



Formation of carbonated apatite in equilibrium system CaO–P₂O₅–H₂CO₃–H₂O at 298 K in air

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Received: 21 March 2023 / Accepted: 26 May 2023 / Published online: 7 June 2023
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Abstract

Equilibrium in the quaternary CaO–P₂O₅–H₂CO₃–H₂O system at 298 K in air was studied in a region of low concentrations of liquid-phase components. We revealed a dependence of the composition of resultant equilibrium solid phases on the Ca/P ratio of the initial components and on pH of the equilibrium liquid phase. It was found that the entire region of the system having low concentrations of liquid-phase components is occupied by variable-composition compounds with apatite structure. Two types of carbonate-containing apatite compounds were detected. The first type of apatite forms at $5.4 \leq \text{pH} \leq 7.0$, contains HPO₄²⁻ groups in the lattice, and has an invariant point with brushite CaHPO₄ · 2H₂O at pH ≈ 5.4. The second type arises at pH > 7.0, does not contain an acidic group, and has an invariant point with CaCO₃ at pH ≥ 8.

Keywords Calcium phosphate system · Equilibrium · Hydroxyapatite · Formation

Introduction

A large number of researchers have been studying carbonate-containing calcium apatites for decades (Le Geros et al. 1968; Labarthe et al. 1973; Elliott et al. 1980; Fox et al. 1995; Rey et al. 1989; Elliott 1994). Interest in these compounds is due to the fact that the mineral component of bone and dental tissues of humans and animals consists of carbonate-containing hydroxyapatite. It is known that in the crystal lattice of hydroxyapatite Ca₁₀(PO₄)₆(OH)₂, which has the Ca/P ratio of 1.67 (hereinafter, an atomic ratio of chemical elements is used), carbonate ion CO₃²⁻ can replace (i) a phosphate group with the formation of carbonate apatite (CAp) of the B-type (Labarthe et al. 1973) or (ii) an OH⁻ group with the formation of A-type CAp (Elliott et al. 1980) or occupy both positions simultaneously, forming AB-type CAp (Elliott 1994). The substitution of the phosphate group alters the Ca/P ratio, whereas the substitution of the hydroxyl group does not change this ratio.

Biological apatites are calcium-deficient B-type CAp nanoparticles. To describe their average composition, the

formula Ca_{8.3}(PO₄)_{4.3}(CO₃)_x(HPO₄)_y(OH)_{0.3} has been proposed, where the carbonate content is 4–8 wt.% (Vallet-Regi and Arcos 2015). Different authors investigate changes in the composition of biological CAPs, where special attention is paid to causes of caries (Vallet-Regi and Arcos 2015; Kunin et al. 2013; Arends and Davidson 1975). Processes of alteration of the composition of bone tissues under the influence of internal and external conditions are researched, including under the influence of microgravity in outer space (Liu et al. 2013; Smith et al. 2014). A detailed review (Combes et al. 2016) has examined processes of evolution of apatite biominerals, bone, and dental tissues during aging of the body. Another important research problem is the formation of calcifications: painful deposits that emerge on the walls of blood vessels and in vitally important organs (LeGeros 2001).

Carbonate-apatites are phosphate ores of sedimentary origin and their weathering products (Baturin and Bezrukov 1979; Baturin 1982). These ores are the main sources of industrial raw materials for the production of phosphorus and its compounds (Ptáček 2016a, 2016b; Van Wazer 1961). Extensive literature is devoted to the genesis of phosphate ores, and various models of their formation and sedimentation have been suggested (Baturin and Bezrukov 1979; Baturin 1982; Ames 1959). In one review (Omelson et al. 2013), researchers discussed how bacteria and marine organisms can help to concentrate phosphate and promote apatite

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crystal nucleation during the formation of phosphorites in seawater and hypothesized that the mechanism of dental tartar deposition may be similar.

One of the methods for investigating the formation of CAP is the analysis of the equilibrium water systems where these compounds are formed. Despite many years of research into the formation of CAP, the CaO–P₂O₅–H₂O system at 298 K in air has barely been investigated.

Authors of ref. (Kelly and Farr 1940) in a study on the CaO–P₂O₅–H₂O system, gave special attention to its “acidic” part, where well-soluble calcium phosphates arise that are used as fertilizers. The composition of equilibrium solid phases of neutral and alkaline parts of the system is less studied. Most authors in this field are inclined to believe that in this region of the system, not stoichiometric compounds but compounds of variable composition are formed.

We have analyzed the region of low concentrations of the CaO–P₂O₅–H₂O ternary system at 298 K in a nitrogen atmosphere, which was created to avoid the formation of CAP under the influence of atmospheric CO₂ (Chaikina and Bulina 2022). When studying the neutral part of this system, we found two types of calcium-deficient apatites of variable composition.

There are studies by Bakher and Kaddami (2018a; 2018b), where the equilibrium of the ternary system CaCO₃–P₂O₅–H₂O at 25, 35, and 70 °C was analyzed using calcium carbonate and phosphoric acid, whose interaction resulted in a carbon dioxide release. Unfortunately, this system has been studied only in the acidic region, where CAP does not form.

