



Article Formation of Fluorapatite in the Equilibrium System CaO–P₂O₅–HF–H₂O at 298 K in a Nitrogen Atmosphere

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Abstract: The process of biomineralization of apatite in nature has been studied by scientists from various fields of science for more than a century. Unlike the volcanogenic, hydrothermal, and other types of igneous apatites, the genesis of which is entirely clear, the formation of phosphate ores of marine sedimentary origin is still debatable. Since phosphate concentrations in water bodies are too low for the spontaneous precipitation of solid phosphates, the study of different ways for their concentration is of particular interest. In this work, phase equilibria in the system $CaO-P_2O_5-$ HF-H₂O at 298 K, involving fluorapatite formation, have been studied. Fluorapatite is known to be the most common phosphate mineral and the main source of phosphorus on Earth, playing an important role in the mineralization process of dental tissues in vertebrates. The equilibrium in the system defined above was studied at a low mass fraction of the liquid phase components, i.e., in conditions close to natural. It has been shown that the compounds of variable composition with the fluorapatite structure containing HPO_4^{2-} ions were formed in the acid region of this system. These compounds are formed at pH \leq 7.0 and have invariant points with monetite, CaHPO₄, and fluorite, CaF₂. Stoichiometric fluorapatite was formed at the lowest concentrations of the liquid phase components in a neutral and weakly alkaline medium and had an invariant point with Ca(OH)₂. The composition of the resulting equilibrium solid phases was found to be dependent on the Ca/P ratio of the initial components and pH of the equilibrium liquid phase. Fluorite CaF₂ was present in each sample obtained in this study.

Keywords: fluorapatite; formation; water system; low concentration; equilibrium; isotherm

1. Introduction

Phosphate ores are the main source used as raw material for manufacturing elemental phosphorus and its compounds [1–6]. Fluorapatite (FAp) with the chemical formula $Ca_{10}(PO_4)_6F_2$ is the main phosphate mineral of igneous origin [1,6,7]. Fluorapatite has a very low solubility in water [7]. This type of apatite has Ca/P and P/F atomic ratios of 1.67 and 3, respectively. Phosphate ores of sedimentary origin and the products of weathering, as a rule, are FAp with the partial replacement of phosphate by carbonate and calcium by other cations, which changes the Ca/P and P/F ratios [1,4]. Fluorapatite is white in color, but sometimes it can be of green, blue, cyan, yellow, purple, and pink hues, which indicate the presence of substituent ions in the FAp structure (Figure 1).

An interesting question is the origin of sedimentary phosphate ores. Phosphorus accumulation in sea and river water occurs from dust, glacial runoff, underground hydrothermal volcanic activity, and deposition of organic material [4]. The primary inflow of dissolved phosphorus is from continental weathering, brought out by rivers to the ocean. The remains of fish and other inhabitants of the underwater world, as well as marsh grass and algae, are also a source of dissolved phosphorus formed during the process of their



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). decomposition with the participation of bacteria and enzymes. When the concentration of phosphorus in water bodies is close to saturation, environmental changes (temperature, pressure, pH) can lead to a sharp precipitation of the phosphates from a supersaturated solution in the form of phosphate minerals, including FAp.



Figure 1. Image of natural fluorapatite from the Slyudyanka deposit (Irkutsk region, Lake Baikal). Element composition of the crystals is presented in Table S1. The collection of M.V. Chaikina.

Nevertheless, most of the phosphorus is generated in the Earth's upper mantle. Magmatic rocks of the mantle and granite shell opened by erosion contain a large number of phosphate minerals, including FAp [4]. Phosphate rock is the major resource mined to produce phosphate fertilizers for the agricultural industry. In this regard, the technology of processing phosphate ores into fertilizers and for the production of double superphosphate and other phosphorus compounds is of great interest.

The aim of the study carried out by Farr et al. [8] was to make phosphate fertilizer by direct interaction of phosphate ore with phosphoric acid and to determine the thermodynamic properties of the resultant equilibrium phases in the system. For this aim, Farr et al. studied the phase equilibria in the CaO–P₂O₅–HF–H₂O system in a region of high mass fraction (*w*) of the liquid phase components at temperatures of 25 °C and 50 °C [8]. The mass fractions $w(P_2O_5)$ and w(CaO) varied from 3.81 to 33.85 wt% and 0.922 to 3.729 wt%, respectively, at pH from 1.90 to 0.26. Farr et al. found that under given experimental conditions, fluorapatite and calcium fluoride CaF₂ were the equilibrium solid phases [8]. In the liquid phase containing $w(P_2O_5) = 25.78$ wt%, w(CaO) = 5.466 wt%, at pH = 0.81, together with fluorapatite and calcium fluoride, the third solid phase Ca(H₂PO₄)₂·H₂O appeared.

