NEW PROPOSAL FOR CO$_3^{2-}$ POSITION IN B-TYPE CARBONATED APATITE

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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 (CO$_3^{2-}$) 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 (%) CO$_3^{2-}$. 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 PO$_4^{3-}$.

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 Á 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 (CO$_3^{2-}$ 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 PO$_4^{3-}$ ion site. The calculated angle between the normal to the plane of CO$_3^{2-}$ ion and c-axis was 30°(3). This configuration for the CO$_3^{2-}$ 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 2.241Á 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 2.241Á 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 CO$_3$A, 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 Á, 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 Á 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 Á 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,0/0.5,0.5√3a,0/0.0,c]], where a and c are the lattice parameters, was used in the present work to turns the hexagonal crystal system (P6/m) into an orthogonal system where the calculus are simplified.