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State of Water in Amorphous Calcium and Calcium–Magnesium Phosphates

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Abstract—Fourier-transform infrared spectra of three samples of deposited amorphous phosphates, calcium monodiphosphate (orthopyrophosphate) with a molar ratio 2P/(2P + 1P) of ~0.3, calcium magnesium monophosphate with an atomic ratio Mg/(Mg + Ca) of ~0.3, and calcium–magnesium monodiphosphate with a molar ratio 2P/(2P + 1P) of ~0.1 and atomic ratio Mg/(Mg + Ca) of ~0.1, were analyzed. On the basis of the observed similarity between the ν(OH), δ(OH) and (δ + ω)(OH) lines in the spectra of these phosphates and liquid water analogous states of water molecules therein were assumed. It was presumed that the formation of amorphous phosphates involves deposition of poorly soluble substances on the surface of water nanoclusters.

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In the recent time calcium phosphates have turned to be inorganic substances that are very important for medi-cine. The reason is that the calcium salt $Ca_5(PO_4)_3(OH)$ which is also called hydroxyapatite is the base material of the human skeleton. Furthermore, previously extensive use of donor materials for the treatment of bone diseases is now terminated. Synthetic calcium phos-phates can be successfully used to obtain various materials and substances for the treatment, regenera-tion, and replacement of affected or lost bone tissues. Hydroxyapatite and its closest analog, tricalcium phosphate, are now widely used as components of various biomaterials [1–6]. Of specific interest are those modifications of calcium phosphates which are close to hydroxyapatite in the chemical composition but are amorphous. This interest originates from enhanced biological activity of amorphous calcium phosphates and their ability to undergo biodegradation [4, 7, 8].

Amorphous calcium phosphates are usually prepared by exchange reactions between phosphoric acid salts and calcium compounds in the presence of substances that prevent formation of crystalline products. The best crystallization inhibitors are biogenic diphosphates (pyrophosphates) and magnesium salts [7–12]. Products of exchange reactions between the above reagents are hydrated substances whose nature is not completely clear.

The present comuunication reports on the results of FTIR study on three samples of amorphous calcium phosphates: calcium monodiphosphate (orthopyro-phosphate) with a molar ratio 2P/(2P + 1P) of about 0.3,[1] calcium magnesium monophosphate with an atomic ratio Mg/(Mg + Ca) of about 0.3, and calcium magnesium monodiphosphate with a molar ratio 2P/(2P + 1P) of ~0.1 and atomic ratio Mg/(Mg + Ca) of ~0.1. The three substances were obtained as thick pastes. Their compositions are given in the table. All substances are amorphous: their X-ray powder patterns contain only one very broad maximum with no reflexes intrinsic to crystalline phase. The IR spectra indicate that the examined amorphous calcium phos-phates contain a large amount of water (Fig. 1). In fact, in keeping with the data of [13], the broadest and strongest absorption band located above 2700–2800 cm^{-1} belongs to symmetric and asymmetric stretching vibrations of O–H bonds in water molecules [(νOH)]. The next intense line with its maximum at 1636–1638 cm^{-1} corresponds to bending vibrations of O–H

[1] In the given formulas 1P stands for monophosphate (ortophos-phate PO_4^{3-}), and 2P, for diphosphate (pyrophosphate $P_2O_7^{4-}$).

Composition of amorphous phosphates

Compound	Molecular weight[a]	Concentration of water, wt %	Molar ratio H_2O–phosphate	Number of water molecules per ion
Calcium monodiphosphate $Ca_1(PO_4)_{0.42}(P_2O_7)_{0.18}$	111.22	80.2	25.0	15.6
Calcium monodiphosphate $Ca_1(PO_4)_{0.42}(P_2O_7)_{0.18}$	140.57	80.5	32.2	13.5
Calcium magnesium monodiphosphate $Ca_1Mg_{0.11}(PO_4)_{0.65}\cdot(P_2O_7)_{0.07}$	116.57	80.1	26.1	14.2

[a] Arbitrary molecular weight of the inorganic salt in the dehydrated substance in accordance with the formula given in this table.

bonds [δ(OH)]. A weak but broad absorption band in the frequency range from 1970 to 2400 cm^{-1} might arise from vibrations of O–H bonds in hydroxonium ions (H_3O^+) or (P)O–H groups. However, fairly high pH value maintained during the synthesis excludes formation of H_3O^+ and (P)O–H-containing species. As noted in [13–17], the above spectral region may also reflect composite vibrations in water molecules like (δ + ω)(OH). Obviously, just those vibrations are responsible for the observed relatively weak absorption.