The authors of refs. (Fox et al. 1995; Hsu et al. 1994) have examined the solubility of synthetic CAP in a series of acetate buffers containing various levels of calcium and phosphate ions. On the basis of the results, they advanced a hypothesis that when CAP is dissolved, a phenomenon known as metastable equilibrium solubility is observed. This phenomenon may arise when crystal dissolution rates are much higher than crystal growth/precipitation rates when compared at equal but opposite (in sign) chemical-potential differences between a crystal phase and solution. According to data from the authors of refs. (Fox et al. 1995; Hsu et al. 1994), the dissolution of CAP can serve as an example of metastable equilibrium solubility that is very far from the true thermodynamic equilibrium. We have to agree with these authors, who believe that months are needed to achieve a true equilibrium in such a system. Our studies on the CaO–P₂O₅–H₂O system have shown that, indeed, in liquid phases with a low concentration of the initial components, the true equilibrium may get established for up to 20 months (Chaikina and Bulina 2022).

The purpose of the present work was to detect stable equilibrium solid phases forming in the region of low concentrations of liquid-phase components of the

CaO–P₂O₅–H₂CO₃–H₂O system at 298 K in an air atmosphere.

Experimental

Materials

The equilibrium in the system in question was studied by the method of isothermal solubility. The system was studied in an air environment where carbon dioxide vapor pressure (P_{CO₂}) was ~3 kPa, which corresponds to an average CO₂ gas concentration of 0.046 wt.%. Characteristics of all initial components are given in Table S1. The system was investigated in three cross-sections.

Cross-section I of the system was studied at a constant initial level of calcium ions (CaO at 0.01 M) with an increase in the Ca/P atomic ratio from 1.0 to 2.5 and a decrease in the P/C atomic ratio from 5 to 2 (Table S2). These conditions are closest to processes of formation of CAP in the human body: with age, the degree of substitution of phosphate by carbonate rises (Arends and Davidson 1975; Combes et al. 2016; Rey et al. 1991).

In cross-section II, concentration of bicarbonate ion C_{HCO₃} in the initial solution was constant, 0.02 M, while the Ca/P ratio was varied from 1 to 2 (Table S3). This concentration of HCO₃⁻ is close to the average concentration in bottom layers of sea water, where apatite of phosphate ores arises (Baturin and Bezrukov 1979; Baturin 1982).

Cross-section III was analyzed at a constant Ca/(P+C) ratio of 1.4 and at different concentrations of phosphorus and carbon, as presented in Table S4. The initial components representing calcium and carbonate in section III were applied in the form of such solid phases as CaO and CaCO₃ in a solution of phosphoric acid. These conditions simulate the formation of CAPs simultaneously with sedimentation of carbonate minerals in the sea and the emergence of CAPs on a continent composed of phosphate-containing carbonate rocks during weathering (Baturin and Bezrukov 1979; Baturin 1982; Ptáček 2016a).

The initial component representing the phosphate ion was a solution of phosphoric acid at a phosphorus concentration of 0.01 M. The phosphoric acid solution was prepared through dilution of 87 wt.% H₃PO₄ with distilled deionized water. This water was prepared by means of a Millipore Q3 device with a product water resistivity of 18.2 MΩ cm. The source of the carbonate ion was a solution of Ca(HCO₃)₂ with an HCO₃⁻ ion concentration of 0.01 M. This solution was obtained by passing purified CO₂ gas through a suspension of CaCO₃. Another source of calcium ions, apart from Ca(HCO₃)₂, was a solution of Ca(OH)₂ in distilled deionized water with a Ca²⁺ concentration of 0.01 M prepared from calcined CaO.

Solutions of the initial components were mixed in certain ratios with a total volume of the mixture of 1 L, placed in special 1.5 L quartz glass vessels equipped with stirrers and mercury locks. The vessels were placed in a thermostatted room having a constant temperature of 298 K and a pressure of 0.1 MPa. The mixtures in the vessels were stirred until an equilibrium got established. The attainment of an equilibrium was assumed when pH in the liquid phase became constant and when there were no changes in the concentration of phosphate and calcium in the liquid phase. The mixtures were checked monthly. An equilibrium was considered established if pH and concentrations of calcium and phosphate ions did not change during testing for 3 months. The establishment of an equilibrium in the sections of the studied system at 298 K lasted for 9–20 months. After an equilibrium in the system got established, the formed solid phases were separated from the liquid phase by filtration through a Buchner funnel equipped with a pump.

Characterization

pH was measured with an LPM-60 M potentiometer (Gomel Instrumentation Factory, Gomel, Belarus).

