

NEW PROPOSAL FOR CO₃²⁻ POSITION IN B-TYPE CARBONATED APATITE

J.C. DE ARAUJO[†], E.L. MOREIRA[§], G.D.A. SOARES[#] and I.N. BASTOS[‡]

[†] Universidade do Estado do Rio de Janeiro, Brazil, jcaraujo@iprj.uerj.br

[§] Centro Brasileiro de Pesquisas Físicas, Rio de Janeiro RJ Brazil, beth@cbpf.br

[#] Universidade Federal do Rio de Janeiro, Rio de Janeiro RJ Brazil, gloria@metalmat.ufrj.br

[‡] Instituto Politécnico, Universidade do Estado do Rio de Janeiro, Nova Friburgo RJ 28.630-050 Brazil, inbastos@iprj.uerj.br

Abstract— The crystal structure of two B-type carbonated apatite samples was re-analyzed, using the data of Wilson *et al* (2006). By applying the least squares method for the determination of carbon and oxygen atoms, a slightly different result was obtained, suggesting that the carbonate ion is not rigorously planar.

Keywords— Carbonated apatite, Carbonate, X-ray diffraction.

I. INTRODUCTION

Apatites are a material of huge importance in biomedical and mineral fields; therefore, a vast number of works is devoted to their studies (López *et al.*, 2008; Araújo *et al.*, 2007; Lima *et al.*, 2006). In spite of these studies, some questions are not a consensus, and one reason for that is the large capability of atom substitution in apatite lattice.

Low content carbonate (CO₃²⁻) is present in many minerals and in synthetic and biological apatites. The precise location of carbonate in the apatite lattice, however, is still controversial. Thus, some authors (Ivanova *et al.*, 2001; Wilson *et al.*, 2004; 2006) have been dedicated their studies to this subject.

Ivanova *et al.* (2001) analyzed by X-ray powder diffraction and Rietveld refinement the crystal structure of a synthetic calcium-deficient carbonate apatite of B-type with 4.4 wt (%) CO₃²⁻. They showed that there are two orientations for the carbonate triangles and that the carbon atom can occupy randomly the adjacent faces (parallel to the axis *c*) of the tetrahedron PO₄³⁻.

Indeed, the C atom was fixed at the center of the triangles of oxygen coordination. However, hard constraint was imposed to the position of the C carbon atom that was fixed at the centers of triangles O1-O3c-O3c' and O2-O3c-O3c'. O3c and O3c' are consequence of the mirror plane at *z* = 1/4 for the refinement at distances of 1.282 Å from each oxygen atoms. This configuration seemed to be a good approximation to the calcite structure.

Wilson *et al.* (2004) proposed in their studies using X-ray and time-of-flight neutron diffraction data collected from a sodium-containing carbonate apatite (CO₃²⁻ content 12.5(7) wt%) a structural model known as face model with the ion in disorder with the mirror symmetry related to the faces of vacant PO₄³⁻ ion site. The calculated angle between the normal to the plane of

CO₃²⁻ ion and *c*-axis was 30°(3). This configuration for the CO₃²⁻ ion corresponded to the best fitting in refinement. In this “face model”, the oxygen coordinates were labeled as Oa, Ob and Oc. The oxygen Oa was no longer constrained to occupy the vertex 1 of carbonate triangle, Ob was placed 2.241 Å from vertex 1 towards vertex 2, and close to vertex 2, while Oc was in the face formed by vertices 1-3 of the phosphate tetrahedron at a distance 2.241 Å from both Oa and Ob. Thus Oa and Ob lie in the mirror plane at *z* = 1/4 while Oc and C were in two folder disorder about the mirror plane.

Later, Wilson *et al.* (2006) studied seven samples of Na-free CO₃A, modeling the carbonate ion with soft constraints. In this sense, a good approximation of calcite structure (C-O and O-O distances with 1.294 and 2.413 Å, respectively) was considered. In this geometry, the hard constrained consideration of ion position, the Oa was taken as O1; Ob was placed on the O1-O2 line, 2.413 Å away from the O1/Oa site, and still constrained by the symmetry to remain in the mirror plane. Oc and C were located in the face formed by vertices 1-3 of the phosphate tetrahedron at an equal distance of 2.241 Å from both Oa and Ob. Besides, with this geometry, the C carbon atom is located on the center of an equilateral triangle of oxygen atoms, maintaining the configuration proposed on the previous paper Wilson *et al.* (2004).

The proposal of this work was to analyze part of the data published by Wilson *et al.* (2006) using a different approach to determine the positions formed by the carbon atom and the oxygen coordination.

II. METHODS

From Wilson *et al.* (2006) data, two samples were chosen: Mon 8 and Mon 10. Table 1 shows the positional parameters of these two samples and the mean of seven samples analyzed by the authors. The results show a slightly difference for the C atom position between Mon 8 and Mon 10. Therefore, Mon 8 was chosen due to the high deviation of positional parameters, while Mon 10 can represent all other samples. The nomenclature of these samples was maintained in order to facilitate the interpretations.

