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IR-SPECTROSCOPIC INVESTIGATIONS OF NANOHYDROXYAPATITE POWDERS

Yurij Sakhno, PhD student and Gianmario Martra, professor Universita di Torino, Torino, Italy

Recently, apatite minerals have gained much attention because of their biological importance. Hydroxyapatite is the major constituent of mammalian bones and tooth enamel. In addition to bone mineral and organic matrix, water is an abundant component of bone, accounting for up to 25% by weight. Attempts have been made to define and understand the role of water present in pore spaces of bones. Simultaneous derivative thermogravimetric analysis and variable temperature X-ray diffraction studies revealed the presence of structural water on carbonated apatite, a synthetic apatite used as a model of bone mineral that contains carbonate ions and is deficient in hydroxide, phosphate, and calcium ions. The unraveling of the ensemble of surface processes and phenomena actually occurring *in vivo* is still a challenge, but there is a general consensus in setting the causal sequence: (i) biomaterial surface structure, (ii) states of adsorbed water molecules, and (iii) states of adsorbed proteins, as one of the main factors ruling the fate of the interaction of the implant (then actually occurring through a hybrid synthetic/proteic interface) with cells [1,2].

Among bioceramic, hydroxyapatite-based materials play a quite relevant role, as they can be considered the synthetic version of the mineral part of bone tissue and enamel, and, indeed, the possibility to prepare them in a nanometric/nanostructured form is considered one of the requisites to fulfill for a "biomimetic" approach to the preparation of optimized materials .

Our target has been to determine the nature of the complex structure of particles IR spectroscopy, augmented by the use of H₂O, D₂O, and CO as probe molecules.

Hydroxyapatite powder, HA (BET specific surface area) 78 m²/g), was synthesized through an aqueous medium procedure, dropping in a Ca(OH)₂ suspension a 1.3 M solution of H₃PO₄, to accomplish the reaction 5Ca(OH)₂ + 3H₃- PO₄ f Ca₅(PO₄)₃OH+9H₂O. The system was continuously stirred at 40 °C; a ripening time of 2 h was used. The precipitate was then washed, filtered, and dried in air at room temperature. For IR measurements, high purity CO (Praxair) was employed without any additional purification except liquid nitrogen trapping, while H₂O and D₂O (99.9 atom % D, Aldrich) were admitted onto the samples after several freeze-pump-thaw cycles. FTIR spectra were obtained using a Bruker Vector 22 spectrometer (resolution: 4 cm⁻¹) equipped with DTGS or MCT detector, for ATR and transmission mode, respectively. Infrared spectra for the analysis of

surface features were performed in transmission on HA powders pressed in self-supporting pellets. The samples were placed in a quartz IR cell equipped with KBr windows designed to carry out spectroscopic measurements both at beam temperature (ca. 50 °C) and low temperature (ca. -170 °C, by cooling with liquid nitrogen). The cell was connected to a conventional vacuum line (residual pressure: 1×10^{-5} mbar, 1 mbar) 10^2 Pa) allowing all thermal treatments and adsorption-desorption experiments to be carried out in situ. The spectra of adsorbed CO are reported in absorbance, after subtraction of the spectra of the samples before adsorption as background.

Figure 1. IR spectra of HA: (a) in contact with H₂O vapor (23.5 mbar) and then outgassed at beam temperature (ca. 50 °C) for (b) 0.5, (c) 2, (d) 15, and (e) 120 min. Curve f is the spectrum obtained after 4 cycles of H₂O/D₂O exchange and subsequent outgassing at beam temperature for 120 min. Insets: zoom of the 3755-3600 cm⁻¹ (left) and 1780-1580 cm⁻¹ ranges; lettering as in the main frame.

