ON THE OBSERVATION OF THE HAP-OCP INTERFACE BY ELECTRON MICROSCOPY

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ABSTRACT

Experimental reports have indicated that octacalcium phosphate and hydroxyapatite produce an interface, which seems to be quite important for some mechanisms of nucleation and crystal growth in the field of biomaterials. Theoretical analyses have generated three models about the way this interface could be built. However, so far the proposed models and the experimental images have not completely matched. In this work we comment on some structural arrangements for this interface deduced from the proposed models and arrangements deduced from the experimental high resolution electron microscope images.

Keywords: Octacalcium phosphate-hydroxyapatite interface, Interface relationship, High resolution electron microscopy.

RESUMEN

Existen reportes experimentales que indican que el fosfato octocálcico y la hidroxiapatita producen una interface, y que ésta juega un papel importante en los mecanismos de nucleación y crecimiento en el campo de los biomateriales. El análisis teórico de la forma en que esta interface se genera ha dado lugar a tres modelos. Sin embargo, hasta el día de hoy ninguno de estos tres modelos ha coincidido completamente con los resultados experimentales. En este trabajo comentamos los arreglos estructurales generados a partir de los tres modelos propuestos y los generados a partir de los resultados experimentales de microscopia electrónica de alta resolución.

Palabras Claves: Interface fosfato calcio-hidroxiapatita, Relaciones estructurales, Microscopia electrónica de alta resolución.

INTRODUCTION

Both octacalcium phosphate (OCP, $Ca8H2(PO4)6{\cdot}5H2O$) and hydroxyapatite (HAP, $Ca10(PO4)6{\cdot}(HO)2$) are of great interest in the field of biomaterials due to their importance in the formation of mineralized tissue [1, 2]. Specifically, HAP is the main constituent of bone, tooth enamel, and dental calculi, whereas OCP plays an important role in HAP formation according to several experimental reports on the transformation reported between them. In recent years many reports have appeared about the role of OCP in the nucleation and growth of HAP. In fact, there have been indications from thermodynamic analyses that OCP is a metastable phase [2, 3], and that OCP is transformed into HAP in order to reach a stable equilibrium [1, 4, 5].

According to some reports, OCP can transform into HAP through two possible processes [5]: the first one is by hydrolysis of OCP, and the second one, by dissolution of OCP after precipitation [6, 7]. Grains containing both OCP and HAP domains can be found in each process, in fact forming an OCP-HAP interface [9]. In addition, Xin et al. [8] have reported the in-situ transformation of OCP into HAP by electron beam radiation in the transmission electron microscope (TEM).

Because of the structural similarities between the unit cells of HAP (hexagonal P63/m, a = 9.418, c = 6.884 A) and OCP (triclinic P1, a = 19.69, b = 9.53, c = 6.85 A; α = 90.13o, β = 92.13o, γ = 108.36o), there have been some suggestions on the way HAP and OCP come together to build an interface. The unit-cell data for HAP and OCP can be found in Kay et al. [10] and Brown et al. [11] respectively, and up to date three approaches for the OCP-HAP interface have been reported in the literature (figure 1). The first one was proposed by Brown [11], where aHAP is parallel to bOCP and a 167° angle is formed between aHAP and aOCP. The second approach was proposed by Fernández et al. [12] where -aHAP is parallel to bOCP and the angle between aHAP and aOCP is 131°. Recently, Xin et al. [8] have proposed a third model, where aHAP is parallel to aOCP and an angle of 128° is formed between aHAP and bOCP, and an angle of 64° is formed between aHAP and aOCP. In all these cases, cOCP is parallel to cHAP and [110]OCP is parallel to [110]HAP. The availability of experimental data will enable the validation of the correct model and the correct relationships.