The maximum with the lowest frequency is located in the region corresponding to stretching vibrations of P–O bonds in phosphate anions PO_4^{3-} and $P_2O_7^{4-}$. Orthophosphate anion PO_4^{3-} usually gives rise to several discrete components [18, 19]. However, insofar as the examined samples are amorphous, particular lines merge together to form one broad asymmetric band.[2] The same applies to diphosphate ion whose spectral maxima overlap each other [20, 21].

The bands corresponding to vibrations of O–H bonds are almost similar for the three samples, while the low-frequency patterns in their spectra differ appreciably due to different contributions of ν(PO) belonging to mono- and diphosphate. One of the examined substances contains both mono- and diphosphate, the second contains only monophosphate, and the concentration of diphosphate in the third sample is smaller than in the first.

Excluding the region of P–O absorption, the spectra of the three amorphous calcium phosphates are almost identical to the spectrum of liquid water in the shape and band intensity (Fig. 1). First of all, this applies to the two low-frequency bands, δ(OH) and (δ + ω)(OH). The ν(OH) lines reveal very weak differences: judging by the second derivatives, their main components have slightly different frequencies (Fig. 2). In addition, the spectra of the magnesium-containing samples display a very weak absorption whose intensity is proportional to the concentration of magnesium. These findings indicate that the state of water molecules in amorphous phosphates is very similar to their state in pure water, though a slight effect of phosphate species exists.

The concentration of water in amorphous calcium phosphates reaches 80 wt % (see table). This means that they contain 25–30 water molecules H_2O per arbitrary phosphate molecule or 13–15 water molecules (on the average) per particular ion (Ca^{2+}, Mg^{2+}, PO_4^{3-}, or $P_2O_7^{4-}$); these values are too large. It is known that a large number of polymeric organic compounds (hydrogels) are capable of retaining a lot

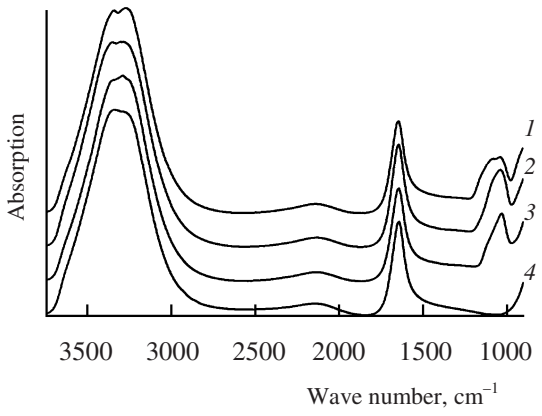

Fig. 1. FTIR spectra of (*1*) amorphous calcium monodiphosphate with a molar ratio 2P/(2P + 1P) of ~0.3, (*2*) calcium magnesium monophosphate with an atomic ratio Mg/(Mg + Ca) of ~0.3, (*3*) calcium magnesium monodiphosphate with a molar ratio 2P/(2P + 1P) of ~0.3 and atomic ratio Mg/(Mg + Ca) of ~0.3, and (*4*) liquid water.

[2] Taking into account complex spectral pattern due to superposition of several P–O bond vibration modes, hereinafter this low-frequency band is denoted as ν(PO).