The matrix $[[a, -0.5a, 0/0, 0.5\sqrt{3}a, 0/0, 0, c]]$, where *a* and *c* are the lattice parameters, was used in the present work to turn the hexagonal crystal system (P6₃/m) into an orthogonal system where the calculus are simplified.

Table 1 – Wilson *et al.* (2006) data for positional parameters (standard deviation). (Values multiplied by 10^4). The C, Ob and Oc atom positions were multiplied by 10^3 .

Positional parameters	Mon 8	Mon 10	Mean of seven CO ₃ Ap
Cx	427(4)	430(4)	430(1)
Cy	419(5)	424(6)	423(2)
Cz	235(8)	211(8)	215(10)
O1x/Oax	3332(8)	3338(8)	3334(4)
O1y/Oay	4896(8)	4902(8)	4898(4)
O2x	5676(16)	5619(16)	5640(22)
O2y	4451(19)	4412(21)	4420(18)
Obx	584(3)	592(2)	591(3)
Oby	494(3)	503(4)	501(4)
O3x	3282(11)	3294(11)	3302(16)
O3y	2412(11)	2442(13)	2441(2)
O3z	742(13)	771(16)	754(12)
Ocx	368(4)	368(4)	369(1)
Ocy	306(4)	288(5)	292(7)
Ocz	92(5)	85(7)	84(4)

The use of least square method to fit the plane of a set of points was early reported by different authors such as Schomaker *et al.* (1959) and Hamilton (1961). We intend to find the best plane in a purely formal sense. The weight is taking as unit in the matrix given by Eq. (8). However, the theoretical treatment is remarkably simplified - as proposed by Giacobozzo *et al.* (2002) - if the Cartesian system is adopted because in this system the metric matrix G is equal the identities I . Therefore, the plane equation is defined by:

$$\alpha \equiv Ax + By + Cz - D = 0 \quad (1)$$

with the unit normal vector $n=(A,B,C)^T$ and D is the distance of the plane from the origin. In an orthogonal frame, the perpendicular distance of i -th atom from the plane is given by:

$$d_i = |Ax_i + By_i + Cz_i - D| \quad (2)$$

The goal is to find the plane that minimizes the weighted sum of squares of distances d_i of points from the plane. The correspondent equation is expressed as:

$$S = \sum_{i=1}^N w_i d_i^2 \quad (3)$$

We use the steady-state points of S and still keeping the condition that n is a unit vector as expressed in the linear functional F with Lagrange's multipliers λ .

The steady-state condition of S , which considers the normal vector unitary, can be expressed by the function F given by the Lagrange multipliers as below:

$$F(A, B, C, D) = \sum_i w_i d_i^2 - \lambda (nn^T - 1) \quad (4)$$

The partial derivative of Eq. (4) with respect to D parameter is given by:

$$D = \frac{1}{\sum_i w_i} \left(A \sum_i w_i x_i + B \sum_i w_i y_i + C \sum_i w_i z_i \right) \quad (5)$$

The meaning of Eq. (5) is the centroid X_0 of the set of atoms. The normal equations

$$\frac{1}{2} \frac{\partial F}{\partial A, B, C} = 0 \quad (6)$$

leads to:

$$\frac{1}{2} \frac{\partial F}{\partial A} = A \sum_i w_i x_i' x_i + B \sum_i w_i x_i' y_i + C \sum_i w_i x_i' z_i = \lambda A \quad (7)$$

where $X_i' = X_i - X_0$ is obtained through the transformation of coordinates. Similar expressions are obtained to partial derivatives with respect the B and C parameters and leads to the linear system:

$$\begin{bmatrix} \sum_i w_i x_i' x_i & \sum_i w_i x_i' y_i & \sum_i w_i x_i' z_i \\ \sum_i w_i y_i' x_i & \sum_i w_i y_i' y_i & \sum_i w_i y_i' z_i \\ \sum_i w_i z_i' x_i & \sum_i w_i z_i' y_i & \sum_i w_i z_i' z_i \end{bmatrix} \begin{bmatrix} A \\ B \\ C \end{bmatrix} = \lambda \begin{bmatrix} A \\ B \\ C \end{bmatrix} \quad (8)$$

The system (8) can be expressed as:

$$(S - \lambda I)N = 0 \quad (9)$$

Multiplying the left-hand side of Eq. (9) by n^T results:

$$\lambda = \sum_i w_i d_i^2 \quad (10)$$

Thus, the best plane corresponds to the eigenvalue λ_1 , passes in the centroid \bar{r}_0 and has the normal vector \bar{N}_{λ_1} . Furthermore:

$$N_{\lambda_1}^T (X_i - X_0) = d_i - D, \quad (11)$$

where $d_i - D$ is the distance of the i -th atom from the best plane.

III. RESULTS AND DISCUSSION

Table 2 shows the comparison of results obtained in this work (re-analyzed the Wilson *et al.*, 2006) and the published results (using face model) for the PO₄³⁻ bond lengths and volume. It is possible to observe the good agreement between data values.

Table 3 showed the A , B , C and D values for best plane $Ax+By+Cz=D$, where x , y and z are the orthogonal coordinates. The small differences observed for Mon 8 and Mon 10 can be attributed to different positional parameters showed in Table 1.

