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The Hydrogen Motion in Nonstoichiometric Hydroxylapatites

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Infrared experimental evidence is presented in favor of a mechanism of continuous and reversible hydrogen motion from $HPO_4^{2-} \cdots OH^-$ to $PO_4^{3-} \cdots H_2O$ in nonstoichiometric hydroxyapatite. It is also shown how such a mechanism is responsible for the presence of a librational OH band at 670 cm^{-1} in the infrared spectrum of fluoroapatite.

1. Introduction

Nonstoichiometric calcium hydroxyapatites form a family of compounds constituting the bones and teeth of humans and many animals (*1*). These compounds are also present in renal and prostatic calculi (*2*); therefore, they have been well studied.

Apart from impurities such as carbonate, Na, Mg, K, Cl, F, and citrate, which are frequently present in the apatites of biological and mineral systems, the generally accepted formula for nonstoichiometric calcium apatites is that proposed by Berry (*3*);

$$Ca_{10-x}(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x}xH_2O,$$

in which the value of x varies between 0 and 2. These compounds crystallize in the hexagonal system and contain hexagono-helicoidad channels throughout their structure; the OH groups and the binary axis of symmetry of the water molecules are situated on the axis of the channels whereas the Ca^{2+} and PO_4^{3-} ions comprise the channel walls, so that each OH group or water molecule is situated between three PO_4^{3-} groups and three Ca^{2+} ions. HPO_4^{2-} ions occupy the same site as PO_4^{3-} ions.

It has been assumed (*5*) that the rotation of the water molecules around the z axis is equivalent to a continuous hydrogen migration from $HPO_4^{2-} \cdots OH^-$ to $PO_4^{3-} \cdots H_2O$ and from $PO_4^{3-} \cdots H_2O$ to $HPO_4^{2-} \cdots OH^-$. When averaged over all possible water rotations in the crystal the numbers of HPO_4^{2-} ions and water molecules become the same in a dynamical equilibrium.

The proposed model of continuous hydrogen migration arises from the full equivalence among the three configurations taking place through the I_B rotation of the water molecule. In other words, the necessary condition for our mechanism is that the water molecule have C_3 symmetry under rotation around the I_B inertia axis (z axis of the crystal).

The proportion of hydrogen migrations per unit cell is expected to increase when the value of x (which is directly related to the number of water molecules per unit cell) increases from 0 to 1. For this last value of x the proportion of hydrogen migrations per unit cell reaches a maximum and then (x running from 1 to 2) must decrease. In fact, when x goes from 1 to 2 the number of groupings $[(PO_4)_2(HPO_4)H_2O]$ in which the C_3 symmetry for water rotation is not realized increases in such a way that no hydrogen migration is allowed for $x = 2$, as confirmed by the infrared spectrum of octacalcium phosphate.

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The C_3 symmetry of water molecule under I_B rotation is also broken when the apatite is deuterated due to the nonequivalence between the groupings $HPO_4^{2-} \cdots OD^-$ and $DPO_4^{2-} \cdots OH^-$. This gives rise to a potential curve for water rotation whose extremals are not situated at the same energy relative to each other, so that the ability of HPO_4^{2-} and OH^- (or H_2O) to be deuterated does not depend on the mechanism of continuous hydrogen migrations.

In order to confirm the existence of such a mechanism in these compounds, measurements of the dimensions of the apatite unit cell and calcination assays have been carried out.

2. Experimental

Ca hydroxyapatites were prepared by the method of Winand (*4*). Ca fluoroapatite was obtained by calcination of a mixture of stoichiometric hydroxyapatite and calcium fluoride at 800°C for 3 hr. The proportion of CaF_2 relative to the hydroxyapatite was close to 4% in weight. α-Tricalcium phosphate was a commercial sample. X-Ray diffraction patterns and infrared spectra were recorded on each sample and showed one-phased apatitic specimens. Chemical wet analysis, including atomic absorption measurements, indicated that original samples possessed the corresponding stoichiometry.