To quantify phosphate, calcium, and bicarbonate ions, the most sensitive methods of chemical analysis were chosen—in accordance with requirements of the State Standards of the Russian Federation (GOST), similar to international standards—that are used for the analysis of water. The phosphate content of the liquid phases was determined by the colorimetric method with a blue molybdenum complex (Interstate Standard 2015a; Standard ISO 2004). This method is based on the interaction of phosphate ions with molybdenum blue complex $\text{MoO}_2 \cdot 4\text{MoO}_3$ with the formation of a stable blue color. This method is applicable to phosphorus concentrations within the range of 0.005–0.8 mg/l. Phosphate in solid phases was quantitated according to a method of precipitation of magnesium ammonium phosphate with subsequent ignition to magnesium pyrophosphate $\text{Mg}_2\text{P}_2\text{O}_7$ (Interstate Standard 2015b), similarly to ref. (Farr et al. 1962). The calcium content of the liquid and solid phases was determined by complexometric titration by means of ethylenediaminetetraacetic acid (EDTA) tetrasodium with indicator Eriochrome Black T according to a method from ref. (Interstate Standard 2014), similarly to ref. (Harris 2003). Carbonate and bicarbonate ions in the liquid phase were quantified by the titrimetric method that is employed to determine total and free alkalinity in water according to GOST (Interstate Standard 2019a; b), similarly to international standards (ISO 1994). The limit of detection of alkalinity (bicarbonate and carbonate) for this method is 0.4 mM (Interstate Standard 2019a). The concentration of carbonate in the solid phases was measured by the gas

volumetric method according to GOST (Interstate Standard 2019b).

The range of concentrations of components of the equilibrium liquid phases in the $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{CO}_3\text{-H}_2\text{O}$ system under study was from 0.0005 to 0.0205 wt.% CaO, from 0.0003 to 0.0214 wt.% P_2O_5 , and from 0.0036 to 0.068 wt.% CO_2 , while pH of the equilibrium liquid phases varied in the range 5.04–12.03. The composition of liquid and solid phases, as determined by the above-mentioned chemical methods, is given in Tables S1–S3.

X-ray diffraction (XRD) patterns were recorded on a D8 Advance powder diffractometer (Bruker, Karlsruhe, Germany) with Bragg–Brentano geometry using $\text{CuK}\alpha$ radiation. X-ray phase analysis of the compounds was carried out with the help of the ICDD PDF-4 database (2011). Unit cell parameters, crystallite size, and the amorphous-phase content were determined by the Rietveld method in the Topas 4.2 software (Bruker, Karlsruhe, Germany).

Functional groups of the solid phases were identified by infrared (IR) spectroscopy on an Infracum-801 instrument (Simex, Novosibirsk, Russia) via compression of each test sample with KBr powder.

Simultaneous thermal analysis (STA) was carried out using a STA 449 F1 Jupiter device (Netzsch, Selb, Germany) equipped with a QMS 403 C Aeolos mass spectrometer. STA included simultaneous detection of mass loss, differential scanning calorimetry (DSC), and registration of the evolved gas using a mass spectrometer. The measurements were performed in a Pt-10wt.-%Rh crucible under an argon-oxygen mixture (80:20) at a heating rate of 10 °C/min.

Results and discussion

Obtained dependences

Results of composition analysis of liquid and solid equilibrium phases of the $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{CO}_3\text{-H}_2\text{O}$ system are given in Tables S2–S4. Based on these data, orthogonal projections of the system's isotherms onto coordinate planes $\text{CaO-H}_2\text{O-P}_2\text{O}_5$ and $\text{CO}_3\text{-H}_2\text{O-P}_2\text{O}_5$ were constructed (Fig. 1). The figure indicates that in all three sections of the $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{CO}_3\text{-H}_2\text{O}$ system—which have different dynamics of changes in concentrations of the initial reagents—behaviors of calcium concentration were identical in solution (Fig. 1a), and the same was true for carbonate concentration (Fig. 1b). Judging by the dynamics of changes in the composition of the liquid phase in the analyzed system, two regions can be distinguished. The first region (Range I) occupies the bulk of the diagrams presented in Fig. 1. With decreasing P_2O_5 concentration in solution (according to the data of Tables S2–S4), at first, there is a gradual decline of calcium concentration and a slight fluctuation of carbonate

