

# The study of temperature effect on the structure and environment of $\text{CO}_2^-$ radical in carbonate hydroxylapatite by computer modeling

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**Abstract.** *The type A carbonate hydroxylapatite (C-HAp) with a  $\text{CO}_2^-$ -radical replaced two hydroxyls in the channel (C-HAp/ $\text{CO}_2^-$  structure) and possible accompanying defects (a  $\text{Ca}^{2+}$  vacancy ( $\square_{\text{Ca}}$ ) and an  $\text{O}^-$ -center (a  $\text{H}^+$  vacancy) have been investigated by computer modeling using the GULP program. The most stable structures at the temperatures  $T = 298, 873, 1073$  and  $1173$  K have been established. The C-HAp/ $\text{CO}_2^-$  structure is the most stable at  $T = 298$  and  $873$  K. The C-HAp/ $\{\text{CO}_2^- + \text{O}^-\}$  structure with the neighbouring  $\text{CO}_2^-$ -radical and  $\text{O}^-$ -center in the channel is the most stable at higher temperatures. The temperature growth leads to noticeable changes of the  $\text{CO}_2^-$ -radical configuration and the nearest structural environment, in accordance with the temperature ranges of transformations of apatite structures: disappearance of  $\square_{\text{Ca}}$  at  $T = 873$  K results in structure ordering, removal of protons at  $T = 1073$  and  $1173$  K – in appearance of oxygen ions in the channels. The obtained data complement and are in agreement with experimental and theoretical investigations of type A C-HAp. The temperature range of existence of the most stable C-HAp/ $\{\text{CO}_2^- + \text{O}^-\}$  structure corresponds to EPR data about the associate forming and growth of precursor amounts of  $\text{CO}_2^-$ -radicals and  $\text{O}^-$ -centers in type A C-HAp at these temperatures.*

## Keywords

Type A carbonate hydroxylapatite structure,  $\text{CO}_2^-$ -radical, temperature stability, computer modeling, GULP.

## 1 Introduction

Various isomorphous substitutions are characteristic for the apatite structures. The  $\text{CO}_3^{2-}$ -ions in carbonate apatites (CAp) of different origin were established to replace  $\text{OH}^-$  ( $\text{F}^-$ )- ions in structural channels (type A CAp) and  $\text{PO}_4^{3-}$ -ions (type B CAp), resulting in structural defects and changes of physical and chemical properties [1 – 6]. Investigations of carbonate substitutions in hydroxylapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  (HAp) are needed for decision of retrospective dosimetry tasks and development of technologies of synthesis of biocompatible materials for bone implants on the HAp basis.

## 2 Related works

Electronic paramagnetic resonance (EPR) is widely used to investigate crystallochemical properties of apatites. The strongest EPR peaks in biogenic and synthetic carbonate apatites are produced by  $\text{CO}_2^-$ -radicals on crystallite surfaces and in the structure [7 – 9]. It is established that  $\text{CO}_2^-$ -radicals in apatite channels are formed from  $\text{CO}_3$ -groups at irradiation. Associate forming of  $\text{O}^-$ -centers and about half of  $\text{CO}_2^-$ -radicals in the nearest structural sites in type A C-HAp has been supposed taking into account similar temperature dependences of precursor amounts of these paramagnetic centers [9]. The growth of the precursor amounts at  $T \approx 873 - 1073$  K has been explained by changes of the structural environment of  $\text{CO}_2^-$ -radical precursors due to apatite structure transformation and diffusion of  $\text{CO}_2$  molecules from an atmosphere in appearing vacancies  $\square_{\text{OH}}$  at these temperatures [9].

At the same time, forming mechanisms, structural environment peculiarities, temperature stability of  $O^-$ -centers and  $CO_2^-$ -radicals in the apatite channels require further investigation. Such researches are needed to develop of methods of division of contributions to the EPR signals of these radicals differed of EPR parameters and temperature stability.

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  $CO_2^-$ -radical forming from a  $CO_3^{2-}$ -ion in the hydroxyl channel causes the substantial change of the electron density distribution in the nearest structural environment in type A C-HAp, but the effective oxygen charges in carbonate impurities are practically identical [8]. The local structure near the  $CO_2^-$ -radical in the type A C-HAp at the subzero substitution degree has been established to be substantially distorted: thr Ca2 vacancy ( $\square_{Ca2}$ ) is present, the  $PO_4$ - tetrahedrons and hydroxyl channel fragments nearest to the radical are deformed notably [11].