At low concentrations of the liquid phase components, the CaO–P₂O₅–HF–H₂O system was studied at 25 °C by Kazakov [9] in order to reconstruct the formation process of FAp in sedimentary rocks with the formation of phosphate ores. Under these conditions, the following equilibrium solid phases were obtained in the system: FAp, fluorhydroxyapatite Ca₁₀(PO₄)₆(F,OH)₂, CaF₂, and Ca(OH)₂. The regions of the stability of these solid phases were defined. It was found that the composition and ratio of phases are dependent on the amount of the introduced fluoride ion and the pH value of the equilibrium liquid phase.

A large number of studies are devoted to fluoride-containing hydroxyapatite and fluorapatite since these materials are essential for dental hard tissues and play an important role in the prevention of dental caries [10–20]. In a number of studies, the positive effect of low levels of fluoride in acid solutions on the demineralization of dental enamel has been shown both in vitro and in vivo [10–12]. In order to identify the reason for dental caries, Duff [16–19] studied the transformation of various phosphates in fluoride-containing solutions. The thermodynamic properties of the solid phase of the CaO–P₂O₅–CaF₂–H₂O system have also been calculated. According to these data, the equilibrium solid phases

of the system are FAp, CaF_2 and $Ca(OH)_2$, and all the phosphates are metastable, except for FAp.

Thus, the reported information about the regions where the phosphates exist as the equilibrium solid phases in $CaO-P_2O_5-HF/CaF_2-H_2O$ system is incomplete. One of the methods to determine the conditions for the formation of solid phases is to study phase equilibria in this system [7].

The purpose of this work is to study the compositions of the equilibrium solid phases in the CaO– P_2O_5 –HF– H_2O system at low mass fractions of the liquid phase components at 298 K and the regions where they exist. In order to prevent the formation of carbonatecontaining apatites, experiments were carried out in a nitrogen atmosphere [7].

Two sections of the CaO–P₂O₅–HF–H₂O system were studied at 298 K. For Section I, the initial ratio of phosphorus to fluorine remained unchanged and was similar to that of the stoichiometric fluorapatite, i.e., P/F = 3, whereas the ratio of calcium to phosphorus (Ca/P) varied from 1 to 2. Section II represents the system in the acid region at a constant ratio of the initial components Ca/(P + F) = 0.5 and at a P/F value varying from 1 to 20. The results of this study can be used to reveal the mechanism of dental caries in an acid environment or fluorosis, with a lack or excess of fluorine, respectively [10,11]. The obtained isotherms can be used to determine the conditions for FAp formation in solutions with low ion concentrations.

2. Materials and Methods

2.1. Sample Preparation

Freshly calcined CaO, CaF₂, HF, an aqueous solution of H_3PO_4 (w = 87 wt%), and distilled and deionized water were the initial components in the synthesis. All reagents were of chemically pure grade supplied by Khimreaktiv LTD (Ekaterinburg, Russia). The initial solutions containing different mass fractions of calcium, phosphate, and fluoride were prepared by mixing the aqueous solutions of the individual ions in the appropriate ratios. A solution containing phosphate with a mass fraction of 0.1126 wt% was obtained by diluting the concentrated H_3PO_4 acid with distilled and deionized water. Distilled deionized water was obtained with a Direct-Q3 (Millipore, Burlington, MA, USA) system with a produced water resistivity of 18.2 M Ω ·cm. The hydrofluoric acid solution was obtained by diluting the concentrated HF acid with distilled and deionized water to a mass fraction of 0.4446 wt%. A calcium solution was prepared by stirring freshly calcined CaO in distilled and deionized water up to a mass fraction of 0.056 wt%.