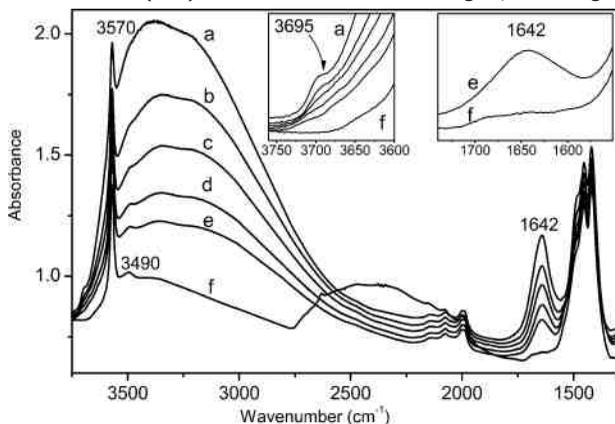


Figure 1 reports the spectra, in the 3750-1350 cm⁻¹ range, recorded during progressive outgassing at room temperature (curves a-e), together with the spectrum obtained at the end of an equivalent outgassing process after contact with D₂O (curve f). The region at lower frequency was not observable, because of the lack of transparency due to the fundamental absorptions of lattice phosphate groups.

In the range shown in the figure other absorption bands due to bulk species are present, namely the sharp peak at 3570 cm⁻¹, due to the stretching of OH⁻ aligned in columns (occupying the 4e position in the hexagonal lattice, hereafter referred to as "columnar" hydroxy groups), a set of weak components in the 2200-1900 cm⁻¹ region, related to overtone and combination modes of the fundamental vibration of phosphate groups absorbing below 1350 cm⁻¹, and bands in the 1550-1350 cm⁻¹, with two main components at 1420 and 1454 cm⁻¹, produced by the stretching modes of carbonate groups. Besides these signals, the spectrum of HA in equilibrium with the water vapor pressure (Figure 1, curve a) exhibits, as main component, a broad band spread over the 3700-2500 cm⁻¹ range, with maximum at ca. 3350 cm⁻¹ and a shoulder at ca. 3100 cm⁻¹, that results from the superposition of the absorption due to the stretching mode of surface hydroxy groups and adsorbed water molecules; these latter are also responsible for the band at 1642 cm⁻¹ (δ H₂O) and the very weak and ill-resolved component at 3695 cm⁻¹, due to the stretching of dangling -OH of water molecules at the end of (H₂O-H₂O)_n polymeric surface chains.

By progressive outgassing at beam temperature (ca. 50°C), the component at 3695 cm⁻¹ disappears, and the bands in the 3600-2500 cm⁻¹ range and at 1642 cm⁻¹ decrease in intensity, monitoring the depletion of physisorbed H₂O liquid-like multilayers (Figure 1, curves b-e). The lower intensity of the broad absorption at high frequency allows the detection of a component at 3490 cm⁻¹. A signal in a similar position has been observed for both geological and synthetic apatites and

assigned to columnar hydroxy groups interacting via H-bond with Cl^- . As such a kind of anion is absent in the material investigated, we propose that the signal at 3490 cm^{-1} could be due to bulk OH^- perturbed by carbonate anions, distorting the structure locally. Some change in shape and relative intensity of the bands of the carbonate groups occurs also, fully reversible by re-admission of water (not shown); such a sensitivity to hydration indicates that some of the carbonate groups are exposed at the surface.

Remarkably, even after prolonged outgassing at beam temperature, a component at 1644 cm^{-1} is still present (Figure 1, curve e), with an integrated intensity of ca. 25% of the initial one (Figure 1, curve a), indicating that the sample retains a significant amount of water molecules (also contributing with their stretching modes to the broad $3600\text{-}2500\text{ cm}^{-1}$ band). Several studies on synthetic hydroxyapatites reported that this kind of material can contain H_2O molecules occluded in the bulk. To assess the actual location of the retained water, the outgassed sample was put in contact with the vapor pressure of D_2O at beam temperature, to selectively replace surface OH groups and H_2O molecules with OD and D_2O species, respectively; a deuteration of the subsurface layers and/or the bulk occurs at a significant extent at temperatures $\geq 150\text{ }^\circ\text{C}$. Several D_2O adsorption/outgassing cycles were performed, until a constant intensity of the $\delta_{\text{H}_2\text{O}}$ band was attained (Figure 4, curve f), corresponding to ca. 10% of that before isotopic exchange (Figure 1, curve e). Also the broad absorption in the $3600\text{-}2500\text{ cm}^{-1}$ range appeared decreased in intensity, in particular, on the low-frequency side, while a broad new component appears in the $2750\text{-}1800\text{ cm}^{-1}$ range, due to the superposition of the stretching bands of surface deuterioxy groups and still adsorbed D_2O molecules. The band due to the deformation mode of these latter, expected at ca. 1200 cm^{-1} , was not observed, because below the transparency cutoff of the material. The sample was then back-exchanged with H_2O and outgassed at beam temperature, and the same spectrum that before contact with D_2O was obtained (not shown).

