

A New Possible Atomic Arrangement for the Carbon Atom in the B-Sites of Ab-Type Carbonate Apatite

Jorge Correa de Araujo^a, Elizabeth Lima Moreira^b, Valeria Conde Alves Moraes^b,

Ana Paula Duarte Moreira^{c*}, Glória Dulce de Almeida Soares^c

^aRio de Janeiro State University – UERJ, CEP 24435-000, São Gonçalo, RJ, Brazil

^bBrazilian Center for Physics Research – CBPF, CEP 22290-180, Rio de Janeiro, RJ, Brazil

^cCOPPE and Polytechnic School, Federal University of Rio de Janeiro – UFRJ, CEP 21941-972, Rio de Janeiro, RJ, Brazil

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The crystal structure of a synthetic AB-type carbonate apatite sample was analyzed by Rietveld refinement including a model with carbon atom not fixed in the B-site of the apatite structure. Only one constraint was applied to this model: the fractional occupancies of the atoms in the CO₃ ion plus PO₄ ion were equal 1.0 per phosphate site with six sites per unit cell. Rietveld refinement of the crystal structure with space group P6₃/m results in cell parameters $a = 9.3583(1) \text{ \AA}$ and $c = 6.9226(5) \text{ \AA}$; $Z = 1$; $R_{wp} = 0.0824$ and 9.5 wt. (%) of carbonate in this structure. The use of simple geometry formulas showed that the C atom is not located at the center of the equilateral triangle of oxygen O2, O3 and O3', but to a distance 0.18 Å of this triangle. The results seem to indicate a new 3-D crystal structure of the carbonated apatite in PO₄ groups.

Keywords: rietveld, refinement, carbonate, crystal structure

1. Introduction

Calcium phosphates are currently employed as bone substitute in several clinical applications due their similarity with bone¹. The crystal structure of hydroxyapatite, (HA - Ca₁₀(PO₄)₆(OH)₂), allows several ionic substitutions. The incorporation of carbonate ions into the HA structure improves its biological properties as it becomes closely to the composition of the mineral part of bone tissue. For instance, a carbonate ion can replace two different sites in HA lattice: the OH ion (A-site or channel site) and the PO₄ site (B-site), increasing apatite solubility.

A deep study in the calcium phosphate structure is important to understand in vivo response. However, the crystal structure of carbonate apatite remains unclear due to uncertainties in the exact localization of the CO₃ ions². As noticed by Fleet and Liu (2003)³ changes in $a (= b)$ and c unit cell parameters of carbonate apatite (CO₃-apatite) were observed, comparing with cell parameters of a pure hydroxyapatite. Suetsugu et al.⁴ analyzed the structure of A-type carbonate apatite with partial occupancy in B sites and observed that a parameter took a middle point of the pure HA and the A-type CO₃-apatite powder reference, while c parameter was larger in comparison with the pure HA. In our previous work⁵, the X-ray diffraction profile of the AB-type CO₃-apatite synthetic powder showed a contraction of the a lattice parameter and an enlargement of c lattice parameter. The decreasing of the occupancy factor (O.F.) of P sites is another partial evidence of the replacement of CO₃ ions in the structure of the apatite².

Elliot⁶ showed that the planes containing CO₃ triangles are nearly parallel to the c axis, when the carbonate ions replace OH groups (A-site) in the channels. When the carbonate ions replace the PO₄ groups, the planes with CO₃ triangles make a $37 \pm 4^\circ$ angle with c -axis, and the triangle occupies the sloping face of the tetrahedron. However, according to Wilson et al.⁷, different locations of the CO₃

ion in the AB- type CO₃-apatite can be obtained, probably due to differences in apatite synthesis.

Ivanova et al.² has analyzed carbonated hydroxyapatite powder samples by X-ray diffraction and has observed that the carbonate ions randomly occupy two adjacent faces of the PO₄ tetrahedron, parallel to the c -axis, indicating that three oxygen atoms O1, O2 and O3 (split in two O3) of the PO₄ tetrahedron make up the coordination for the two carbon atoms labelled C1 and C2. The discrepancies amidst the data of different authors seem to indicate that carbonate triangles may occupy any of the tetrahedral faces, but in each specific case, they can be found to stick to a certain face².