### 3 Changes in structural environment of the $CO_2^-$ radical at temperature growth

The aim of this research was to study the changes in the type A C-HAp structure with a  $CO_2^-$ -radical replaced two hydroxyls in the channel (C-HAp/ $CO_2^-$  structure) or, in addition, an  $O^-$ -center (C-HAp/ $\{CO_2^- + O^-\}$  structure), at  $T = 298, 873, 1073$  and  $1173$  K using computer modeling.

#### 3.1 Methodology of computer modeling

The type A C-HAp structure with  $CO_2^-$ -radical or, in addition, an  $O^-$ -center and a possible vacancy  $\square_{Ca}$  were modeled by the semiempiric method, using interatomic potential-based simulation techniques. Interactions between ions in the type A CHAp structure and the  $CO_2^-$ -radical 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 equal to formula value:  $q^{eff}(CO_2^-) = -0.955e$ . The oxygen ion in the hydroxyl oxygen O(h) site near the proton vacancy ( $\square_H$ ) was been considered to simulate an  $O^-$ -center. The effective charges  $q^{eff}(O^-) = -1.4e = q^{eff}(O(h))$  and  $-1.0e$  (at proportional decrease of core - shell charges) and the Buckingham parameters of an O(h) ion were used for this ion.

The  $3 \times 3 \times 3$  supercells with composition  $[Ca_{270-x}\square_x]_{270}[PO_4]_{162}[OH_{52-y}(CO_2^-)_1O^-_y]_{54}$  (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 [2], presumed coordinates of radical ions [8] and parameters of the elementary HAp cell at considered temperatures [4] were used.

Optimization of structure variants differed distribution of structural defects at considered temperatures had been carried out using GULP [10]. The Helmholtz free energies ( $F$ ) of optimized structures have been calculated in order to determine the most stable structures with the  $\min(F)$ .

#### 3.2 The temperature effect on the structure of type A C-HAp with a $CO_2^-$ radical

Optimization of about of 100 structure variants had been carried out, from which 25 structures have been optimized.

Helmholtz free energy of the most stable structures of C-HAp/ $CO_2^-$  and C-HAp/ $\{CO_2^- + O^-\}$  at considered temperatures are listed in table 1. Figure 1 shows the structures of the hydroxyl channel with the  $CO_2^-$ -radical in the most stable structures. The higher probability of forming of paramagnetic centers in type A C-HAp at  $T = 298$  K must be noted: optimized structures are more notably stable, than HAp ( $F = -481.68$  eV for the HAp structure optimized at used potential parameters).