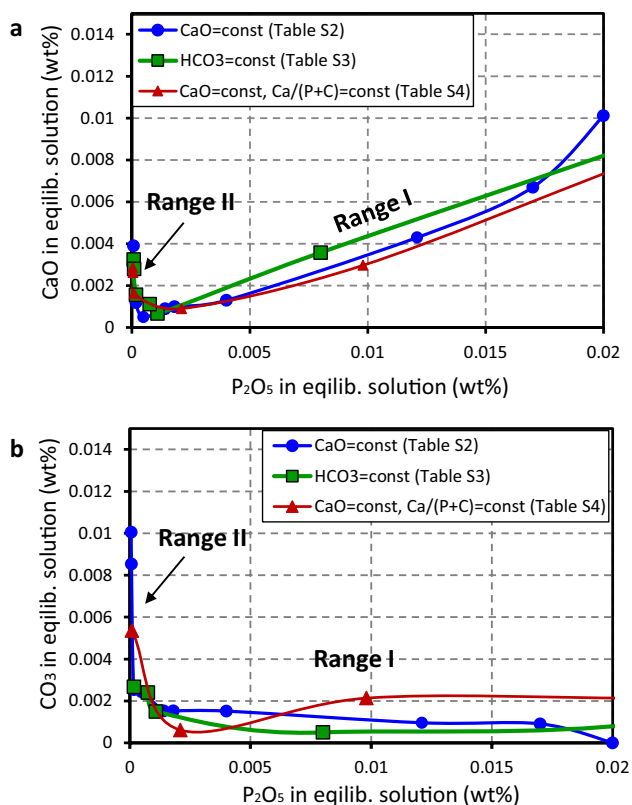


Fig. 1 Orthogonal projection of isotherms on the CaO–P₂O₅ coordinate plane (a) and CO₃–P₂O₅ plane (b) for the CaO–P₂O₅–H₂CO₃–H₂O system

concentration in solution: range I. At low concentrations, starting from P₂O₅ concentration of 0.0014 wt.% in solution, there is a sharp increase in the concentrations of calcium and carbonate in the liquid phase: range II. These radically different dynamics of liquid-phase composition point to the formation of a solid phase differing in composition between these solutions.

If we present the results on changes in elemental composition of the solid phase in all obtained samples (see Tables S2–S4) in graphical form (Figs. 2, 3 and 4), then we can see that the composition of the samples from the three studied sections changes in the same way (the dynamics are identical). The same was true for the liquid phase of these samples (Fig. 1).

From the data in Fig. 2, it follows that with an increase in pH of the equilibrium solution, in all cross-sections there is an increase in the Ca/P ratio in the solid phase. In this context, as Tables S2–S4 indicate, in the range $5.7 < \text{pH} \leq 8.0$, crystallites of only the apatite phase are detectable: a single-phase region. In this region, the Ca/P ratio in the solid phase rises slightly, yielding a plateau with a weak slope in the plot of the solid-phase Ca/P ratio against pH of the equilibrium solution (Fig. 2). Outside

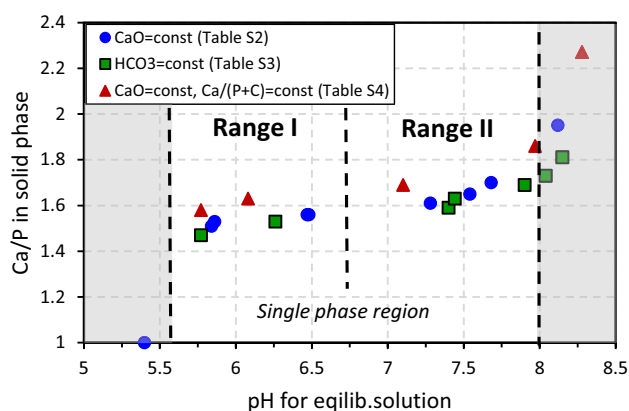


Fig. 2 The dependence of the Ca/P ratio in the solid phase on pH of the equilibrium solution for samples from different sections (see Tables S2–S4)

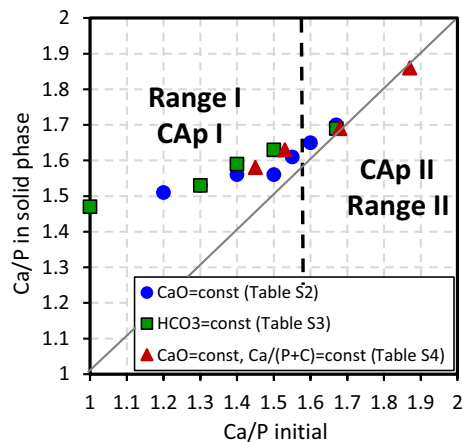


Fig. 3 The dependence of the Ca/P ratio in the solid phase on the initial Ca/P ratio for samples from different sections (see Tables S2–S4)

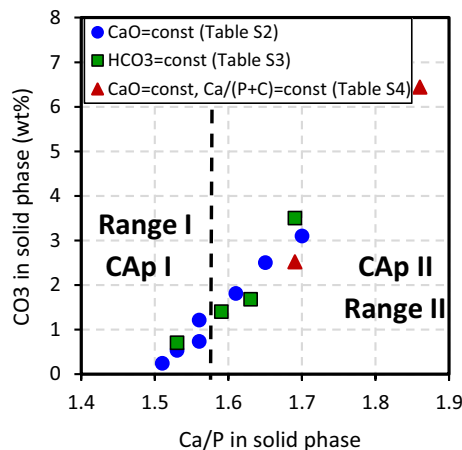


Fig. 4 The dependence of CO₃²⁻ concentration on the solid-phase Ca/P ratio for samples from different sections (see Tables S2–S4)

this range, the Ca/P ratio of the solid phase is either substantially higher or considerably lower. From Fig. 2, we can conclude that in the range $5.7 < \text{pH} < 8.0$, the formed solid phase is a continuous series of solid solutions with a Ca/P ratio smoothly changing in a narrow range of 1.4–1.65.