The concentration of calcium ions in the initially investigated solutions of Section I was varied, while the concentration of fluoride and phosphorus ions remained constant with the ratio P/F = 3, similar to that for stoichiometric FAp. Therefore, conditions for the formation of calcium-deficient FAp and FAp with excess calcium cations were created in the solutions of Section I. In the solutions of Section II, the calcium concentration remained constant, but the P/F ratio was varied, maintaining the Ca/P + F ratio at a value of 0.5, which is the case in the oral cavity environment.

The resulting initial solutions were poured into polyethylene containers with mixers and placed in a thermostat chamber at a constant temperature of 298 (± 0.1) K and a pressure of 0.1 MPa to achieve an equilibrium state. To create an inert atmosphere, nitrogen gas purified from CO₂ and H₂O using an absorber with CaCl₂ was bubbled into the containers with solutions.

Equilibrium was considered to have been achieved when the pH value and the concentration of calcium and phosphate ions did not change after being sampled and analyzed at least three times with an interval of at least a month. Phase equilibrium in the system has been achieved in 9 to 20 months. After equilibration, the solid phases of the samples were filtered on a Buchner funnel using a vacuum pump, placed in a desiccator, and analyzed by chemical and physical methods.

2.2. Characterization

Due to very low concentration, the analysis of liquid phase components was performed using the most sensitive methods of the State Standards of the Russian Federation [21] applied for the analysis of water purity, similar to International Standards [22].

The phosphate content in the liquid phases was determined by the colorimetric method using the molybdenum blue reaction [21,22]. This method is based on the interaction of phosphate ions with the molybdenum blue complex $MoO_2 \cdot 4MoO_3$ with the formation of a stable blue color. This method can be used in the phosphorus concentration range from 0.005 mg/L to 0.8 mg/L [22]. Phosphate ion contents in the solid phases were determined according to the published method [23] by the precipitation of magnesium ammonium phosphate followed by its ignition to magnesium pyrophosphate $Mg_2P_2O_7$ [8]. Calcium content in the liquid and solid phases was determined by titration using Ethylenediaminete-traacetic acid tetrasodium (EDTA) with an Eriochrome Black T indicator according to the published method [24,25].

Fluoride ions were separated from the solid phases by distillation according to the State Standard [26]. The apparatus used consists of a reaction flask made of heat-resistant glass, with a pocket for a thermometer, placed in a heating mantle connected to a relay for controlling the distillation temperature. A sample of the solid phase was placed in the reaction flask containing 50 mL of sulfuric acid. The flask was closed with a rubber stopper with two glass tubes, one of which was connected to a steam generator and the other to a ball cooler and a condensate receiver for the evaporated fluorine. The temperature of the reaction mixture was maintained at 130–135 °C. Fluorine in the condensate obtained from the solid phase and fluorine in the liquid phases of the incubated sample were determined by the potentiometric method [27] on a pH-121 pH-meter using a fluoride-selective electrode of the EF-VI type and an auxiliary silver chloride electrode EVL-1M3 (ZIP, Gomel, Russia). The chemical compositions of the equilibrium liquid and solid phases are shown in Tables 1 and 2.

No	Ca/P Ratio of Starting Components		Equi	librium Liquid P	hase	Equilibrium Solid Phase			
		pН	Chemical Composition, wt%			Chemical Composition, wt%			Phase
			CaO	P_2O_5	F	CaO	P_2O_5	F	Composition
1	1.0	2.0	1.0750	4.1877	$2.15 imes 10^{-3}$	58.91	9.84	31.25	A.P. + CaF ₂ + CaHPO ₄
2	1.1	1.84	1.0400	3.1270	$1.85 imes 10^{-3}$	52.44	15.80	31.76	HPFAp + CaF ₂ + CaHPO ₄
3	1.3	5.34	0.0045	$7.2 imes10^{-3}$	$1.50 imes10^{-3}$	55.06	26.24	18.70	HPFAp + CaF_2
4	1.4	5.44	0.0031	$4.2 imes 10^{-3}$	$1.43 imes 10^{-3}$	56.51	20.34	23.15	$HPFAp + CaF_2$
5	1.5	5.52	0.0030	$3.4 imes10^{-3}$	$1.33 imes10^{-3}$	56.92	24.81	18.27	$HPFAp + CaF_2$
6	1.6	6.24	0.0024	$0.47 imes10^{-3}$	$1.18 imes10^{-3}$	60.41	32.15	7.44	$HPFAp + CaF_2$
7	1.7	7.10	0.0019	$0.10 imes10^{-3}$	$0.92 imes 10^{-3}$	52.84	39.02	8.14	$FAp + CaF_2$
8	1.8	7.14	0.0027	$0.015 imes 10^{-3}$	$0.90 imes 10^{-3}$	60.42	21.74	17.84	$FAp + CaF_2$
9	1.9	7.58	0.0033	$0.013 imes10^{-3}$	$0.67 imes10^{-3}$	61.75	19.52	18.73	$FAp + CaF_2$
10	2.0	11.54	0.0111	$0.010 imes 10^{-3}$	$0.41 imes 10^{-3}$	69.81	13.84	16.35	$FAp + CaF_2 + Ca(OH)_2$

