HAL open science

Formation and evolution of hydrated surface layers of apatites

Diane Eichert, Christèle Combes, Christophe Drouet, Christian Rey

To cite this version:

Diane Eichert, Christèle Combes, Christophe Drouet, Christian Rey. Formation and evolution of hydrated surface layers of apatites. Key Engineering Materials, 2005, vols. 284-286 ., pp. 3-6 available on : http://oatao.univ-toulouse.fr/429/1/58.pdf. hal-00474890

HAL Id: hal-00474890

https://hal.science/hal-00474890v1

Submitted on 11 Mar 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Formation and evolution of hydrated surface layers of apatites

D. Eichert[1a], C. Combes[1b], C. Drouet[1c], C. Rey[1d]

[1]CIRIMAT, INPT-ENSIACET, UMR CNRS 5085, 118 route de Narbonne, 31077 Toulouse Cedex, France

[a]eichert@esrf.fr, [b]Christele.Combes@ensiacet.fr, [c]Christophe.Drouet@ensiacet.fr, [d]Christian.Rey@ensiacet.fr

Keywords: Apatite, surface properties, carbonate, magnesium

Abstract. Nanocrystalline apatites exhibit a very fragile structured hydrated surface layer which is only observed in aqueous media. This surface layer contains mobile ionic species which can be easily exchanged with ions from the surrounding fluids. Although the precise structure of this surface layer is still unknown, it presents very specific spectroscopic characteristics. The structure of the hydrated surface layer depends on the constitutive mineral ions: ion exchanges of HPO_4^{2-} ions by CO_3^{2-} ions or of Ca^{2+} by Mg^{2+} ions result in a de-structuration of the hydrated layer and modifies its spectroscopic characteristics. However, the original structure can be retrieved by reverse exchange reaction. These alterations do not seem to affect the apatitic lattice. Stoichiometric apatite also shows HPO_4^{2-} on their surface due to a surface hydrolysis after contact with aqueous solutions. Ion exchange is also observed and the environments of the surface carbonate ions seem analogous to that observed in nanocrystalline apatites. The formation of a hydrated layer in aqueous media appears to be a property common to apatites which has to be taken into account in their reactivity and biological behavior.

Introduction

The surface properties of apatites play a crucial role in their biological behavior, however the alterations of the surface structure in aqueous media have not been extensively studied. The study of poorly crystalline apatites analogous to bone mineral has revealed the existence of a hydrated layer probably located on the surface of the nanocrystals, associated with very specific spectroscopic characteristics observed by FTIR and MAS-NMR [1]. This hydrated unstable layer is especially developed at early stages of apatite formation and decreases on aging due to the development of more stable apatite domains. This evolution appears however to be limited and never reach an end: the surface layer seems always present even in very mature apatites. The ions of the hydrated layer can be easily replaced by other ions from the solution [2,3] and several ion exchange reactions have been described. The object of the present report is to analyze the alterations of the surface layer by ion substitution and to determine if the hydrated layer occurs only in poorly crystalline apatites or if it is a general feature also found in well crystallized apatites exposed to an aqueous media.

Materials and methods

Sample preparation. The nanocrystalline apatites were prepared by double decomposition between a calcium nitrate solution ($Ca(NO_3)_2$, $4H_2O$ 17,7 g in 250 ml deionized water) and an ammonium phosphate solution ($(NH_4)_2HPO_4$, 40g in 500 ml deionized water). The calcium solution was rapidly poured into the phosphate solution. The precipitate was filtered and washed immediately. The ion exchange reactions were performed on the wet suspension by exposing the precipitate to solution of

ammonium bicarbonate or magnesium nitrate (1 M) during 5 minutes. The reverse reactions were made by immersing the carbonate- and magnesium-exchanged precipitates into 1 M solutions of ammonium hydrogenophosphate or calcium nitrate respectively. The precipitates were washed after exchange and reverse reactions, a part was freeze-dried for chemical analysis. All samples were analyzed, wet, by FTIR spectroscopy.

Chemical analysis. Calcium and magnesium were determined by complexometry with EDTA. Mg alone was analyzed by atomic absorption spectroscopy in the presence of Lathanum chloride. The carbonate content was obtained by coulometry of the CO_2 evolved during sample dissolution. Phosphate was determined by spectrophotometry of the phosphovanodomolybdic acid [3].

Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra of the wet gel-like samples were obtained by ATR (Attenuated Total Reflectance) on a ZnSe crystal. The water content was close to 90%. The spectrum of water was subtracted to isolated the absorption due to the apatite precipitate corresponding to the ν_3-ν_1 PO_4 domain and the ν_2 domain of CO_3. The spectral treatments were performed with Grams 32 (Galactic, Salem, NH, USA).