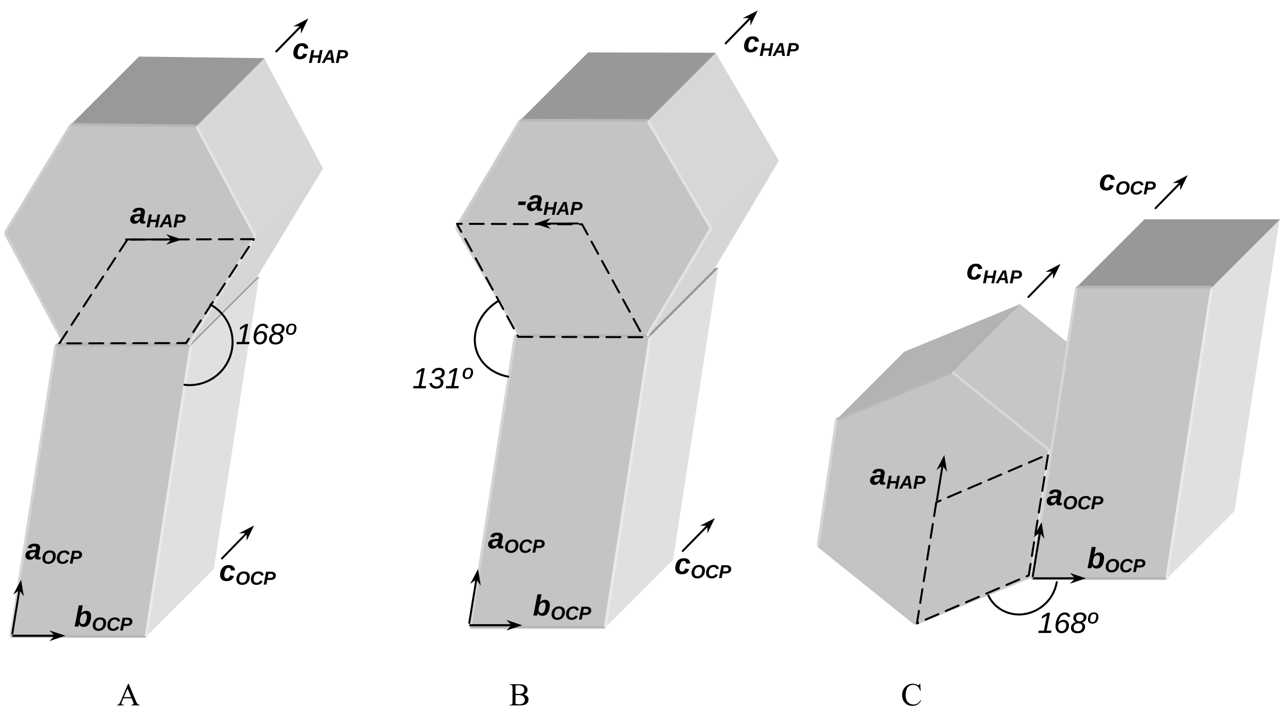

Fig. 1. Schematic 3-D presentation of the three models so far available for the OCP-HAP interface. A) Brown [11], B) Fernández [12] and C) Xin [8].

In this work we comment on the structural relationships that should be observed experimentally for the OCP-HAP interface in the high resolution electron microscope (HTEM) images, according to each one of the three proposed models. On the basis of these comparisons, the need of more experimental and theoretical works to elucidate the correct structural relationships of the OCP-HAP interface is evident.

STRUCTURAL CONSIDERATIONS

The arrangement proposed in Brown's model [11] imply a misfit of 1.2% between OCP and HAP lattices, taking into account that aHAP is 0.942 nm and bOCP is 0.953 nm. The model by Fernández et al. [12] has similar characteristics. On the other hand, the misfit associated to the model of Xin et al. [8] is 4.5% considering that aOCP is 0.985 nm. In any case, those differences are enough to give rise to several types of defects at the interface, such as dislocations. However, as yet no experimental evidence has been provided to indicate their existence or nonexistence.

Additionally, the structural relationships that the OCP-HAP interface must show can be deduced from the arrangement presented in each model. Figure 2 shows the case of Brown [11] and Fernandez et al. [12] along the [010] OCP and [001] OCP zone axes. It is evident that cOCP is parallel to cHAP along the [010]OCP axis. Then, when OCP shows the [010] zone axis, HAP must show the [-12-10] zone axis, and the periodicities shown in figure 2 have to be measured in the HRTEM images. Also, when the interface is oriented so that the electron beam is parallel to the [001] zone axis of OCP, HAP must show the [0001] zone axis.

