChemShell with built-in module must be compiled and then GULP can be started by ordinary (theory=gulp).

All tasks were performed using grid-infrastructure that accelerated calculations considerably (a calculation time of one task (one structure variant) was 1.5 - 8 hours compared to 24 hours by the personal computer). As the GULP software does not support multithreading, many GULP instances need to be launched, each instance processing a different CHAP structure. The administrator obtained data as *.gin files, divided all input files (all names are index numbers) into two cycles (with pair and odd files) to parallel of task, each separate file was processed on a grid node in its own instance of GULP software and simulation results were returned as *.gout files. The administrator obtained a file with expansion *.gout on an exit and directed its back to the researcher. A total of 160 different CHAP structures have been processed this way.

The web-sites of uagrid.org.ua and grid.inpracom.kiev.ua were used. All calculations were executed in the virtual organization "GEOPARD", developed by Glushkov Institute of Cybernetic of NAS of Ukraine, Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of NAS of Ukraine and Subbotin Institute of Geophysics of NAS of Ukraine.

3.3 The type A CHAP structures with the carbonate group and CO_2^- -radical

Helmholtz free energy of the most stable structures is approximately the same order of magnitude with higher probability of carbonate substitutions: F (per one elementary cell) = -483.43 , -482.82 and -481.68 eV for CHAp/ CO_3^{2-} , CHAp/ CO_2^- and HAp, respectively. The optimization accuracy is high: $G_{\text{norm}} = 7.34 \cdot 10^{-5}$, $6.73 \cdot 10^{-5}$ and $4.35 \cdot 10^{-6}$, respectively. The a -parameter of the CHAp/ CO_3^{2-} and CHAp/ CO_2^- lattices (9.325 and 9.345 \AA , respectively)

go down relative to HAp, the *c*-parameter is practically the same. In these structures, H and O atoms in hydroxyls have the biggest displacements of up to 0.7 Å, C atom is displaced by up to 0.3 Å, displacement for other atoms does not exceed 0.1 Å from initial sites (in HAp).

Figure 1 shows the channel structures with the CO₃²⁻-group and the CO₂⁻-radical in the most stable structures (atoms of Ca1 and PO₄-groups are not shown). Coordinates of carbonate oxygen atoms in CHAp/CO₃²⁻ are close to these in bioapatite (axial O1 and O2 occupy hydroxyl O sites in the channel, O3 lies in the outer wall of the channel) [4]. Coordinates of radical oxygen in CHAp/CO₂⁻ are noticeably different (the axial O2 occupies approximately hydroxyl O site in the channel, but the off-axis O3 is located near □_{OH} so that the O–O axis is oriented at an angle of 5.51° with the *c*-axis). C atom lies in the channel at *z* = 0.5 in both structures

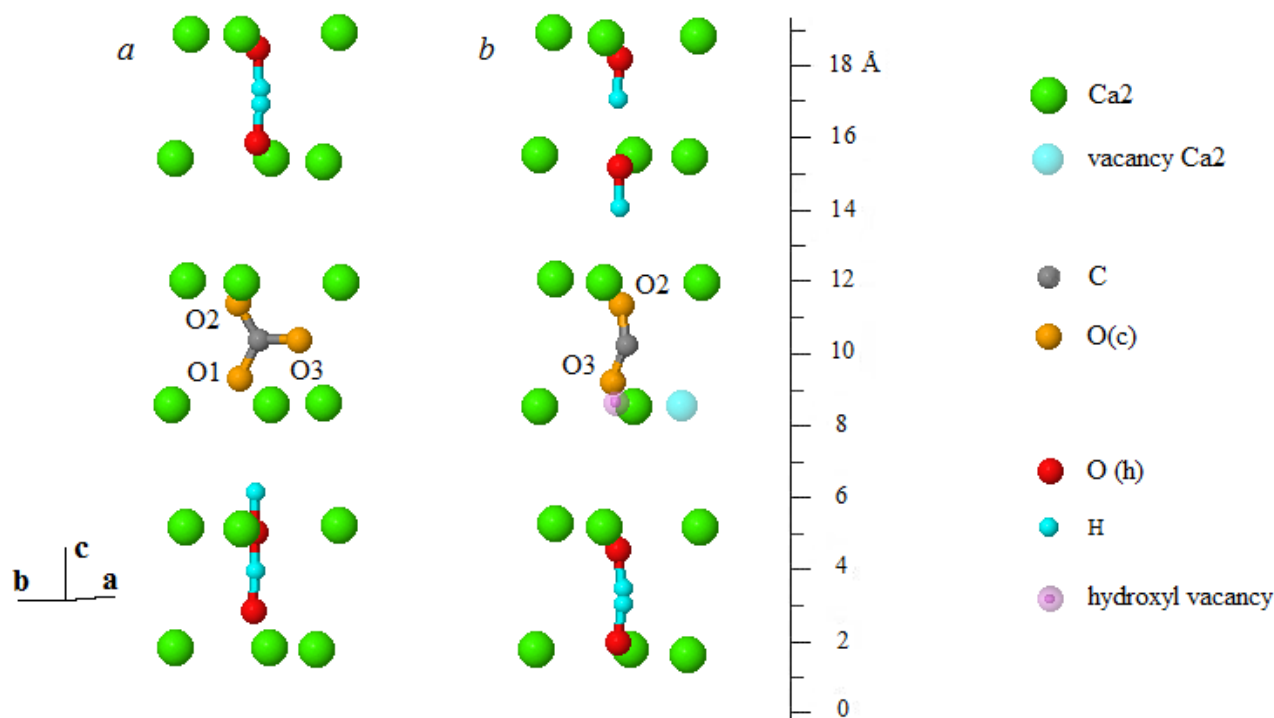


Fig. 1. The channel structures in the most stable type A CHAp structures: with the CO₃²⁻-group (a) and the CO₂⁻-radical (b). The Ca2 atoms are at $z = 1/4 + n/2$, where $n = 0 - 5$. The atoms of Ca1 and PO₄-groups are not shown. The numbering of O in carbonate impurities is shown.

