SILICON DOPED HYDROXYAPATITES

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The use of implants for bone filling and replacement has acquired a great importance during the last three decades in the developed countries. Actually, the high development of our societies has led to an increase of the lifespan and, consequently, an increase of the osteoporosis incidence and other illness related with advanced ages. As an example, it is estimated that about 40% of asian and caucasian women older than 50 years will suffer an osteoporotic fracture. In this sense, the bioceramics for filling and restoring damaged bones and teeth are one of the most important topics in the field of orthopaedic and oral surgery.

Between the different bioceramics, the hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is the most important calcium phosphate used for bone replacement (1,2). From the point of view of the *biocompatibility*, the hydroxyapatite shows an excellent performance, due to its similarity with the mineral component of the bone. However its *bioactive behaviour*, that is, the ability to join to the living bone when they are implanted, is lower compared to other biomaterials such as bioactive glasses. One of the alternatives to improve the *bioactivity* of hydroxyapatite, is to incorporate silicon into the apatite structure (3). The experimental results have demonstrated the better bioactive behaviour of these *silicon doped* apatites, but the chemical and structural effects on the hydroxyapatite host matrix were not well known (4,5).

From these evidences, we have used powder neutron and X-ray diffraction techniques to carry out a deep structural characterization of these improved bioceramics. Structural analyses were carried out by combining X-ray and neutron diffraction (ND). The structure was refined by the Rietveld method.

Figure 1 shows a scheme of the HA structure. An important feature of neutron diffraction is that neutrons are highly scattered by H atoms. For this reason we can quantify, even if it is small quantity, the amount of H that takes part in the hydroxyls groups (OH^-) at the *4e* position. Our results indicate that SiHA are more hydroxylated than non-substituted HA. That is, the OH^-/O^{2-} ratio characteristic of these compounds (6) when are treated at high temperature, is higher for SiHA.

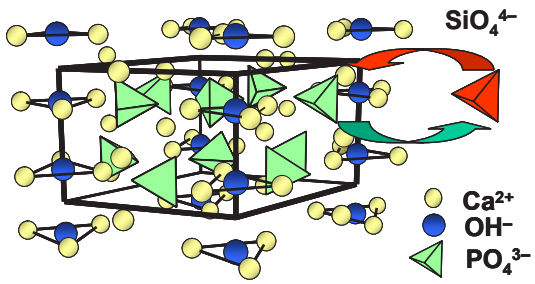

Figure 1. Structure of HA. The SiO_4^{4-} substitution for PO_4^{3-} in Si substituted hydroxyapatite is indicated.

These OH groups sited at the *4e* Wyckoff position are one of the most important sites for the HA reactivity (7). Figure 2 shows the displacement ellipsoids for HA and SiHA calculated from the refined anisotropic displacement parameters. The thermal displacement of the H atom along the c-axis is more than twice for SiHA. The authors did not report on the static or dynamic disorder that yield this volume increase of the displacement ellipsoids. However, this disorder could contribute to the higher reactivity of SiHA (8).

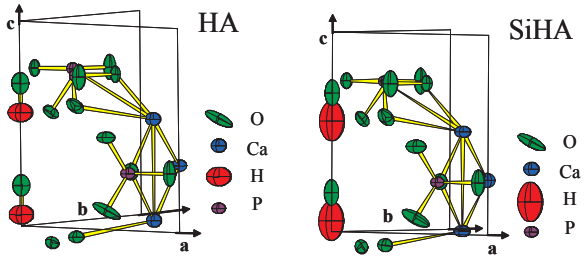

Figure 2. Thermal displacement ellipsoids for HA and SiHA

Under the synthesis conditions used in this work (high temperature and air atmosphere), the formation of HPO_4^{2-} from PO_4^{3-} is possible through the following mechanism

$$PO_4^{3-} + H_2O \longleftrightarrow HPO_4^{2-} + OH^-$$

Although this is a widely accepted statement, there is no reference in the scientific literature providing atomic coordinates for the H atom of the HPO_4^{2-} group. Figure 3 shows the scattering density (SD) Fourier difference maps, calculated from the structural model proposed for HA and SiHA. In the case of SiHA sample, the projection over the mirror plane, parallel to (0 0 1) and sited at ¼ and ¾ of the c axis, clearly show negative SD positions close to the O2 atoms, sited on the mirror plane. These sites correspond to H atoms (they are the only ones that have negative Fermi lengths in this compound) and are sited at the *6h* Wyckoff position. For SiHA, the H atoms seem to be clearly localized at 0.4746, 0.1666 and 0.25 for x, y and z respectively (next to O2 atoms), whereas in HA the negative density sites have lower intensity and appear scattered at the mirror plane at z = 0.25. The negative SD points out that our initial structural model is not complete and additional H atoms should be included. New refinements were carried out for SiHA including H atoms at the position described above, obtaining a better adjustment during the Rietveld refinement (9).
Even if the fraction of the SD of the additional H atoms is quite small, we clearly see them in the Fourier maps. These results demonstrate the presence of HPO_4^{2-} in SiHA. The presence of SiO_4^{4-} in SiHA seems to fix higher amount of H atoms, next to the O2 sites. The stronger charge attraction of the SiO_4^{4-} respect to PO_4^{3-} would explain this difference, facilitating the H^+ incorporation to the PO_4 (or SiO_4) tetrahedrons following the mechanism:

$$2\ PO_4^{3-} \longleftrightarrow SiO_4^{4-} + HPO_4^{2-}$$

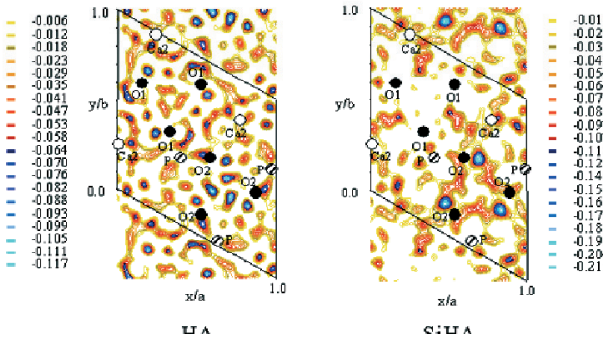

Figure 3. Difference Fourier maps for neutron SD in HA and SiHA. The negative SD (in blue) in SiHA correspond to H atoms (see text).

In this study we have provided a direct evidence of this kind of substitution mechanism, taking into account that HA obtained by ceramic method under air atmosphere are not pure hydroxyapatites but oxy-hydroxyapatites, $Ca_{10}(PO_4)_6(OH)_xO_y$, or more exactly $Ca_{10}(PO_4)_{6-x}(HPO_4)_x(OH)_yO_z$. For first time, we have calculated the hydroxylation degree in oxy-hydroxyapatites and provide crystallographic positions for the H atoms of the HPO_4^{2-} groups by means of a neutron diffraction study.

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