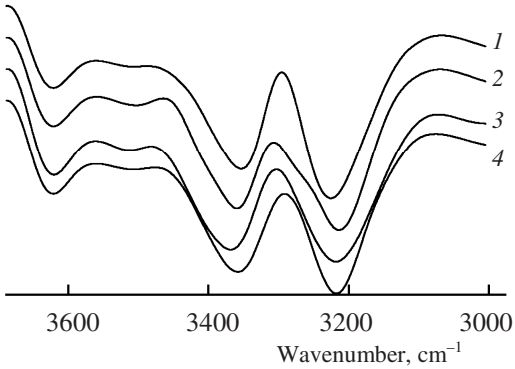

Fig. 2. Second derivatives of the FTIR spectra of (*1*) amorphous calcium monodiphosphate with a molar ratio 2P/(2P + 1P) of ~0.3, (*2*) calcium magnesium monophosphate with an atomic ratio Mg/(Mg + Ca) of ~0.3, (*3*) calcium magnesium monodiphosphate with a molar ratio 2P/(2P + 1P) of ~0.3 and atomic ratio Mg/(Mg + Ca) of ~0.3, and (*4*) liquid water.

of moisture. Inorganic hydrogels are also known, for example, silicates or vanadates which are also polymeric compounds. Amorphous calcium phosphates are not polymeric salts; therefore, a considerable concentration of water therein should be rationalized in a different way. It is hardly probable that there are ions surrounded by multilayered hydrate shells. According to [22], high degree of hydration of amorphous calcium phosphates is related to a large diameter (5–50 nm) of mesopores therein, which are capable of accommodating water molecules. As a result, water present in phosphates keeps properties intrinsic to liquids. However, this model implies that the concentration of water should be considerably lower than in amorphous calcium phosphates, even though monomolecular thickness of walls of the phosphate material is assumed. Moreover, the formation and stability of such a thin inorganic network could not be rationalized. Presumably, the formation of amorphous calcium phosphates involves localization of inorganic ions on the surface of water clusters persisting in liquid water [23, 24], thus inducing their aggregation, rather than water molecules are incorporated into phosphate pores. If this is the case, removal of water from amorphous calcium phosphates should leave voids with a size comparable with the diameter of water clusters. In fact, the products obtained by dehydration of the examined amorphous calcium phosphates in air at room temperature had pores with a diameter of 1.5–2 nm. This value is somewhat smaller that the size of water clusters (3 nm) described in [25]. Assuming that the dehydration process is accompanied by shrinkage of the inorganic material, the resulting pores are likely to be smaller than those in the initial hydrated samples.

According to calculations, at a phosphate–water ratio of 20:80, inorganic ions in amorphous calcium phosphates completely cover the surface of water clusters if the diameter of the latter approaches 100 nm. However, taking into account that the effective radius of ions in solution exceeds the crystallographic radius due to the presence of hydrate shells, the size of the clusters should be smaller. The size will be even smaller if we assume that blocking of only a part of the cluster surface is sufficient for consolidation of particular clusters (i.e., formation of amorphous calcium phosphates).

Regardless of actual factors controlling formation of hydrated amorphous calcium phosphates, it is clear that water clusters coated with a thin layer of poorly soluble phosphate material persist for a long time in the deposited substances. It was found experimentally that paste-like amorphous calcium phosphates did not change their consistency, composition, and state of the principal chemical bonds on storage in a hermetically closed vessel at room temperature for several years. Insofar as the phosphate shell surrounding water clusters cannot be mechanically strong, such clusters are likely to be stable. Obviously, the phosphate shell acts simultaneously as separating and consolidating medium.

EXPERIMENTAL

Amorphous calcium phosphates were prepared according to the procedures described in [11, 12, 26]. The reactant ratios indicated above ensured formation of X-ray amorphous products at a minimal concentration of crystallization inhibitor. Samples of amorphous calcium phosphates were examined by FTIR spectroscopy using attenuated total reflectance technique on a Nicolet 5700 instrument equipped with a horizontal Zn–Se crystal add-on; resolution 4 cm^{-1}, accuracy ±0.5 cm^{-1}, scan number 32. Sodium monophosphate $Na_2HPO_4 \cdot 12H_2O$, calcium chloride $CaCl_2 \cdot 6H_2O$, and magnesium chloride $MgCl_2 \cdot 6H_2O$ of analytical grade were used. Sodium diphosphate was synthesized from $Na_2HPO_4 \cdot 2H_2O$ according to the procedure described in [27].

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