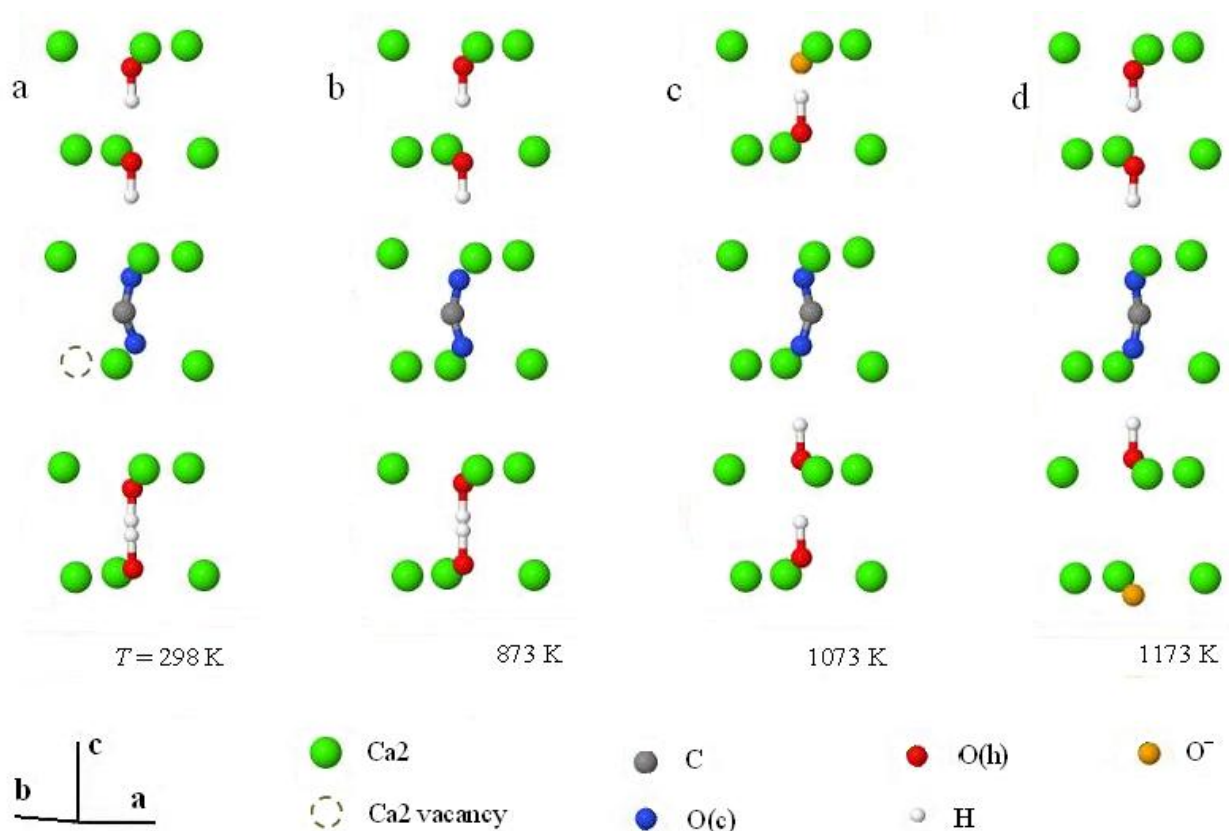
The most stable C-HAp/ $CO_2^-$  structure at  $T = 298$  K had been obtained earlier [11] using of the elementary HAp cell parameters [2] as an initial approximation. Other structures have been obtained with parameters [4]. The C-HAp/ $CO_2^-$  structures optimized with these parameters at  $T = 298$  K are less stable. The most stable structures C-HAp/ $\{CO_2^- + O^-\}$  have been optimized at  $q^{eff}(O^-) = -1e$ , except the structure at  $T = 1073$  K.

The C-HAp/ $CO_2^-$  structures are the most stable at  $T = 298$  and  $873$  K (fig. 1 a, b). There is the Ca2 vacancy near the  $CO_2^-$ -radical in this structure at  $T = 298$  K. The increase temperature to  $T = 873$  K leads to a bit changes of the  $CO_2^-$ -radical configuration and disappearance of  $\square_{Ca2}$ , however the hydroxyl channel structure does not change substantially. The C-HAp/ $\{CO_2^- + O^-\}$  structures at these temperatures are less stable:  $\Delta F \approx 0.4$  and  $0.3$  eV, respectively (tab. 1). The paramagnetic centers incorporate in the nearest structural sites in the channel in these structures (tab. 1). The differences  $\Delta F$  between the most stable structures C-HAp/ $CO_2^-$  and C-HAp/ $\{CO_2^- + O^-\}$  are the same order with the O-H-bond reorientation energy in HAp [12].

**Tab.1.** Helmholtz free energy  $F$  (eV) of the most stable structures

<i>Hydroxyl channel structure</i>	<i>Temperature, K</i>			
	298	873	1073	1173
	<b>C-HAp/ CO<sub>2</sub><sup>-</sup></b>			
OH HO CO <sub>2</sub> <sup>-</sup> HO HO [9] □ <sub>Ca2</sub>	- 482.82			
OH HO CO <sub>2</sub> <sup>-</sup> HO HO		- 492.03		
OH HO CO <sub>2</sub> <sup>-</sup> HO HO □ <sub>Ca2</sub>			-	- 497.81
	<b>C-HAp / {CO<sub>2</sub><sup>-</sup> + O<sup>-</sup>}</b>			
OH OH CO <sub>2</sub> <sup>-</sup> O <sup>-</sup> HO	- 482.39	- 491.73		
O <sup>-</sup> OH CO <sub>2</sub> <sup>-</sup> HO HO				- 498.05
OH OH CO <sub>2</sub> <sup>-</sup> OH O <sup>-</sup> *			- 496.33	

Note:  $q^{\text{eff}}(\text{O}^-) = -1.4e$ .