Figure 3 shows the solid-phase Ca/P ratio as a function of the Ca/P ratio in the initial solution. Readers can see in the figure that in Range II for solid-phase samples, the Ca/P ratio is close to the Ca/P ratio of the initial solution (the experimental data points lie near the diagonal). Range I is characterized by a different dependence. In this case, solid-phase Ca/P ratios are above the diagonal line. Furthermore, the lower the Ca/P ratio in the initial solution, the greater is the observed deviation. Consequently, the solid phase has different compositions in these ranges. Let us designate the solid phase formed in Range I as CAP I, and the one arising in Range II as CAP II.

It follows from Fig. 4 that carbonate concentration in samples from different sections gradually goes up with an increase in the Ca/P ratio in them, transitioning from Range I to Range II. It is evident that at the solid-phase Ca/P ratio of less than 1.5, the CO_3 group is not detectable in the samples.

Thus, we can conclude that in the liquid phase of the $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{CO}_3\text{-H}_2\text{O}$ system, in the region of low concentrations of liquid-phase components under equilibrium conditions, CAPs crystallize that have variable composition of two types: CAP I in the range $5.7 < \text{pH} < 6.5$ and CAP II in the range $7.0 < \text{pH} < 8.0$. There is a smooth transition from CAP I composition to CAP II composition. In CAP I, the Ca/P ratio is much higher than that in the initial solution, whereas in CAP II, the Ca/P ratio is comparable to that in the initial solution. The composition of CAP I and CAP II,

as determined by chemical, XRD, IR, and STA analyses, is discussed in more detail below.

CAP of type I

Let us examine the composition of CAP I, which form in the weakly acidic region of the system at $5.7 < \text{pH} < 6.5$ (Fig. 2). The Ca/P ratio in these samples is in the range $1.5 < \text{Ca/P} < 1.56$, and the carbonate content is no more than 1.21 wt.% (Fig. 4, Table S2). As mentioned above, this type of apatite is characterized by a higher Ca/P ratio than that in the initial solution (Fig. 3).

Diffraction patterns of CAP I samples contain reflections belonging to an apatite phase having low crystallinity. In Fig. 5a, a diffraction pattern of sample 4 is presented as an example. Positions of the reflections and the distribution of intensities are consistent with PDF file card 40-11-9308.

According to FTIR spectroscopy, CAP I samples in all three sections contain not only a carbonate group but also a HPO_4^{2-} group (Fig. 5b, sample 4). The presence of HPO_4^{2-} groups is indicated by an absorption band in the $860\text{--}875\text{ cm}^{-1}$ region, and this band may overlap with an absorption band of bending vibrations of O–C–O bonds of the CO_3^{2-} ion (Arends and Davidson 1975; Hayek and Link 1975; Wilson et al. 2005). Figure 5b depicts IR spectra of equilibrium solid phases that form at different pH values in samples from different sections of the $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{CO}_3\text{-H}_2\text{O}$ system. In the IR spectrum of sample 18, in addition to absorption bands belonging to vibrations of bonds of the PO_4 tetrahedron in the apatite lattice (bending vibrations ν_4 of O–P–O bonds at 565 and 605 cm^{-1} and stretching vibrations ν_3 and ν_1 of P–O bonds at 1050 , 1100 , and 960 cm^{-1}), there is a broad absorption