Middle infrared absorption spectra were obtained on samples in KBr pellets using a Perkin–Elmer 457 spectrophotometer. X-Ray diffraction patterns were recorded on a PW 1050 X-ray diffractometer, using Ni-filtered radiation. Electron diffraction patterns were obtained in a Siemens Elmiscop 1A electron microscope.

3. Results and Discussion

Using synthetic calcium apatites of known x in which neither CO_3^{2-} nor any other substituting species occurred, the variation of the characteristic dimensions of the unit cell against x has been studied for hexagonal calcium apatites. The values of x were fixed between 0 and 2. The measured a $(=b)$ and c hexagonal parameters are plotted in Fig. 1 against x. It can be observed that c continuously decreases when x increases from 0 to 2, whereas a $(=b)$ first decreases from $x = 0$ to $x = 1$ and afterwards increases from $x = 1$ to $x = 2$. The trend of c with x can be easily explained considering that when x increases the number of O–H bonds nonparallel to the z axis and the "calcium holes" is made greater. In order to explain the form of the curve for the parameter a $(=b)$ we note:

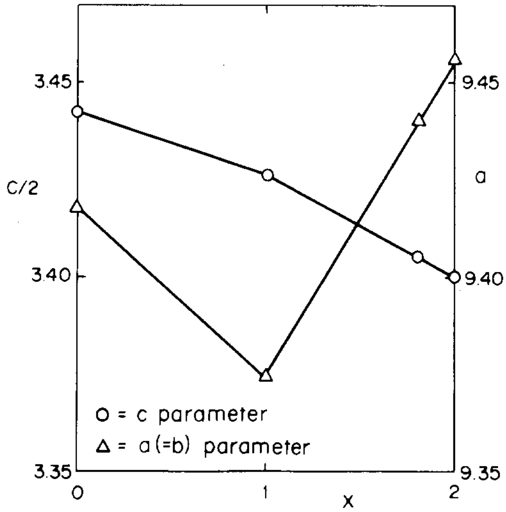

FIG. 1. Variation of the hexagonal parameters of the unit cell of calcium apatites with x.

1. The continuous hydrogen migration can be assimilated to a proton resonance in which successive proton bonds are formed between an OH group and each of the three PO_4^{3-} ions surrounding it. In a way similar to that in which π-electrons make the C–C bonds in conjugated organic systems more stable and shorter, "resonant protons" will make the bonds between an OH group and each of the three PO_4^{3-} ions surrounding it more stable and shorter, so that when the proportion of the continuous hydrogen motion increases, a decrease must be expected for the averaged a $(=b)$ parameter.