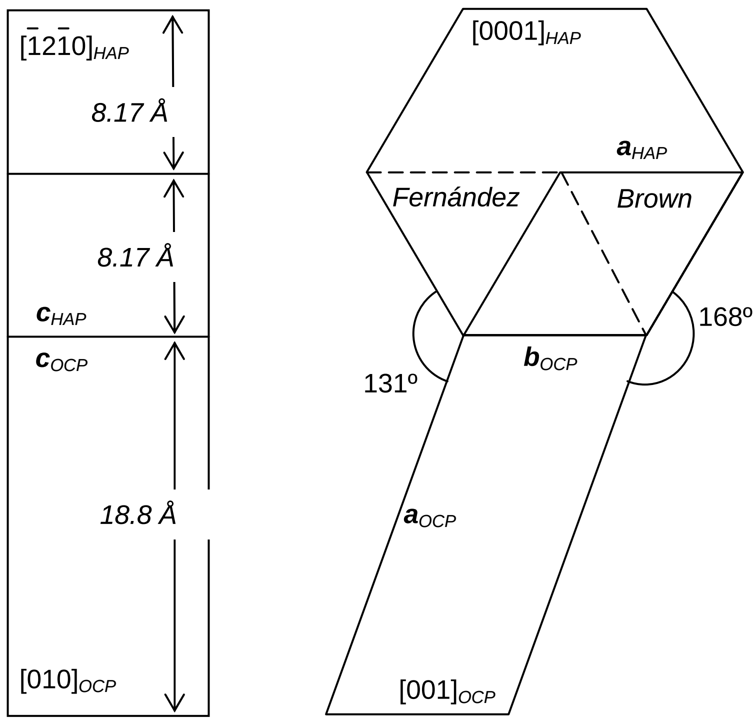

Fig. 2. Structural considerations according to the models proposed by Brown [11] and Fernández [12].

In the case of the model proposed by Xin [8], figure 3 indicates it is not possible to look at the interface when the electron beam is parallel to the [010] OCP zone axis, because of the HAP and OCP structure overlapping. Nevertheless, the interface must be observed on the [100] OCP zone axis, in which case HAP will present the [-12-10] zone axis. Along the [001] OCP zone axis, HAP must present the [0001] zone axis with the arrangement shown in figure 3.

EXPERIMENTAL OBSERVATIONS

There are few experimental HRTEM images of the OCP-HAP interface reported in the literature. Some of them are those described by Iijima et al. [13], Xin et al [8] and Arellano-Jiménez et al. [14].

Iijima et al [13] synthesized lamellar mixed crystals of OCP and HAP with thin plate-like morphology in such a way that distinct OCP lamellas were set at the center of a HAP matrix. The synthesis was carried out in the presence of 1 ppm F- considering the indication that F- causes the growth of apatites in lamellar mode. The structural analysis of the stacking of lamellas indicated that cOCP grew parallel to cHAP in all cases. In particular, figure 3 of reference [13], which is reproduced in figure 7 of reference [12] after image processing, shows a clear lattice-resolution image of the OCP-HAP interface. In this figure we realize that aHAP is parallel to bOCP at the interface and that HAP shows the arrangement along the [1-213]HAP zone axis, whereas OCP shows an arrangement close to the [001]OCP zone axis. The interface was smooth, keeping the epitaxial relationship between OCP and HAP as the most probable. However, looking this figure at glancing incidence, we note a slight mismatch along directions crossing the interface, a clear indication of dislocation-like defects along the interface.

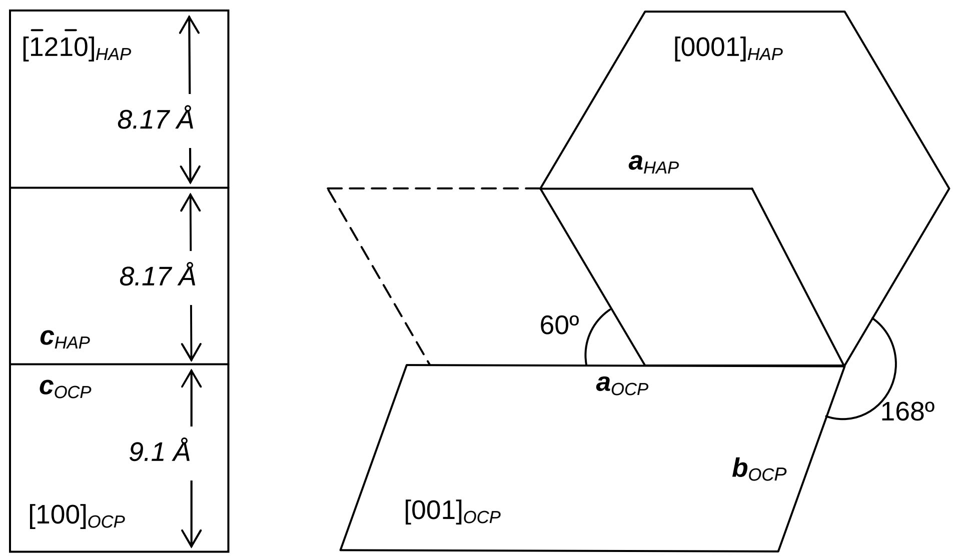

Fig. 3. Structural considerations according to the model proposed by Xin [8].