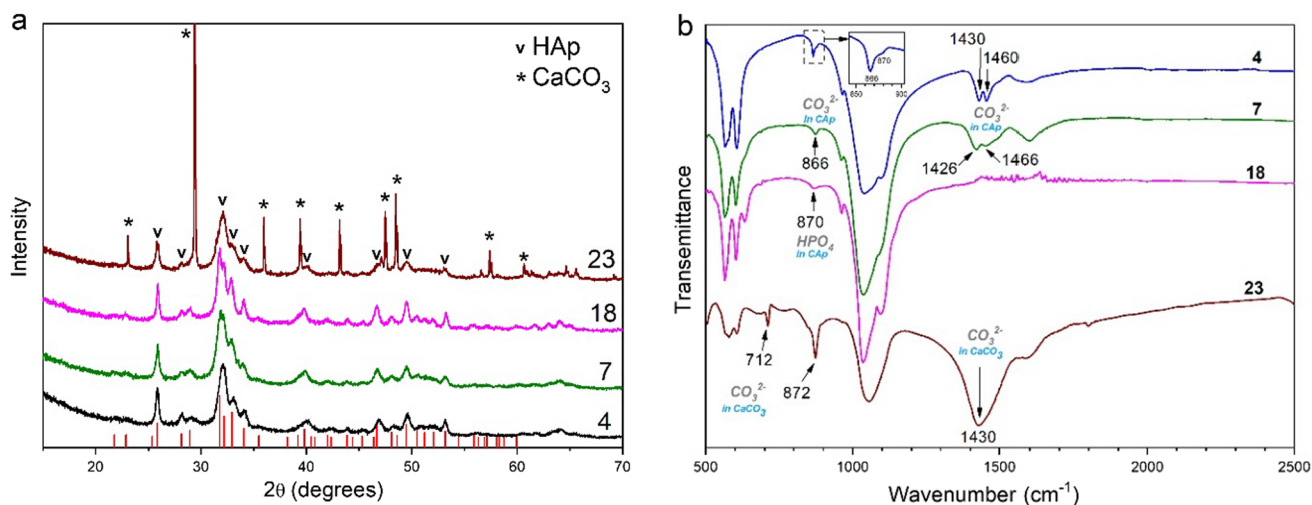


Fig. 5 XRD patterns (a) and FTIR spectra (b) of equilibrium solid phases in samples from different sections. The numbers correspond to the sample ID numbers in Tables S2–4. The bar chart corresponds to PDF file 40–11–9308 (ICDD PDF-4) of crystalline hydroxyapatite (HAp)

band with a wavenumber of 870 cm^{-1} . This indicates the presence of HPO_4^{2-} groups in the apatite lattice (Arends and Davidson 1975). In this sample, there are no absorption bands of the carbonate group. When the CO_3^{2-} ion enters the apatite lattice, a narrower band (with a wavenumber of 866 cm^{-1}) of bending vibrations of O–C–O bonds in the carbonate ion appears in apatite on a relatively wide band at 870 cm^{-1} (Fig. 5b, sample 4). As the concentration of the carbonate ion increases, the intensity of this band rises, as does the intensity of absorption bands of stretching vibrations of C–O bonds at 1430 and 1460 cm^{-1} (Fig. 5b) characteristic of B-type CAP (Bonel 1975). It is worth noting that the shape of the C–O stretching vibration bands in CAP I and their positioning differ from those observed by us in samples of CAP II (Fig. 5b, sample 7) and from literature data on CAPs not containing an acidic group (Bonel et al. 1975). It is possible that the change in the shape and positions of the absorption bands are explained by the presence of an HPO_4^{2-} group in the immediate environment of a carbonate group.

Caps containing an HPO_4^{2-} group are a mineral component of human bone and dental tissues, and such CAPs were named by the authors of ref. (Hayek and Link 1975) as hydrogenphosphate-carbonate-apatite. Their composition is characterized by the ratio $1.33 < \text{Ca/P} \leq 1.63$. These compounds are similar to calcium-deficient hydroxyapatites (Wilson et al. 2005) but contain carbonate CO_3^{2-} group in the lattice that replace PO_4^{3-} group with the formation of B-type CAP (Bonel et al. 1975). The charge of the heterovalent substitution is compensated by the emergence of vacancies at positions of calcium ions and of OH groups (Elliott 1994; Hayek and Link 1975).

Discussions about the incorporation of water into apatite of bone tissues have been going on for decades (Pasteris 2012). The role of water in the structure of synthesized carbonate hydroxyapatites and its dynamics are also demonstrated in refs. (Hayek and Link 1975; Bonel et al. 1975; Moreno et al. 1968). Those authors believe that the presence of water in apatite promotes the hydrolysis of PO_4^{3-} groups into HPO_4^{2-} . As the Ca/P ratio increases and pH goes up in the equilibrium liquid phases, HPO_4^{2-} groups are isovalently replaced by carbonate ion CO_3^{2-} . The resulting product can be described by the formula $\text{Ca}_{10-x+u}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{H}_2\text{O})_z(\text{OH})_{2-x+2u}$, where $0 \leq x \leq 2$ and $0 \leq u \leq x/2$ (Bonel et al. 1975). In our case, spectra of CAP I samples also contain a wide band of bending vibrations of water molecules in the region of 1600 cm^{-1} (Fig. 5b, sample 4), confirming the presence of structural water in these samples, which promotes the formation of HPO_4^{2-} .

Results of thermogravimetric analysis of the CAP I samples also confirm the presence of adsorbed water, whose maximum release corresponds to $150\text{ }^\circ\text{C}$ (Fig. 6). With

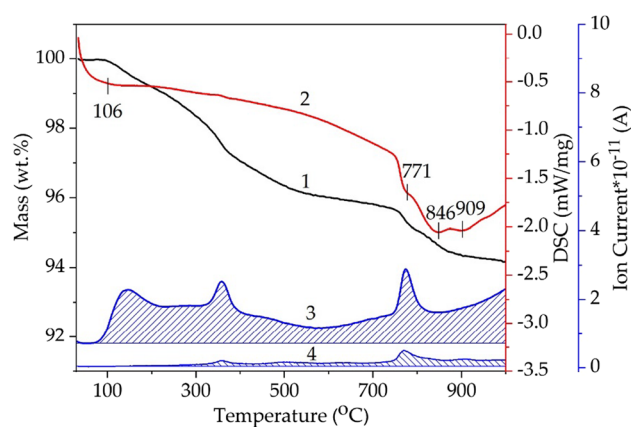


Fig. 6 STA of sample 19 (CAP I): weight loss (1); DSC (2); evolution of water (3); evolution of CO_2 (4)