In this paper, XRD data of an AB-type CO₃-apatite sample was analyzed by Rietveld refinement⁸, using a different approach in which, the CO₃ ion is allowed to move freely during the refinement, in order to determine the C position and the oxygen coordination in PO₄ group.

2. Materials and Method

2.1. AB-type carbonated apatite sample (CO₃-apatite)

CO₃-apatite was synthesized by wet precipitation method using calcium nitrate (Ca(NO₃)₂·4H₂O), diammonium hydrogen phosphate ((NH₄)₂HPO₄) and ammonium carbonate ((NH₄)₂CO₃) solutions as precursors. The temperature and pH were maintained at 3 °C and 12, respectively⁵. This sample was heat treated at 500 °C for 6 hours and examined by X-ray diffraction using a XRD Rotaflex (Rigaku, Japan) with CuK_α radiation and graphite monochromator, spectra 2θ 10°-100° with the step of 0.02/5s per data point. The CO₃ content on green and calcined powder was determined by temperature-programmed desorption coupled to mass spectrometer (TPD-MS) being equal to 16.2 and 12.8 wt. (%), respectively. As the green sample was submitted to thermal treatment at 500 °C,

*e-mail: anapauladm@metalmat.ufrj.br

any carbonate bonding superficially was eliminated, decreasing the carbonate content of the calcined sample. The complete description of synthesis and characterization results can be found elsewhere⁹.

2.2. Rietveld refinement

Rietveld refinements were carried out employing the FULLPROF program¹⁰ and a Pearson VII function was used particularly to fit anisotropic broadening of Bragg $00l$ reflections caused by the strain in the reticulate, the crystallite size and the instrument. Initially, for the refinement of the apatite structure without explicit inclusion of CO_3 ion, the structure of Holly Springs hydroxyapatite single crystal structure¹¹ was used. This model, called A model, space group $\text{P6}_3/\text{m}$, was used as the starting model for refinement.

Another model, B model, also space group $\text{P6}_3/\text{m}$, was created adding C atom in the structure of the refined A model, with the CO_3 ion occupying PO_4 sites. The model for the CO_3 ion (model B), similar to the calcite structure, was proposed considering that the z position of the C atom can be varied. This strategy was firstly adopted by Wilson et al.¹² that proposed an initial triangular geometry for the CO_3 ion, with C-O and O-O distances of 1.294 and 2.413 Å, respectively. In their studies, these distances were maintained by the soft constraints, while the O1 position of the CO_3 ion was hard constrained to have the same position of O1 in the PO_4 ion. Contrary, in our study, the initial geometry for the CO_3 ion in model B was allowed to move freely during the refinement. Only one constraint was applied: the fractional occupancies of the atoms in the CO_3 ion plus PO_4 ion were equal 1.0 per phosphate site with six sites per unit cell.

The isotropic displacement parameters were refined in all refinements performed. The preferred orientation (March-Dollase) parameter was allowed to vary, but it was fixed at 1.0 because the refinement indicated no preferred orientation. The background was modeled with the linear polynomial¹³.

3. Results and Discussion

The refinement of the observed and calculated XRD patterns of CO_3 -apatite is shown in Figure 1 and was in good agreement as the average R_{wp} , R_{B} and R_{F} values were, respectively, 0.0824, 0.0256 and 0.0195.

Table 1 shows some crystal data obtained for CO_3 -apatite sample using Model A and Model B. Data from the literature for HA¹¹ and B-type CO_3 -ap² are also included.

As told before, the A model was used only as the starting model for refinement of the B model with the inclusion of the C atom in the structure. Both models showed an important and similar reduction in P occupancy (~20% for model A and ~18% for model B). However, the two models are not directly comparable. For example, the model B has a constraint about the complementary crystallography condition of the occupation factors of P and C (B-site) while the A model has no constraint about these occupancies factors.