Results

The chemical composition of the precipitated and exchanged nanocrystalline apatites are reported in Table 1. The precipitated apatite exhibited a very low Ca/P ratio, close to that of OCP, however the specific X-ray diffraction pattern and spectroscopic features of the triclinic OCP structure were not detected [1]. The amount of HPO_4^{2-} ions was rather high (18% of total P) and these ions appeared mainly located on the surface of the nanocrystals in non-apatitic sites [1]. The carbonate-exchanged samples exhibited the same (Ca+Mg)/(P+C) ratio than the original samples. The carbonate ions appeared also mainly located in the hydrated layer where they substituted for HPO_4^{2-} ions (data not shown). The reverse reaction removed most of the carbonate ions without altering the cations/anions ratio. Similar observations can be made on magnesium exchanged samples. The substitution ratio appeared higher for carbonate than for Mg ions.

Table 1

Chemical composition of the samples (atomic ratios)

Samples	(Ca+Mg)/(P+C)	C/(P+C)	Mg/(Ca+Mg)
As precipitated	1.39	0.004	-
Carbonate-exchanged	1.40	0.124	-
Carbonate reverse	1.39	0.021	-
Mg-exchanged	1.38	0.007	0.062
Mg reverse	1.39	0.007	0.007

The FTIR spectrum of the precipitated fresh sample is shown in Fig.1. It exhibits very thin phosphate bands which were assigned to the hydrated layer and disappeared on aging [1]. The spectrum has been shown to be close to that of OCP although some shifts in bands positions and the absence of specific bands were noticed [1]. The substitution of HPO_4^{2-} ions by CO_3^{2-} modified the appearance of the spectrum. The bands broadened, several bands were shifted, especially the maximum of the peak, and new bands appeared. The observation of the ν_3 carbonate domain revealed two broad bands at 1465 and 1415 cm^{-1} different from those in the freeze-dried sample (figure 2). In the case of Mg-exchanged samples two broad bands appeared at 1400 and 1340 cm^{-1} assigned to water molecules, which almost disappeared in the freeze-dried samples. The substitution of calcium by magnesium also induced band broadening and shifts. However, the reversed exchange

re-established in both cases the exact original spectrum despite the few amount of foreign ions remaining in the samples (Figure 1).

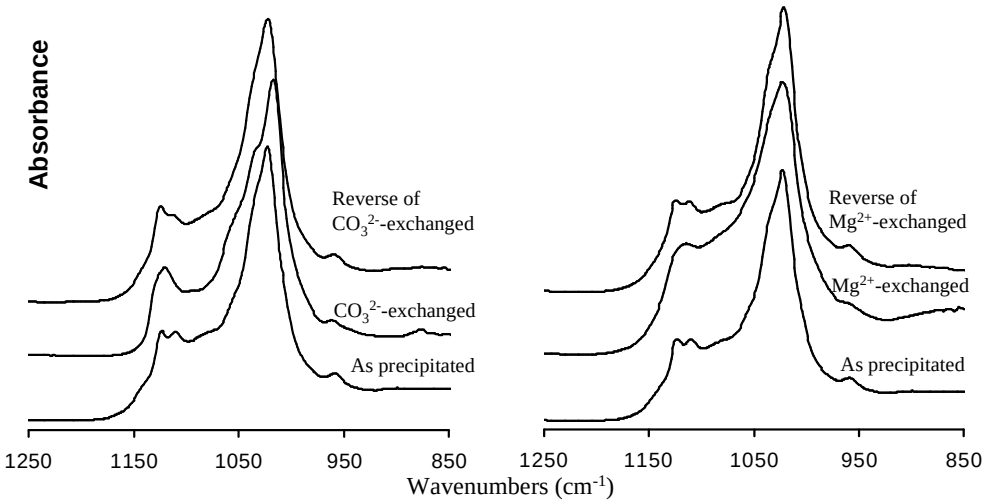

Figure 1: ATR-FTIR spectra of the wet samples showing the reversible alteration of the precipitates submitted to fast ion exchange reactions.

The fast exchange reactions described here did not involve a modification of the apatite domains. The X-ray diffraction data (data not shown) indicated the presence of poorly crystalline apatite with very similar crystal dimensions and characteristics.

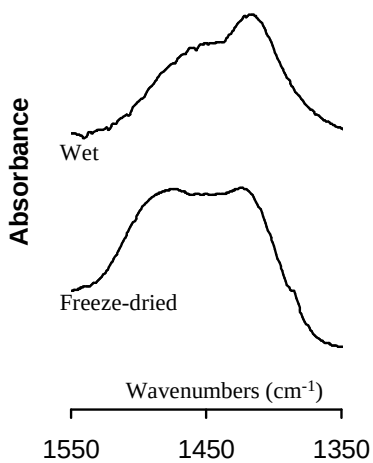

Figure 2 : FTIR spectra of the wet and freeze-dried carbonate exchanged samples illustrating the change in carbonate bands related to drying.