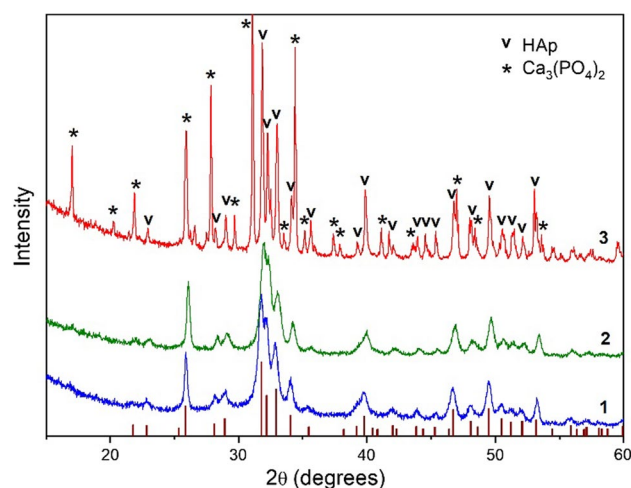


Fig. 7 XRD patterns of sample 19 (CAP I) before heating (1), after heat treatment at $400\text{ }^\circ\text{C}$ (2), and after STA analysis (3). The bar chart corresponds to PDF file 40-11-9308 (ICDD PDF-4) of crystalline hydroxyapatite (HAp)

a further increase in temperature, along with the loss of adsorbed water, there is a gradual loss of structurally bound water in the range of $200\text{--}600\text{ }^\circ\text{C}$. At $350\text{ }^\circ\text{C}$, an additional portion of structural water and a small amount of carbon dioxide separate out, and this finding is obviously due to some structural transformations in the sample. At $760\text{ }^\circ\text{C}$, the acidic and carbonate groups are removed from the CAP I lattice with the formation of the β -phase of tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$. The presence of this phase is confirmed by the results of X-ray phase analysis (Fig. 7). Heating of the CAP I samples at $400\text{ }^\circ\text{C}$ did not lead to structural transformations.

On the basis of published data and our experimental results for CAP I, we can propose a formula where the substitution of PO_4^{3-} groups by HPO_4^{2-} groups and

CO_3^{2-} ions is compensated by vacancies of calcium ions and OH groups with the formation of apatite of composition $\text{Ca}_{10-(x+z)}(\text{PO}_4)_{6-(x+z)}(\text{HPO}_4)_x(\text{CO}_3)_z(\text{OH})_{2-(x+z)}$, where $0 \leq x \leq 1$ and $0 \leq z \leq 0.5$. Examples of such apatites are samples **2–5** from cross-section I (Table S2), sample **12** from cross-section II (Table S3), and sample **19** from cross-section III (Table S4).

CAp of type II

The second type of compounds of variable composition with the structure of apatite, CAp II, forms in the alkaline region of the $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{CO}_3\text{-H}_2\text{O}$ system at $\text{pH} > 7.0$ and does not contain an HPO_4^{2-} group (Tables S2–S4). The equilibrium liquid phase in this region of the system is characterized by a low concentration of calcium ions and a very low level of phosphate but a high carbonate content (Fig. 1). When an equilibrium got established in these solutions, crystallites precipitated whose diffraction patterns show reflections of only an apatite phase (Fig. 5a, sample 7). In contrast to CAp I, in the samples of CAp II, the Ca/P ratio is > 1.59 , and they contain more than 1.2 wt.% of the carbonate ion (Fig. 4).

IR spectra of samples from the CAp II series show absorption bands of carbonate ion CO_3^{2-} (Fig. 5b, sample 7). There is a narrow absorption band of bending vibrations of O–C–O bonds at 866 cm^{-1} and bands of stretching vibrations of C–O bonds with maxima at 1426 and 1466 cm^{-1} (Fig. 6). These values are typical for B-type CAPs (Bonel et al. 1975). Absorption bands of the HPO_4^{2-} group are absent in the spectra. As pH of the liquid phases of the system under study increases, the concentration of the carbonate ion in CAp II goes up. At $\text{pH} \geq 8$, CaCO_3 begins to precipitate as calcite along with CAp II (Table S2–S4). In diffraction patterns of these samples, there are narrow reflections of well-crystallized CaCO_3 (Fig. 5a, sample 23). In the IR spectra, the presence of calcium carbonate is manifested by the absorption bands characteristic of calcite: bending vibrations of O–C–O bonds at 712 and 872 cm^{-1} (Vagenas et al. 2003; Al-Hosney and Grassian 2005) and stretching vibrations of C–O bonds at 1430 cm^{-1} (Fig. 5b, sample 23).