A second significant insight results from the lower effect of the H/D exchange on the intensity of the νOH component spread on the $3450\text{-}2500\text{ cm}^{-1}$ range with respect to the $\delta_{\text{H}_2\text{O}}$ band at 1642 cm^{-1} . This behavior could be due to a higher extinction coefficient of the stretching absorptions of occluded water with respect to that on the surface, or to the presence in the bulk of hydroxy groups involved in hydrogen bonding, responsible for the broadness of the signal. The first hypothesis can be ruled out because of the position at higher frequency of the maximum of the νOH band left after H/D exchange (Figure 1, curve f), that indicates the presence of OH oscillators involved in weaker hydrogen bonds, and then with a lower νOH extinction coefficient. It can be then concluded that hydroxy groups chemically and/or structurally different from bulk columnar OH^- are present in the material.

The behavior of the $\delta_{\text{H}_2\text{O}}$ band will be described first, as this signal is specific for water molecules, and then the evolution of the complex νOH signal in the $3700\text{-}2500\text{ cm}^{-1}$ region, related to the presence of both water and hydroxy groups, will be considered.

Finally, bulk phosphate and carbonate groups, responsible for the sets of signals in the $2200\text{-}1900$ and $1600\text{-}1350\text{ cm}^{-1}$ ranges, respectively, appeared essentially stable up to outgassing at $300\text{ }^\circ\text{C}$. In contrast, such bands and the signals related to columnar OH^- (3570 cm^{-1} and 3490 cm^{-1}) progressively decreased in intensity and changed in shape by raising the outgassing temperature up to $800\text{ }^\circ\text{C}$, indicating the occurrence of a transformation of the bulk structure.

The ν_{CO} band observed must be then essentially attributed to CO molecules adsorbed on surface Ca^{2+} sites by electrostatic/ polarization interaction that re-

sults in an upward shift of the stretching frequency of adsorbed CO, increasing as the Lewis acid strength of the adsorbing center increases. The two components at 2170 and 2180 cm^{-1} monitor the presence of two families of Lewis acid centers, the stronger ones constituting a minor fraction.

For the sake of completeness, IR spectra of CO adsorbed on HA pre-outgassed at 300 °C were also recorded, as this treatment resulted in the complete desorption of water molecules from the surface accompanied by a severe modification of the surface itself. Surprisingly, the spectra of adsorbed CO at decreasing coverage were not so markedly different from those obtained for the sample pre-outgassed at 130 °C: the component at high frequency appeared more intense and slightly up-shifted, but the overall intensity of the spectral pattern at high coverage was essentially equivalent to the previous case. By assuming that the molar extinction coefficient of adsorbed CO species is independent of frequency changes in the 2185-2165 cm^{-1} interval, such spectral pattern indicated that the amount of surface Ca^{2+} probed by CO was essentially unaffected by the pre-outgassing at higher temperature, while a change in the local structure of a significant part of them occurred, resulting in an increase of their Lewis acid strength.