Table 1. Composition of equilibrium liquid and solid phases at P/F = 3 (Section I).

Note: A.P.—amorphous phase; FAp—fluorapatite; HPFAp—hydrogenphosphate-fluorapatite.

Powder X-ray diffraction (XRD) was used to identify the phase composition of the solid phases obtained. The diffraction patterns were recorded on a D8 Advance diffractometer (Bruker, Mannheim, Germany) with Bragg–Brentano geometry using CuK α radiation, a nickel K β filter, and a position-sensitive one-dimensional Lynx-Eye detector. The crystallite size was refined by the Rietveld method using Topas 4.2 software (Bruker, Germany). The fundamental parameter approach was used to account for the instrumental contribution [28].

No	P/F Ratio of Starting Components	Equilibrium Liquid Phase				Equilibrium Solid Phase				
		pH –	Chemical Composition, wt%			Chemical Composition, wt%			Phase	
			CaO	P_2O_5	F	CaO	P_2O_5	F	Composition	
11	1	3.26	0.097	0.252	$0.46 imes 10^{-3}$	59.35	11.04	29.61	A.P. + CaF_2	
12	1.5	3.50	0.114	0.300	$0.41 imes 10^{-3}$	58.31	12.55	29.14	HPFAp + CaF_2	
13	3	3.08	0.286	0.775	$0.47 imes10^{-3}$	56.31	15.18	28.51	$HPFAp + CaF_2$	
14	4	3.07	0.300	0.800	$0.44 imes10^{-3}$	56.84	18.33	24.83	HPFAp + CaF_2	
15	9	3.03	0.335	0.890	$0.48 imes10^{-3}$	54.65	28.91	16.44	$HPFAp + CaF_2$	
16	10	2.97	0.371	1.010	$0.48 imes10^{-3}$	52.41	33.58	14.01	$HPFAp + CaF_2$	

Table 2. Composition of equilibrium liquid and solid phases at Ca/(P + F) = 0.5 (Section II).

Note: A.P.—amorphous phase; HPFAp—hydrogenphosphate-fluorapatite.

The functional groups in the solid phases were identified by IR spectroscopy. The spectra were recorded on an Infralum-801 instrument using the KBr pellet method.

A high-resolution JEM-2010 electron microscope (JEOL, Tokyo, Japan) at an accelerating voltage of 200 kV and a resolution of 1.4 Å was used to study the microstructure of the solid phases. A suspension of the particles in alcohol was deposited onto a copper substrate using an ultrasonic disperser. Local analysis of the elemental composition of the sample was carried out using a QUANTAX 200-TEM energy-dispersive EDS spectrometer (Bruker, Germany) with an XFLASH detector and an energy resolution of about 130 eV.

3. Results

A part of the isotherm of the CaO–P₂O₅–HF–H₂O system has been studied at 298 K in a nitrogen atmosphere for the equilibrium liquid phase containing w(CaO) = 0.0019-1.0750 wt%, $w(P_2O_5) = 0.01 \times 10^{-3}$ –4.1877 wt%, $w(F) = 0.41 \times 10^{-3}$ –2.15 × 10⁻³ wt%, and at pH changing from 1.84 to 11.54 (Tables 1 and 2). It was found that the compounds of variable composition with the fluorapatite and fluorite structures mostly exist in this region. In this system, the region of fluorapatite is much wider than the region of the existence of hydroxyapatite and carbonate apatite observed in the ternary [29] and quaternary [30] systems, respectively. Thus, calcium-deficient hydroxyapatites of variable composition, which form an invariant point with octacalcium phosphate Ca₈H₂(PO₄)₆·5H₂O, were found in the ternary system CaO–P₂O₅–H₂O whose liquid phase at equilibrium contained w(CaO) = 0.0026 wt%, $w(P_2O_5) = 0.0058 \text{ wt\%}$ and had pH = 6.64 [29]. In the quaternary CaO–H₃PO₄–H₂CO₃–H₂O system, carbonate apatites of variable composition are formed, having an invariant point with brushite CaHPO₄·2H₂O at equilibrium values w(CaO) = 0.0101 wt%, $w(P_2O_5) = 0.0202 \text{ wt\%}$, and pH = 5.40 [30].