Two main carbonate bands are observed in the ν_3 CO_3 domain suggesting a local symmetry lower than that of the free carbonate ion (D_{3h}). The bands position shifts from 1415, 1465 cm^{-1} in the wet sample to 1420, 1480 cm^{-1} in the freeze-dried sample. This phenomenon is not related to the technique used (ATR for the wet sample and KBr pellets for the freeze-dried sample).

Mis en forme

Discussion

These data confirm the high reactivity and the structural complexity of apatite nanocrystals [1,3]. Dehydration as well as ions exchange modify the local ionic environments and the structure of the hydrated layer. The modifications observed by FTIR on the wet samples concern essentially the phosphate and carbonate groups. The details of these transformations are difficult to determine in the absence of structural model. However, based on the analogy of the spectrum of the precipitated apatite with that of OCP, a preliminary assignment of the phosphate bands can be proposed based on Fowler's work [4]. It appears then that the strongest alterations are related to band assigned to

HPO_4^{2-} ions. The specific shoulder assigned to HPO_4^{2-} ions, at 1140 cm^{-1} especially, is observed in all samples except in the carbonate exchanged sample, confirming the replacement of HPO_4^{2-} groups by carbonate. However, the data cannot be interpreted as a superimposition of altered and original domains. The entirely different spectra in ion exchanged samples suggest a complete structural modification of the phosphate environment related to the carbonate and Mg uptake probably due to a reorganization of water molecules and ions in the hydrated layer. This phenomenon is attested by the alterations of the phosphate and carbonate bands on drying. The effect of ion exchange seems however reversible and the reorganization of the hydrated layer is probably related to a minimum amount of foreign ions, thus the small amount of carbonate and Mg^{2+} ions remaining after the reverse exchange, cannot prevent the original organization of the layer to prevail. These changes could be described as surface phase transformations. The original OCP-like surface structure probably accepts ion substitution to a certain level, however, when the proportion of foreign ions is too large, a de-structuration and possibly a re-structuration occur.

One may wonder if the surface reactivity of nanocrystalline apatites can be extended to well crystallized samples or if it is a specificity related to a peculiar mode of formation. Stoichiometric apatites obtained at high temperature exhibit surfaces that are not in equilibrium with biological fluids. XPS data and the solubility behavior of well crystallized apatite indicate a surface hydrolysis of PO_4^{3-} ions into HPO_4^{2-} [5,6,7]. Such a reaction has been proposed as an initial step of apatite dissolution [7]. The hydration of this modified surface layer can be observed by FTIR and probably participates in a decrease of the surface energy. These surfaces can also bind, like nanocrystals surfaces, small amounts of carbonate groups the IR spectra of which are very analogous to those of carbonate-exchanged apatite nanocrystals [5]. No data is available for Mg ions. These observations suggest that all the HA surfaces in aqueous media react in a very similar way and probably show a similar surface structure. The main difference between well and poorly crystalline apatite lies in the capabilities of evolution of the apatite domains, in nanocrystals, leading to a progressive decrease of the hydrated layer, but not to its complete disappearance.

Conclusion

Apatite surface could be considered as formed of a bi-dimensional hydrated layer containing calcium and HPO_4^{2-} ions, and exhibiting a variable structure depending on the ions composition. The next challenging step is to determine the structures associated with these layers and the conditions of their transformation.

References

[1] D. Eichert, H. Sfihi, C. Combes, C. Rey: Key Eng. Mater. Vols. 254-256 (2003), p. 927

[2] S. Cazalbou, C. Combes, D. Eichert, C. Rey: J. Mater Chem. Vol. 14, (2004), p. 2148

[3] C. Rey, A. Hina, A. Tofighi, M.J. Glimcher: Cells and Materials Vol. 5 (1995), p. 345.

[4] B.O. Fowler, M. Markovic, W.E. Brown: Chem. Mater. Vol. 5 (1993), p. 1417.

[5] C. Rey, A. Hina, S. Amrah-Bouali, X. Ranz: *Fourth Euro-ceramics, Bioceramics* (Faenza Editrice, Italy, 1995)Vol.8, p.301

[6] S. Amrah-Bouali, C. Rey, D. Bernache, A. Lebugle: Biomaterials Vol. 15 (1994), p. 269.

[7] J. Christoffersen: J. Crystal Growth Vol. 49 (1980), p. 29.