There is then a relevant discrepancy between the indication on the effect of outgassing at 300 °C on the surface structure provided by the rehydration test, i.e., by H_2O as probe molecules, and the adsorption of CO. However, it can be proposed that a part of surface Ca^{2+} dehydrated by outgassing at 130 °C relaxed inward the surface, in an extent large enough to render them unable to adsorb a weak probe molecule as CO, that then can monitor the Ca^{2+} ions remained more exposed at the surface. However, the relaxation can be reversed by interaction with H_2O , definitely stronger as ligand, and then in rehydration tests water molecules probed the presence of a larger amount of surface Ca^{2+} sites. By increasing the outgassing temperature up to 300 °C, a more severe modifications of the surface structure could have occurred, resulting in an inward relaxation, irreversible by rehydration, of ca. 60% of surface cations, that then cannot be longer probed neither by CO nor H_2O .

The use of IR spectroscopy and the control of the atmosphere surrounding the samples in both kind of experiments was useful for a quantitative estimation of the amount of hydroxyl groups and water constituting the first surface hydration layer. Such a layer, for the as-prepared material, appeared mainly constituted by H_2O molecules coordinated to surface Ca^{2+} ions, approximately in a 1:1 ratio. Removal of water by outgassing at increasing temperature produced a progressive modification of the surface structure, with an increased level of irreversibility as the temperature increased, resulting in the loss of sites able to coordinate H_2O molecules by subsequent rehydration. In turn, such changes in the first hydration layer resulted in the decrease of the extension of water overlayers. This result indicated that it can be possible to modify in a controlled way the behavior toward water of synthetic HA materials, one of the main aspects ruling their interaction with the biological media.

References and Notes

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ПОДГОТОВКУ УЧИТЕЛЕЙ – НА УРОВЕНЬ СОВРЕМЕННЫХ ТРЕБОВАНИЙ

Асадуллин Р.М. (Уфа, Россия)

Принципиальные изменения, происходящие в настоящее время в России в социальной и экономической сферах, в частности вхождение страны во Всемирную торговую организацию, ставят задачу модернизации системы образования во всех ее звеньях.

Очевидно, что интеграция в мировую практику образования — это проблема, поставленная жизнью, а не выдумка реформаторов. Вопрос «быть или не быть» состоит не в том, присоединиться или нет к Болонскому соглашению, а в выборе стратегии, которая не позволит отстать от экспресса истории, стремительно уходящего в будущее. При этом, однако, важно сохранить «особую стать» нашей сформировавшейся системы образования.

Современная ситуация в образовании складывается таким образом, что реформы следуют одна за другой, однако ни одно из выбранных направлений не доводится до конца, поэтому и результаты не являются базой, на которую можно было бы опираться, прогнозируя новую реформу. Сегодня нельзя подходить к реформам с традиционных позиций. В настоящее время заказчиком образования является не только государство, но и личность, и работодатель, а образование может рассматриваться как образовательная услуга. Отсутствие традиций в этом вопросе, помноженное на менталитет россиян и традиционно скудное финансирование, может привести к частичному, усеченному решению образовательных задач. Поэтому чрезвычайно важно, реформируя систему образования, не спешить, разобраться в каждой детали. Запутавшись в стратегиях, можно вместо ожидаемых светлых перемен получить удручающие результаты. Первые шаги реформ, в том числе реализация национального проекта, как справедливо отметил министр образования и науки РФ А.А.Фурсенко, всего лишь старт системным изменениям во всех звеньях российского образования. В этих условиях современный педагогический университет должен рассматриваться как источник образовательных инноваций, способствовать развитию новых образовательных проектов, стать центром интеграции с региональной образовательной системой. Основное направление инноваций, определенных стандартами второго и особенно ожидаемого третьего поколения государственных образовательных стандартов в области профессионального образования, будет связано с переориентацией образовательного процесса с предметоцентризма на функциональную подготовку специалистов. Вузам предлагается сохранить преимущества в фундаментальной и теоретической подготовке студентов и одновременно формировать компетентного, т.е. способного к профессиональной деятельности специалиста. Разумеется, что это возможно лишь при обновлении содержания образования и выборе адекватных решаемым задачам образовательных технологий.

Как известно, система высшего профессионального образования в России занимает одно из лидирующих мест в мире. Однако, несмотря на это, ей присущ ряд серьезных недостатков, а именно:

- технологическая необеспеченность формирования профессиональ-