3.1. Section I

Under acid conditions, in the CaO–P₂O₅–HF–H₂O system, fluorapatite is bordered by monetite CaHPO₄, where, at equilibrium w(CaO) = 1.075 wt%, w(P₂O₅) = 4.1877 wt%, and w(F) = 2.15 × 10⁻³ wt%, and pH = 2.00, fluorite, monetite, and nanosized amorphous phosphate are formed (Figure 2, Table 1 sample #1). According to the XRD data, the invariant point (sample #2) involves fluorite, monetite, and fluorapatite (Figure 2, Table 1, sample #2). CaF₂, with an average crystallite size of 12 nm, is the predominant solid phase (90 wt%) in the sample. The concentration of fluorapatite in this sample is only 8 wt%, and the average crystallite size is ~170 nm. TEM image of the equilibrium solid phase of sample #2 reveals the presence of a finely dispersed CaF₂ phase and large fluorapatite particles (Figure 3).



Figure 2. X-ray diffraction patterns of the solid phases of samples #1 and #2.



Figure 3. Electron microscopy image of the solid phase of sample #2 containing nanocrystalline fluorite (1) and a block of fluorapatite (2).

It should be noted that even in the presence of calcium, phosphorus, and fluoride ions in sufficient concentrations in the solution with the required P/F ratio, the formation of fluorapatite almost does not occur in the solid phase of sample #2, and a significant amount of the calcium and phosphorus ions remains in the solution (Table 1). In this case, the determining factor for the FAp formation is the high acidity of the liquid phase.

Figure 4 shows the IR spectra of the solid phases of samples #1 and #2. As seen, sample #1 has a specific IR spectrum; it has two intense absorption bands at 1080 and 1130 cm⁻¹ and a shoulder at 960 cm⁻¹. Similar IR spectra of amorphous calcium phosphates were obtained by Holt et al. [31]. According to this study, the intense absorption band at 1080 cm⁻¹ can be explained by the effects of site symmetry in partially lifting the degeneracy of the asymmetric stretching mode of the phosphate tetrahedron. The shoulder at 950 cm⁻¹ can be attributed to the symmetric stretching vibration of the bonds of the phosphate tetrahedron PO₄³⁻ species when the effects of site asymmetry make the mode active in the infrared [31].



Figure 4. IR spectra of the solid phases of samples #1 and #2.

The IR spectrum of the solid phase of sample #2 is typical for fluorapatite, although the splitting of the absorption bands of the O–P–O bending vibrations v_4 at 560 and 578 cm⁻¹ occurs. Apart from that, the absorption bands of the P–O stretching vibrations v_3 at 1007 cm⁻¹ and 1050 cm⁻¹ are shifted and split (Figure 4). An increase in the number of absorption bands in the IR spectrum of the phosphate tetrahedron indicates a change in the coordination environment and a decrease in the symmetry of the phosphate ion. The absorption band at 870 cm⁻¹ may indicate the presence of the HPO₄^{2–} group [13].

As the pH values of the equilibrium liquid phase increase (Table 1, samples #3 and #4), the absorption bands of the P–O stretching vibrations in the IR spectra change their positions; as a result, the spectra become more similar to those of the FAp (Figure 5). However, the splitting of the absorption bands of the O–P–O bending vibrations remains unchanged. This can be explained by the formation of nonstoichiometric fluorapatites of variable composition in the acid region of the CaO- P_2O_5 -HF- H_2O system at pH < 7 with partial replacement of the PO_4^{3-} ions by the HPO_4^{2-} groups. An absorption band at 870 cm⁻¹ in the IR spectra indicates the presence of HPO₄^{2–} groups in the fluorapatite structure (Figure 4). As known, the mineral component of bone tissue consists of apatite, in the structure of which some of the PO_4^{3-} groups are replaced by HPO_4^{2-} and CO_3^{2-} ions [32]. Hayek and Link called these apatites "hydrogenphosphate-carbonate-apatite", abbreviated as HPCA. By analogy with these compounds, fluorapatites containing HPO4²⁻ groups can be called "hydrogenphosphate-fluorapatite" and denoted as HPFAp. Since the experiments in this study were carried out in a nitrogen atmosphere, the HPFAp structure should not contain the carbonate groups. Apart from that, if these groups were in the apatite structure, together with the band at 870 cm⁻¹, more intense bands at 1400–1470 cm⁻¹ would appear in the IR spectra [30], which is not the case (Figures 4 and 5).