**Fig. 1.** The structure of the hydroxyl channel with the CO<sub>2</sub><sup>-</sup>-radical in the most stable structures at considered temperatures. The Ca2 atoms are at  $z = 1/4 + n/2$ , where  $n = 0 - 5$ . The atoms of Ca1 and PO<sub>4</sub>-groups are not shown.

The C-HAp/{CO<sub>2</sub><sup>-</sup> + O<sup>-</sup>} structures are the most stable when  $T = 1073$  and  $1173 \text{ K}$ . The paramagnetic centers in these structures are more distanced (fig. 1 c, d). The considered variants of C-HAp/CO<sub>2</sub><sup>-</sup> and C-HAp/{CO<sub>2</sub><sup>-</sup> + O<sup>-</sup>}

structures with  $q^{\text{eff}}(\text{O}^-) = -1e$  have not been optimized at  $T = 1073$  K. This can be explained by substantial changes of electron density and, in particular, the  $\text{O}^-$ -center effective charge at  $T = 1073$  K. The C-HAp/ $\text{CO}_2^-$  structure at  $T = 1173$  K is less stable:  $\Delta F \approx 0.25$  eV (tab. 1).

Temperature growth leads to substantial changes of the  $\text{CO}_2^-$ -radical configuration and transformations of the local structural environment in type A C-HAp. The Ca2 vacancy disappearances at  $T = 873$  K (fig. 1 b), the  $\text{O}^-$ -center is present in the channel at  $T \geq 1073$  K (fig. 1 c, d). These changes are corresponded to temperature ranges of transformation of apatite structure during dehydration and partial dehydroxylation: disappearance of vacancies at  $T \approx 873 - 973$  K leads to structure ordering, removal of protons and OH-groups at  $T \approx 973 - 1073$  K – to appearance of oxygen ions (proton vacancies) and hydroxyl vacancies [2, 4, 6, 9].

The hydroxyl channel structure is transformed noticeably. The hydroxyl protons are oriented in the same direction in the channel fragment near the  $\text{CO}_2^-$ -radical at  $T \leq 1073$  K (fig. 1 a – c). The similar structure of hydroxyl channel near a structural defect is characteristic for apatites of different composition [12]. One O-H-bond is oriented to the radical at  $T \leq 1073$  K (fig. 1 a – c) and the both O-H- bonds – at  $T = 1173$  K (fig. 1 d). The structures of the hydroxyl channel near the  $\text{O}^-$ -center are differed substantially: at  $T = 1073$  K one proton of nearest hydroxy groups lies towards the  $\text{O}^-$ -center, but at  $T = 1173$  K both nearest protons are located aside from the  $\text{O}^-$ -center. This allows to suppose the substantial differences in mechanism of proton removal resulting in an oxygen ion appearance in the channel at these temperatures.

## 4 Conclusion

The type A C-HAp structure with a  $\text{CO}_2^-$ -radical replaced two hydroxyls in the channel or, in addition, an  $\text{O}^-$ -center, at  $T = 298, 873, 1073$  and  $1173$  K has been investigated by computer modeling using the GULP program. It is established that the C-HAp/ $\text{CO}_2^-$  structure is the most stable at  $T = 298$  and  $873$  K, the C-HAp/ $\{\text{CO}_2^- + \text{O}^-\}$  structure – at  $T = 1073$  and  $1173$  K. The temperature growth results in substantial changes in the  $\text{CO}_2^-$ -radical configuration and the radical environment in accordance with temperature ranges of apatite structure transformation.

Obtained data complement and are in agreement with experimental and theoretical studies of type A C-HAp. The temperature range of existence of the most stable C-HAp/ $\{\text{CO}_2^- + \text{O}^-\}$  structure corresponds to EPR data about the associate growth of precursor amounts of  $\text{CO}_2^-$ -radicals and  $\text{O}^-$ -centers in type A C-HAp annealed at such temperatures.

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