The description of the composition of CAPs that do not contain the HPO_4^{2-} group, just as the mechanism of replacement of phosphate by carbonate, is the subject of abundant literature, where various formulas have been proposed (Hayek and Link 1975; Wilson et al. 2005; Bonel et al. 1975; Vignoles et al. 1988; Kühl and Nebergall 1963; Rey et al. 2007). According to findings of some authors (Wilson et al. 2005; Vignoles et al. 1988), CAP can be synthesized with a carbonate content of up to 14 wt.%.

To compensate the charge of the heterovalent substitution of phosphate by carbonate during the formation of B-type CAP, according to Vignoles et al. (Vignoles et al. 1988),

there are two mechanisms: (1) due to vacancies of calcium, of an OH group, and of one oxygen in the phosphate tetrahedron; (2) replacement of phosphate by a carbonate ion together with an OH group: $\text{CO}_3^{2-} + \text{OH}^- \rightarrow \text{PO}_4^{3-}$.

In ref. (Kühl and Nebergall 1963), it is suggested that the change in charge is compensated by simultaneous vacancy of calcium cations and of a hydroxyl group with the formation of apatite of composition $\text{Ca}_{10-x+y}(\text{CO}_3)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x+2y}$, where $0 \leq x \leq 2$ and $2y \leq x$. On the other hand, Bonel et al. (1975) believe that water should be present in the general formula: $\text{Ca}_{10-x+u}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{H}_2\text{O})_u(\text{OH})_{2-x+2u}$; $0 \leq x \leq 2$ and $0 \leq u \leq x/2$, and this water probably fills the space of nascent vacancies.

Formula $\text{Ca}_{10-x+u}(\text{PO}_4)_{6-x-y}(\text{HPO}_4)^{2-}$ or $\text{CO}_3^{2-})_{x+y}(\text{OH})_{2-x+2u+y}$ with $0 \leq x \leq 2$ and $0 \leq 2u+y \leq x$ from the authors of ref. (Rey et al. 2007) can describe the composition of both calcium-deficient apatites and carbonate-substituted apatites.

In most studies in this field, not all experimental data are presented; therefore, the question of whether the proposed formula matches the composition of the sample remains open.

According to our data, in the investigated $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{CO}_3\text{-H}_2\text{O}$ system, the degree of substitution of phosphate by carbonate is the highest in CAp II that form in an alkaline medium. The highest value is one phosphate group out of six in the unit cell of apatite: approximately 5–6 wt.%. This is close to literature data on the carbonate content of apatites of bone tissues (Elliott 1994; Combes et al. 2016).

It is known that carbonate-substituted hydroxyapatite is more soluble than stoichiometric hydroxyapatite (Elliott 1994). In a comparison of the region of existence of CAp I and CAp II in the $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{CO}_3\text{-H}_2\text{O}$ system with the region of existence of calcium-deficient hydroxyapatite in $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ system (Chaikina and Bulina 2022), it was found that the region of existence of compounds having apatite structure is wider in the quaternary system than in the ternary system. In the ternary system, calcium-deficient apatites had an invariant point with octacalcium phosphate at $\text{pH} = 6.64$ (Chaikina and Bulina 2022). In the quaternary system, CAPs “rise” to the invariant point with brushite at $\text{pH} = 5.40$ (Table S2, sample 1).

Conclusions

An equilibrium in quaternary system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{CO}_3\text{-H}_2\text{O}$ was examined at 298 K in an air atmosphere in the region of low concentrations of liquid-phase components. It was revealed that carbonate-containing compounds of variable composition with apatite structure are formed throughout the

analyzed region. These are stable phases with an equilibration duration of 9 to 20 months.

The existence of carbonate-substituted apatites of two types was demonstrated. Both types dissolve incongruently. In a weakly acidic part of the system, CAPs of the first type (CAP I) were found containing HPO_4^{2-} groups and a small amount of carbonate in the lattice (0.1–0.2 mol of CO_3^{2-} per mole of apatite); this carbonate replaces the phosphate ion thereby giving rise to B-type CAP. At pH less than 5.8 in the equilibrium liquid phase, the carbonate ion is absent in the apatite; only an acidic group is present in the lattice. Apatites of this type have an invariant point with brushite $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ at $\text{pH} \approx 5.4$.

The second type of carbonate-containing apatites, CAP II, arises in neutral and alkaline regions of the system and does not contain an HPO_4^{2-} group. In CAP II apatites, there is substantially more carbonate replacing the phosphate group, with the formation of B-type CAP as well. It is possible to substitute as many as one in six phosphate groups in the apatite lattice with a carbonate ion. At pH of the equilibrium liquid phase of > 8.0 , calcite precipitates along with CAP II; therefore, carbonate-bearing apatites of the second type have an invariant point with calcite CaCO_3 .

CAPs of the two types forming in the $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{CO}_3\text{-H}_2\text{O}$ system reflect the composition of natural CAPs of various origins and confirm the diversity of natural and synthetic CAP types.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11696-023-02895-0>.

Acknowledgements This research was carried out within a state assignment to the Institute of Solid State Chemistry and Mechanochemistry SB RAS (Project No. 121032500064-8).

Declarations

Conflict of interest The authors declare that there is no conflict of interest.

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