Figure 5. IR spectra of samples #3 and #4, containing HPO_4^{2-} groups, and samples #8 and #9 not containing these groups.

The as-synthesized compounds of variable composition can be represented by the general formula $Ca_{10-x}(PO_4)_{6-x}(HPO_4)_xF_{2-x}$, where $0 < x \le 1$. Non-stoichiometric apatites with partial substitution of PO_4^{3-} by the HPO_4^{2-} ion are formed in the surface layers of hydroxyapatite upon its dissolution [33], and they were observed in the ternary and quaternary phosphate aqueous systems we had studied earlier [29,30].

As the pH of the equilibrium liquid phase increases to pH = 7.0, the concentration of calcium, phosphorus, and fluoride ions in it decreases (Table 1). In an alkaline environment, the content of calcium ions begins to increase (Table 1, samples #8–#10), while the concentration of phosphorus and fluoride ions continues to decrease. The invariant point with Ca(OH)₂ is reached at pH = 11.57 in the equilibrium liquid phase containing w(CaO) = 0.0111 wt%, w(P₂O₅) = 0.1 × 10⁻⁴ wt%, and w(F) = 0.41 × 10⁻³ wt% (Table 1, sample #10).

The lowest concentration of phosphate and calcium ions in the liquid phase was reached at the neutral point of the isotherm at pH = 7.1 (Table 1, sample #7). At this point of the isotherm, at pH~7 and above, the stoichiometric FAp with the chemical formula $Ca_{10}(PO_4)_6F_2$ is formed. In the IR spectra of the solid samples formed under neutral and alkaline conditions, an absorption band at 875 cm⁻¹, assigned to the HPO₄^{2–} group, is absent (Figure 5, samples #8 and #9). The spectra become more similar to the FAp spectrum.

It should also be noted that FAp, which does not contain the acid groups, precipitates from the initial solution at a Ca/P ratio of >1.67, which is needed for FAp to form.

Based on the data obtained, an orthogonal projection of the isotherm of the CaO–P₂O₅– HF–H₂O system onto the CaO–H₂O–P₂O₅ coordinate plane was drawn (Figure 6). This diagram clearly shows that the composition of the solid phases, which are in equilibrium with the liquid phase, depends on the equilibrium pH, which in turn, is determined by the ratio of the components in the initial solution. Thus, in an acid medium, fluorapatite containing the HPO₄^{2–} group (HPFAp) is formed, while in a neutral and alkaline medium, the formation of stoichiometric fluorapatite (FAp) takes place. Similar phase diagrams of the quaternary CaO–P₂O₅–HF–H₂O and the ternary CaO–P₂O₅–H₂O systems were reported in studies [8,9] and [34], respectively.



Figure 6. Orthogonal projection of the CaO–P₂O₅–HF–H₂O isotherm at 298 K onto the CaO–P₂O₅–H₂O coordinate plane, based on the data in Tables 1 and 2. Numbers on the graph indicate the sample numbers. Multi-colored arrows show the direction of increasing the ratio of the components in the initial solution, as well as the pH of the medium in the equilibrium state. The brown arrow indicates the transition region between FAp and HPFAp.

3.2. Section II

Unlike Section I, where the P/F ratio in the initial solution was a stoichiometric and constant value of 3, in Section II, this ratio varied from 1 to 20 (Table 2). The data in Table 2 show that an increase in the P/F ratio in the initial solution results in a decrease in the pH of the equilibrium liquid phase and changes the composition of the equilibrium liquid and solid phases. As seen in Figure 6, the compositions of the equilibrium liquid phase of the samples from Section II (points #11–#16, taken from Table 2) fall on the isotherm in the interval between samples #2 and #3 from Section I (Table 1). The composition of the liquid phase of the samples from Section II complements the diagram of the composition of the liquid phase of the samples from Section II complements the diagram of the composition of the liquid phase of the samples from Section I.