Table 2 - PO₄³⁻ bond lengths (Å) and volume (Å³) for analyzed samples.

Sample	P-O1	P-O2	P-O3	PO ₄ vol
Mon 8	1.498(8) ^a	1.442(13) ^a	1.590(10) ^a	1.819(18) ^a
	1.495(5) ^b	1.442(8) ^b	1.590(1) ^b	1.809(7) ^b
Mon10	1.494(9) ^a	1.396(13) ^a	1.562(12) ^a	1.716(19) ^a
	1.494(1) ^b	1.396(2) ^b	1.563(9) ^b	1.714(9) ^b

^a - Data published by Wilson *et al.* (2006).

^b - Results obtained from the re-analysis of published parameters of crystal.

Table 3 - Best least square planes in orthogonal coordinates. Displacements are expressed in Å.

	Plane coefficients - plane 1			
Mon 8	A=-0.0059	B=-0.5923	C=-0.8057	D=-0.8917(4)
	Displacement of atoms C(1), Oa, Ob and Oc, respectively 0.1880(8) -0.0763(1) 0.0837(2) -0.0614(1)			
	Plane coefficients -plane 2			
Mon 10	A=-0.247	B=-0.5665	C=-0.8233	D=-0.7920(4)
	Displacement of atoms C(1), Oa, Ob and Oc, respectively -0.0849(8) 0.0289(2) 0.0295(1) 0.0017(6)			

The results of plane 1, obtained for sample Mon 8, show that the CO_3^{2-} ion is not truly planar. Indeed, the CO_3^{2-} ion in Mon 8 occupies a little tetrahedral volume (0.19 \AA^3). For the Mon 10 sample, the CO_3^{2-} ion can be seen as having a non-significant tetrahedral volume (0.086 \AA^3), being thus nearly planar with the face plane formed by Oa, Ob and Oc oxygen making $\psi \approx 33.62^\circ$ with the c-axis.

IV. CONCLUSIONS

From the data published by Wilson *et al.* (2006) related to the Rietveld refinement with soft restrictions of carbonate atomic positions in samples 8 and 10 of carbonated B-apatite, it was shown, in the present work, with the use of least square method, that the configuration of carbonate ions is not rigorously planar as previously considered, especially for the sample named 8.

We think that a rigorous planarity for the CO_3^{2-} triangles, similar that of calcite structures can only be obtained with hard constrained for the C carbon atom position in the Rietveld refinement. In other words, carbon positions have to be fixed in the center of the oxygen coordination during all the Rietveld refinement as suggested by Ivanova *et al.* (2001). The soft constraint seems to be more realistic as it allows the C atom to move slightly out of the face plane formed by the oxygen atoms. Anyway, a further detailed investigation of Mon 8 crystal structure would be desirable.

ACKNOWLEDGMENT

The authors thank the financial support of Brazilian agencies such as CNPq, FAPERJ and CAPES.

REFERENCES

Araújo, J.C., L. Sena, I.N. Bastos and G.D.A. Soares, "Synthesis of hydroxyapatite and structural re-

- finement of X-ray diffraction," *Quím. Nova*, **30**(8), 1853-1859 (2007).
- Giacovazzo, C., H.L. Monaco, G. Artioli, D. Viterbo, G. Gilli, G. Zanotti and M. Catti, *Fundamentals of Crystallography*, 2nd edition, International Union of Crystallography, Oxford University Press, England (2002).
- Hamilton, W.C., "On the least-squares plane through a set of points". *Acta Cryst.*, **14**, 185-189 (1961).
- Ivanova, T.I., O.V. Frank-Kamenetskaya, A.B. Kol'tsov and V.L. Ugolkov, "Crystal structure of calcium deficient carbonated hydroxyapatite," *J. Solid State Chem.*, **160**, 340-349 (2001).
- Lima, I.R., A.M. Costa, I.N. Bastos, J.M. Granjeiro and G.D.A. Soares, "Development and characterization of 5% mol Zn bioceramic in granular form," *Mat. Res.*, **9**, 399-403 (2006).
- López, M., G. Fuentes, R. González, J. González, E. Peón and C. Toledo, "PMMA/ Ca^{2+} bone cements. Thermoanalytical characterization," *Lat. Am. Appl. Res.*, **38**, 227-234 (2008).
- Schomaker, V., J. Waser, R.E. Marsh and G. Bergman, "To fit a plane or a line to a set of points by least squares," *Acta Cryst.*, **12**, 600-604 (1959).
- Wilson, R.M., J.C. Elliott, S.E.P. Dowker and R.I. Smith, "Rietveld structure refinement of precipitated carbonate apatite using neutron diffraction data," *Biomaterials*, **25**, 2205-2213 (2004).
- Wilson, R.M., S.E.P. Dowker and J.C. Elliott, "Rietveld refinements and spectroscopic structural studies of a Na-free carbonate apatite made by hydrolysis of monetite," *Biomaterials*, **27**, 4682-4692 (2006).

Received: August 20, 2011

Accepted: May 29, 2012

Recommended by Subject Editor: Orlando Alfano