Xin et al. [8] studied the solid-state transformation of OCP into HAP induced by the electron beam irradiation inside a TEM. Figure 7 in reference [8] shows an HRTEM image of both OCP and HAP structures contained in a flake-like grain after its exposition to the electron beam. The analysis of this image was reported as HAP along the [1-10] zone axis and OCP along the [110] zone axis. However, in contrast to the image shown in reference [12], where a smooth interface is displayed, this figure shows a stepped boundary between HAP and OCP. Taking into account the structural relationship reported for this figure and looking it at glancing incidence, we note a slight mismatch along the c-axis, but a severe mismatch along the [110]-axis.

Arellano-Jimenez et al. [14] reported the transformation of OCP into HAP by hydrolysis of OCP powder. Figure 10d of reference [14] and figure 4 show the interface between [010] zone axis of OCP and a set of {10-10} planes of HAP corresponding to the [1-210] zone axis of HAP, but the electron beam has been slightly out of the exact zone axis. As seen in figure 4, the OCP-HAP interface shows a stepped boundary and its contrast is quite similar to figure 7 of reference [8]. However, as in figure 7 of reference [8], figure 4 shows an angle of 56º between cOCP and cHAP, and an angle of 143º between aOCP and cHAP. Of course, these experimentally deduced orientation relationships are not in accordance with any of the three models. It is clear, therefore, that more experimental observations are required in order to elucidate the real structural relationship in the OCP-HAP interface. We are working now in this direction.

It is worth to mention here the experimental trouble we have found when we have analyzed the OCP-HAP by TEM, mainly HRTEM: when the electron beam interacts with these materials, they present electron beam damage. The electron beam damage of these materials is well known and some researchers have suggested the use of a carbon thin film in order to get enough time to carry out the TEM observation. In fact, Xin et al. [8] have also reported the transition phase from OCP to HAP by electron beam interaction. Therefore, this electron process has to be considered when performing the TEM analysis of the OCP-HAP interface. We suggest the use of a video system.

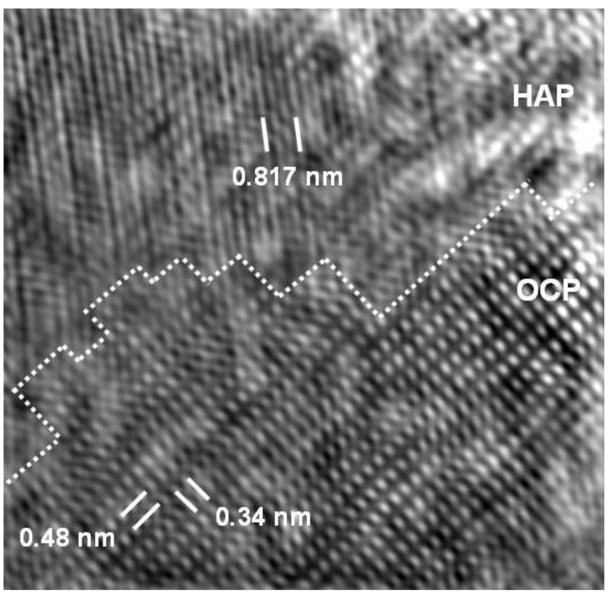

Fig. 4. The HRTEM image of a grain of the sample obtained after thirty minutes of hydrolysis where coexistence of HAP and OCP is observed. Dashed lines indicate a boundary between HAP (along the [10-10] zone axis) and OCP (along the [010] zone axis) phases.

CONCLUSIONS

As discussed above, it is clear that a detailed structural analysis of the interface OCP-HAP remains an open research field. Of course, controlled experimental synthesis and analysis are needed in order to perform a detailed examination of the OCP-HAP interface, and also to determine which model can explain the behavior.

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