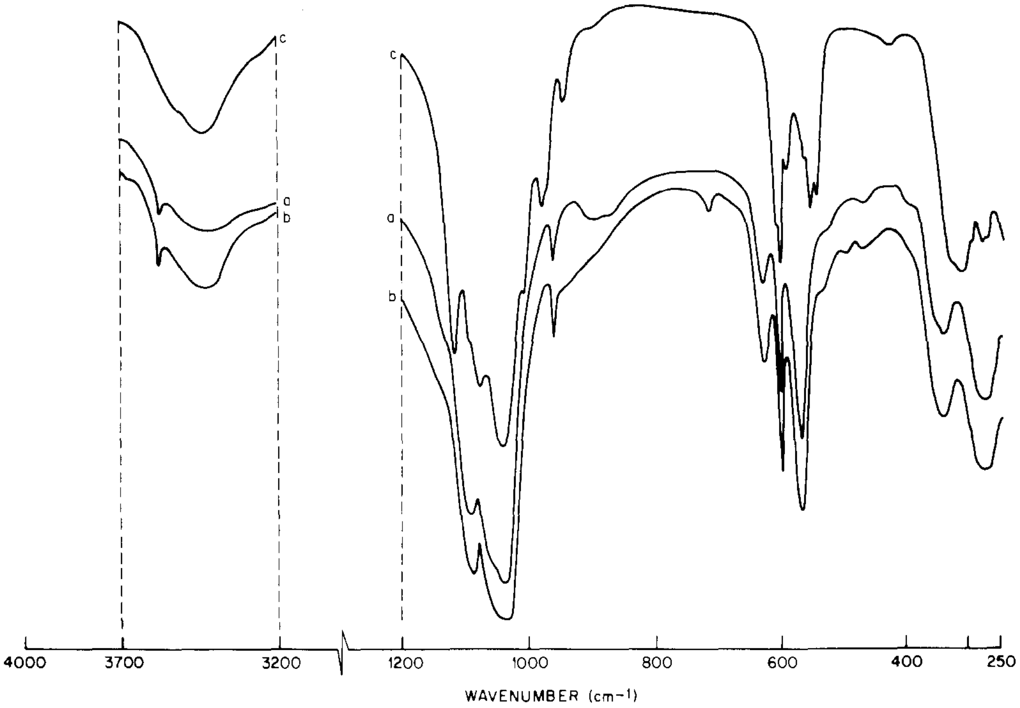

FIG. 2. Infrared absorption spectra of: (a) α-tricalcium phosphate, (b) the same sample heated at 300°C for 3 hr, (c) the same sample heated at 800°C for 3 hr.

2. If the hydrogen migrations do not occur, HPO_4^{2-} ions with a static O–H bond approximately parallel to the plane a, b, and permanent water molecules appear. From geometric considerations one can see that this is equivalent to an increase of the averaged cross section of the apatitic channels.

So, since the proportion of hydrogen migrations per unit cell increases from $x = 0$ to $x = 1$ and decreases from $x = 1$ to $x = 2$, the curve giving the variation of the a ($=b$) parameter vs x seems justified only if the mechanism of continuous hydrogen migration is assumed to be operative in nonstoichiometric hydroxyapatites.

A characteristic term of the apatitic family is the α-tricalcium phosphate:

$$Ca_9(PO_4)_5(HPO_4)(OH)H_2O. \qquad (1)$$

Under heating at 800°C this compound transforms into β-tricalcium phosphate [$Ca_3(PO_4)_2$]. How α-tricalcium phosphate becomes β-tricalcium phosphate is not clearly explained at present. One knows that the HPO_4^{2-} ions convert to $P_2O_7^{4-}$ ions upon heating, and it has been checked that the $Ca_2P_2O_7$ reacts with stoichiometric hydroxyapatite at 700°C to give β-tricalcium phosphate.

Figure 2a shows the infrared spectrum of α-tricalcium phosphate and Figs. 2b and c, the spectra of α-tricalcium phosphate heated at 300 and 800°C, respectively. In the former, one can observe the characteristic bands of the OH groups (3572 and 630 cm^{-1}) and of the HPO_4^{2-} ions (864 cm^{-1}). The formation of internal $P_2O_7^{4-}$ ions is indicated in the spectrum of Fig. 2b by the band at 715 cm^{-1}, attributed to a P–O–P vibration (*6*). The spectrum of Fig. 2c corresponds to the β-tricalcium phosphate.

Since HPO_4^{2-} ions are present in α-

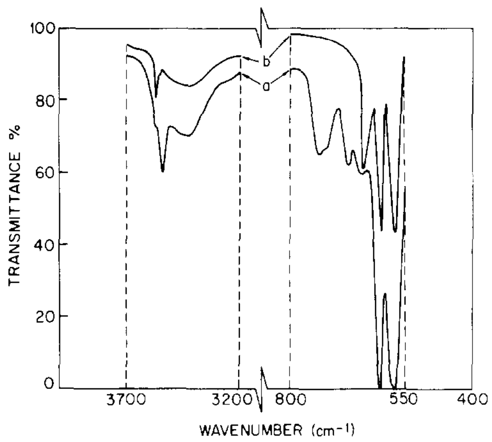

FIG. 3. Infrared absorption spectra of: (a) nearly stoichiometric fluoroapatite, (b) nearly stoichiometric hydroxylapatite.

tricalcium phosphate, the formation of β-tricalcium phosphate has been attributed to this reaction between $Ca_2P_2O_7$ and stoichiometric hydroxyapatite.

However, it is not clear how equal quantities of $Ca_2P_2O_7$ and $Ca_{10}(PO_4)_6(OH)_2$ can be formed from (1) to yield only β-tricalcium phosphate.