The O-H-bonds near carbonate impurities mainly orient in one direction (similar to monoclinic HAp) in both structures, however sites of hydroxyls ions differ substantially (Fig.1). The O-H-bond orientations in other channels are similar to the hexagonal HAp (O – H – H – O), with small deviations in channels closest to the channel with the structural defect. Hydroxyl ions in these fragments are located in sites close to such in HAp with the following distances between them: Oh–H = 1.086 Å, Oh–Oh = 2.62 – 2.64 Å, H–H = 0.46 Å (Oh = an hydroxyl oxygen). In channel fragments similar to monoclinic HAp, unidirectional orientation of O-H bonds leads to strong hydrogen bonds between O and H of different hydroxyls and approximately linear alignment O–H .. O–H (Fig. 1 - OH..OH = 1.11 and 1.54 Å in CHAp/CO₃²⁻ and CHAp/ CO₂⁻, respectively). The O-H bond distances in these fragments are approximately identical (1.12 - 1.13 Å), though some higher, than in HAp.

Vacancies □_{OH} and □_{Ca} have low probability in the CHAp/CO₃²⁻ structure. On the contrary, there are close-spaced vacancies □_{OH} (close to O3) and □_{Ca} in the vicinity of the radical in CHAp/CO₂⁻.

Presence of a radical leads to significant changes in the distances between ions of a carbonate impurity and in nearest structure relative to CHAp/CO₃²⁻ structure. C–Oc (Oc = carbonate O) distances diminish from 1.19 to 1.15 Å, C–H - from 4.18 to 3.79 Å. Distances to the nearest hydroxyl ions increase considerably: C–O h = 4.91, 5.78 Å and O3–Oh = 4.73, 5.96 Å in contrast to 5.30, 5.57 Å and 5.51, 5.64 Å in CHAp/CO₃²⁻. Distances Oc–Oc = 2.17 Å, O3–H = 4.83 Å and Oh–Oh = 3.10 Å and H–H = 3.10 Å (in hydroxyl fragments with unidirected O-H bonds) increase substantially in comparison to 2.09, 4.43, 2.24 and 2.23 Å in CHAp/ CO₃²⁻.

Obtained data complement and are partly in agreement with experimental and theoretical studies of CHAp structures. The most stable obtained CO₂⁻-radical structure approximately corresponds to the expected structure of radicals responsible for axial signals in EPR spectra of CAp (with a larger angle between the Oc–Oc axis and the *c* axis (≈ 25°)) [8]. The distance H–C in the most stable CHAp/ CO₂⁻ structure is less than expected value C–H ≥ 4.1 Å [8].

Structural sites of (CO₃)⁻-group atoms and O-H bond orientations of the nearest hydroxyls in the channel in CHAp/CO₃²⁻ are close to such in monoclinic CHAp obtained by MD simulation [5]. Closely spaced protons in approximately linear aligned O-H .. O-H structure (H..O ≈ O-H ≈ 1.1 Å) in the CHAp/CO₃²⁻ channel can be responsible for the doublet signal in ¹H NMR spectra of type A CHAp. The origin of doublet signal remains unclear and can be explained by incorporation of H₂O molecules into □_{OH} in channels [10]. Unidirected O-H bonds in channels near carbonate impurities are in keeping with data about orientations of O-H bonds near structural defects in the hexagonal apatite structures with substitutions of different types [12].

4 Conclusion

The structure of type A CHAp (3x3x3 supercell) with CO₃²⁻-group or CO₂⁻-radical in the channel (0.16 wt % CO₂) was studied by computer modeling using GULP software and grid-techniques. The hydroxyl fragments with unidirected O-H bonds have been found to form near structural defects in the most stable hexagonal CHAp/CO₃²⁻ and CHAp/CO₂⁻ structures. The C atom is located in the channel at z ≤ 0.5. The sites of carbonate oxygen atoms in CHAp/CO₃²⁻ are close to those in bioapatite, but they are significantly different in CHAp/CO₂⁻. The radical structure is approximately aligned (O2-C-O3), but O3 does not occupy the hydroxyl vacancy unlike the axial O2. It is shown, that the radical formed by removal of one carbonate oxygen leads to additional structural defects (closely spaced □_{OH} and □_{Ca}), noticeable atom displacements and structure deformations, relative to the CHAp/CO₃²⁻ structure. Obtained data complement and are partly in agreement with experimental and theoretical studies of type A CHAp. Obtained CO₂⁻-radical structure is similar to expected structure of radicals responsible for axial peaks in EPR spectra of type A CHAp.

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