Comparing cell parameters of B model with data for HA (Table 1), a reduction in the a parameter, and a large increasing in the c parameter is observed. The a parameter is smaller than that reported by Ivanova² (9.437 Å), but agrees with Wilson et al.¹² data ($a = 9.3446(3)$ Å and $c = (6.9199(4))$ Å) for a carbonate apatite with CO_3 content equal to 12.6 wt. (%) and some residual sodium. In this case, the reduction of a parameter occurs because the carbonate ion is smaller than phosphate ion. According to Wilson et al.¹², the a-axis contraction for a CO_3 -apatite depends on the method and conditions of precipitation. The replacement by carbonate ion generates a large structural disorder creating vacancies of Ca and OH ions. This disorder is also reflected in periodicity of the crystallographic planes observed by X-ray¹⁴, resulting in a decrease of the a parameter.

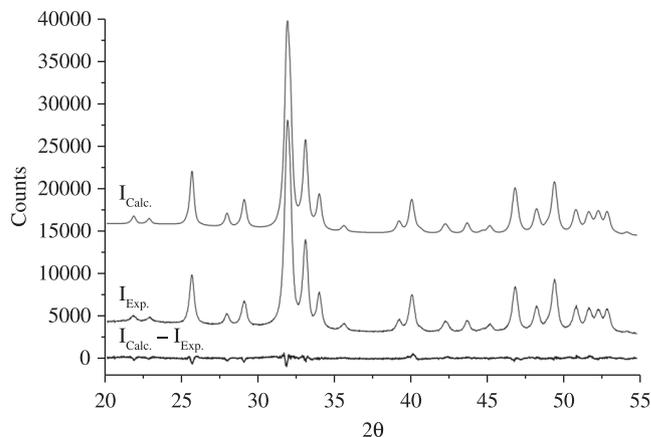


Figure 1. Final fit between experimental and B model calculated XRD pattern of the CO_3 -apatite calcined at 500 °C during 6 hours.

The results for C2 atom position using model B is in reasonable agreement with those obtained by Ivanova et al.² for B-type CO_3 -apatite and with the (0.408(1), 0.398(1), 0.187(2)) position for atom C obtained by Wilson et al.¹².

In the B model, the reduced occupancy values, 0.82 and 0.39 for P and O4h atoms, respectively, are partial evidence of the incorporation of CO_3 ions in sites A and B. No vacancy was observed in O1 sites, which exhibit an occupancy factor (O.F.) equal to 1.02(4). Therefore, we suggested that the CO_3 ions occupy the sites O2 and O3' of a replaced PO_4 ion, with O.F. equal to 0.054(8) and 0.08(1), respectively.

From occupancies factors obtained by refinement for Ca, P, C2 and O4 atoms (Table 1), the chemical formula for CO_3 -apatite employed in this study is $\text{Ca}_{9.408}[(\text{PO}_4)_{4.92}(\text{CO}_3)_{1.08}][(\text{OH})_{1.56}(\text{CO}_3)_{0.44}]$, resulting in approximately 9.5 wt. (%) of carbonate in this structure and Ca/P ratio equal to 1.912. The theoretical value (obtained by refinement) for carbonate content is quite different from the experimental data (12.8 wt. (%)).

The maximum and minimum residual electron densities for the eight atomic cell positions in the B model were, respectively, $\Delta\rho = 0.16$ ($\text{e}\text{\AA}^{-3}$) and $\Delta\rho = -0.15$ ($\text{e}\text{\AA}^{-3}$). This data shows that $F_0 \approx F_c$, where F_0 is the observed structure factor and F_c is the structure factor calculated by the model. Unfortunately, the C position in coordination with the O2-O3-O3' oxygen was not clearly determined by X-Fourier maps (not shown). Consequently, the lower residual scattering around the P atom was not undoubtedly identified as a CO_3 ion.

The application of simply analytical geometry formulas and geometrical transformations of three dimensions confirm that the C atom is not fixed in the center of the O2-O3-O3' triangles, but at 0.18 Å of this tetrahedral face. The transformation matrix $[a, 0, 0 / -0.5a, 0.5\sqrt{3}a, 0 / 0, 0, c]$ turns the hexagonal crystal system into an orthogonal system.

The plane face of CO_3 ion formed by only O2-O3-O3' triangle is parallel to c axis in agreement with the results obtained by Ivanova et al.². It seems that the environment around the C atom is not strictly distorted, although the distance for C-O bond (1.36 Å) suggests that the C atom is weakly bounded with the oxygen coordination. Therefore, the geometry for CO_3 ion in PO_4 vacancies sites is a small tetrahedron of 0.164 Å³ in comparison with 1.70 Å³ for the PO_4 tetrahedral volume.