Analysis of the data obtained showed that the ratio of the components in the equilibrium solid phases is dependent on the P/F ratio in the initial solution (Figure 7). Thus, an increase in the phosphorus concentration in the initial solution results in an increase in the concentration of fluorapatite and a decrease in the content of fluorite. This can be seen when comparing the intensities of the reflections of the phases in the XRD patterns shown in Figure 7. It should be noted that as the fraction of the fluorapatite phase increases, its crystallite size decreases from 100 nm (sample #12) to 35 nm (sample #16). The latter sample is composed of 78 wt% apatite phase.



Figure 7. XRD patterns of solid phases of the samples from Section II.

Figure 8 shows the IR spectra of the samples from Section II. As seen, they are very much similar to those obtained in the same range of the liquid phase concentrations from Section I (Figure 5). Analysis of the spectra of the equilibrium solid phases of the samples from Section II revealed that the P/F ratio in the initial solution affects the phosphate structure. Thus, the IR spectrum of sample #11, which, according to the XRD data, mainly consists of fluorite with a small content of amorphous apatite, has triply degenerated bending vibrations of phosphate and a band at 1073 cm⁻¹ attributed to the P–O stretching vibrations v_3 (Figure 8), which is close to a similar band of the sample #1 (Figure 3). With an increase in the concentration of phosphorus in the initial solution up to a stoichiometric value of fluorapatite (P/F = 3) and higher, fluorapatite containing the HPO₄^{2–} group (HPFAp) is formed. In the IR spectra of these samples, the bands attributed to the O-P vibrations v_3 appear in the 1000–1060 cm⁻¹ range (Figure 8). A characteristic feature of the IR absorption in HPFAp is the splitting of the bands of the O–P–O bending vibrations v_4 in the 500–620 cm⁻¹ range (Figure 8). It can be assumed that the presence of both the HPO₄^{2–} groups and fluoride ions in the structure of fluorapatite lowers the symmetry of a PO₄³⁻ tetrahedron, which is evident in the splitting of the absorption bands in the IR spectra. The shift of the phosphate bands is due to the variable composition of the samples, which is most likely caused by the different concentrations of the $\mathrm{HPO_4}^{2-}$ group.



Figure 8. IR spectra of solid phases of the samples from Section II.

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4. Conclusions

The phase equilibria in the CaO–P₂O₅–HF–H₂O system at 298 K in an atmosphere of nitrogen gas at low concentrations of the liquid phase components have been studied. The concentration range started at the invariant point between fluorapatite and monetite and ended at the levels limited by the sensitivity of analytical methods used. It has been established that all of the as-synthesized samples showed the presence of the fluorapatite structure are present in the acid and neutral regions of the isotherm. Depending on the ratio of the components in the initial solution and pH in the equilibrium state, the following equilibrium solid phases with the fluorapatite structure were found:

(1) Hydrogen phosphate fluorapatite, HPFAp, existing in an acid environment, at $7.1 > pH \ge 1.9$, with a part of the PO₄³⁻ groups replaced by HPO₄²⁻ ions. The excess charge of this heterovalent substitution is compensated by the calcium ion vacancies. The HPFAp composition can be described by the formula $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}F_{2-x}$, where $0 < x \le 1$. The invariant point between three solid phases, HPFAp, CaHPO₄ and CaF₂, exists when the equilibrium liquid phase contains w(CaO) = 1.040 wt%, $w(P_2O_5) = 3.127$ wt%, $w(F) = 1.85 \times 10^{-3}$ wt% and pH = 1.84;

(2) Stoichiometric fluorapatite Ca₁₀(PO₄)₆F₂ is formed at pH = 7.1–7.58 at the lowest concentration of phosphate and calcium in the equilibrium solution. Under alkaline conditions, for the equilibrium liquid phase at pH = 11.54 containing w(CaO) = 0.040 wt%, w(P₂O₅) = 0.1 × 10⁻⁴ wt%, and w(F) = 0.41 × 10⁻³ wt%, fluorapatite has the invariant point with Ca(OH)₂.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst13081264/s1. Table S1. EDX analysis of element composition of the crystals.

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