Let us consider that the mechanism of continuous hydrogen migrations, described above, takes place in (1). If so, when certain amounts of HPO_4^{2-} are transformed into $P_2O_7^{4-}$ above 250°C, the equilibrium between HPO_4^{2-} and water molecules, assumed by the proposed mechanism, is broken. To recover this equilibrium the hydrogen migrations are displaced toward the formation of HPO_4^{2-};

$$Ca_9(PO_4)_5(P_2O_7)_{0.5}(OH)H_2O,$$

$$Ca_9(PO_4)_{4.5}(P_2O_7)_{0.5}(HPO_4)_{0.5}(OH)_{1.5}0.5H_2O \quad (2)$$

so that the equilibrium is restored. The HPO_4^{2-}, present again in (2), undergoes dehydration and new $P_2O_7^{4-}$ ions are formed:

$$Ca_9(PO_4)_{4.5}(P_2O_7)_{0.75}(OH)_{1.5}\,0.5H_2O. \quad (3)$$

Dehydration of (3) directly gives β-tricalcium phosphate.

On the other hand, the infrared spectrum (Fig. 3a) of a compound obtained by heating at 800°C a mixture of nearly stoichiometric hydroxyapatite (Fig. 3b) which contained a small amount of HPO_4^{2-} ions, evidenced by infrared spectroscopy[1] and calcium fluoride, shows a stretching OH band at 3540 cm^{-1}. Since the theoretical curve relating $\Delta\nu(OH)$ to the O···F distance in O–H···F distance in O–H···F hydrogen bonds (*7*) reproduces well the observed O···F distance (3·14 Å) (*8*) for the shift corresponding to the band at 3540 cm^{-1}, that band can be attributed to the presence of an O–H···F hydrogen bonding mechanism along the apatitic channels in partially fluorided hydroxyapatite. Nevertheless, bands at around 730 and 670 cm^{-1} in the same spectrum indicate (*9*) that a remarkable quantity of $P_2O_7^{4-}$ ions is formed and remains within the apatitic lattice.

To explain how these $P_2O_7^{4-}$ ions can be formed it is necessary to consider that the number of HPO_4^{2-} ions per unit volume becomes greater when fluorine is introduced in the apatitic lattice; so, the reaction $2HPO_4^{2-} \xrightarrow{a} P_2O_7^{4-} + H_2O$ at 800°C can be allowed. This could be justified only if a part of the small proportion of water molecules present in the sample converts into OH groups (a part, at least, of which is substituted by fluorine), giving rise to an additional quantity of HPO_4^{2-} ions. This is just a consequence of the mechanism of the continuous hydrogen migration.

The bending P–O–P mode of γ-calcium pyrophosphate appears at 715 cm^{-1}. If the $P_2O_7^{4-}$ ions are included within the apatitic lattice and are, furthermore, perturbed by a certain amount of fluorine, it is not surprising that the bending P–O–P mode is shifted to 730 cm^{-1} in calcium fluoroapatite. It is well known that there is strong dependence of the bending

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[1] Because of the small quantity of HPO_4^{2-} ions present in this sample, the spatial separation among these ions is probably large enough to preclude reaction $2HPO_4^{2-} \xrightarrow{a} P_2O_7^{4-} + H_2O$ at 800°C.

vibrational levels of quasi-linear systems on the valence angle.

OH groups bonded to fluorine in fluoroapatite cannot rotate around the *z* axis. Therefore no librational band can arise from these kinds of OH groups, so that the librational band at 670 cm^{-1} has to originate in the OH groups situated in reduced channels (*9*) which are not bonded to fluorine atoms.

Since the band at 670 cm^{-1} is assigned to the OH librational mode always associated with the OH stretching mode appearing, as in the case of OH···F, at 3540 cm^{-1} (*9*), the band at 3540 cm^{-1} in the infrared spectrum of Fig. 3a must be either a pure stretching band of the OH situated within the channels with reduced cross section, or else a band composed of the O–H···F and O–H stretching modes.

So, we have shown that hydrogen migration is necessary to explain the results of the calcination assays as well as to justify the hexagonal unit cell parameters for different calcium apatites.

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