This little tetrahedral configuration for the CO_3 ion seems to contradict the previous Rietveld studies realized by Ivanova et al.² and Wilson et al.¹², but in their investigations, the constraints were

Table 1. Cell, positional and occupancy parameters of the crystal structure.

Method of Refinement	CO ₃ -apatite sample				
	Model A	Model B	HA ¹¹	B-type CO ₃ -apatite ²	
	Rietveld	Rietveld	Refinement with neutrons	Rietveld	
Cell parameters (Å)					
<i>a</i> (= <i>b</i>)	9.3576(4)	9.3583 (4)	9.424(4)	9.437(1)	
<i>c</i>	6.9222(3)	6.9226 (4)	6.879(4)	6.881(1)	
Positional and occupancy factors parameters and Wyckoff index					
Ca1 4f					
<i>z</i>	0.0020(0)	0.0020(0)	0.0015(1)	0.0011(3)	
Occupancy	0.981(5)	0.957(2)	1.0	0.848(2)	
Ca2 6h					
<i>x</i>	0.2430(2)	0.2437(2)	0.2468(2)	0.2457(2)	
<i>y</i>	0.9884(3)	0.9877(3)	0.9934(1)	0.9879(2)	
Occupancy	0.910(1)	0.93(1)	1.0	0.985(2)	
P 6h					
<i>x</i>	0.3964(6)	0.4018(6)	0.3987(2)	0.3991(3)	
<i>y</i>	0.3705(4)	0.3770(4)	0.3658(1)	0.3692(3)	
Occupancy	0.796(5)	0.820(9)	1.0	0.824(3)	
O1 6h					
<i>x</i>	0.3290(6)	0.3290(6)	0.3284(2)	0.3264(5)	
<i>y</i>	0.4863(9)	0.4863(9)	0.4848(2)	0.4829(5)	
Occupancy	1.188(9)	1.02(4)	1.0	0.932(5)	
O2 6h					
<i>x</i>	0.5851(5)	0.5893(5)	0.5873(2)	0.5879(6)	
<i>y</i>	0.4620(8)	0.4625(8)	0.4651(2)	0.4695(6)	
Occupancy	1.144(8)	0.946(8)	1.0	0.945(5)	
O3 12i*					
				O3p	O3c
<i>x</i>	0.3448(5)	0.3481(5)	0.3437(2)	0.3409(4)	0.362(4)
<i>y</i>	0.2612(4)	0.2613(4)	0.2579(1)	0.2579(4)	0.299(4)
<i>z</i>	0.0693(4)	0.0693(4)	0.0702(2)	0.0668(4)	0.089(4)
Occupancy	0.883(9)	0.928(1)	1.0	0.832(9)	0.187(9)
O4 4e					
<i>z</i>	0.182(2)	0.170(1)	0.1978(7)	0.1884(2)	
Occupancy	0.360(3)	0.390(4)	0.5	0.602(4)	
C2 6h					
	N.I.		N.I.		
<i>x</i>		0.4435(5)		0.4380**	
<i>y</i>		0.3190(6)		0.3550**	
<i>z</i>		0.2256(2)		0.2500**	
Occupancy		0.18(2)		0.09(1)	

N.I. = not included in the refinement. *The O3 atom was splitted into two O3p and O3c by D-Fourier maps. **Not refined by Ivanova et al. (2001).

applied in the CO₃ ion geometry to maintain the C carbon atom in the center of the equilateral triangle of oxygen atoms.

4. Conclusions

The Rietveld refinement of XRD data of the carbonated apatite crystal structure with explicit inclusion of CO₃ ions considering B model showed that the C atom is weakly bounded with the only O2, O3 and O3' oxygen of the replaced PO₄ ions and 0.18 Å distant of this plane face. The refinement in occupancies for the CO₃ and PO₄ ions resulted in ~9.5 wt. (%) of carbonate in this structure. The results seem to indicate a new possible crystal structure of carbonate group in phosphate site with CO₃ ion occupying a small tetrahedral volume (0.164 Å³) when compared with the PO₄ tetrahedral (1.70 Å³).

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