

# Dissolution of Gibbsite and Its Transformation to Taranakite Depending on the Concentration of Phosphate Anions in the Solution

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**Abstract**—Structural changes of gibbsite at the binding of phosphate anions from  $\text{NH}_4\text{H}_2\text{PO}_4$  solutions of different concentrations (from  $10^{-6}$  to 2 mol P/L) have been studied using an X-ray diffractometer and an electron scanning microscope with a spectrometric microanalyzer. It has been shown that, beginning from a concentration of  $10^{-3}$  mol P/L, the binding of phosphate anions has been accompanied by the release of anionic aluminum–phosphate complexes into the liquid phase. The content of these complexes has increased with the phosphate solution concentration and the time of its contact with gibbsite. The treatment of gibbsite with a 1 M phosphate solution for two months has resulted in the pronounced dissolution of the gibbsite crystal surface, accompanied by the formation of ammonium taranakite (ammonium salt of complex aluminophosphoric acid). Successive changes in size and form of the initially formed ammonium taranakite crystal has occurred in a 2 M phosphate solution. The degradation of the layered structure of taranakite and the enrichment of degradation products with phosphorus and nitrogen have been revealed. The significant increase of the P/Al ratios in the degradation products compared to the corresponding ratio in the initially formed taranakite indicates the formation of new phosphate phases resulting from the transformation of taranakite under the impact of free phosphate anions in a high-concentration solution.

**Keywords:** chemisorption, complex aluminophosphate anions, ammonium taranakite formation

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## INTRODUCTION

In spite of the well-known increasing eutrophication of water bodies (visually manifested as blossoming) because of the input of soluble phosphorus compounds, the concept of the strong binding (chemisorption) of phosphate anions on the surfaces of Al- and Fe-containing soil compounds (sorbents) remains widely accepted. The use of aluminum and iron salts for the purification of water from phosphorus by its precipitation as solid Al(Fe) phosphates is based on the high chemical affinity of phosphate anions for these metals. However, the secondary (internal) eutrophication of water usually purified with Al and Fe sulfates [18] indicates the potential transformation of aluminum (iron) phosphate precipitates to soluble P-containing compounds.

Soluble (migration-capable) phosphorus compounds can be formed in acid soils, where Al and Fe compounds (metal oxides and hydroxides, clay minerals, metal-humus derivatives) operate as the main sorption barriers for exogenic phosphate anions [9, 12]. The decrease in the activity of soil barriers under a high load with fertilizer phosphates is related to the formation of negatively charged Al(Fe)-phosphate complexes and their involvement in the migra-

tion process [12, 13]. This implies that the products resulting from the interaction of phosphate anions with soil sorbents are subjected to migration.

The properties of sorbent transformation products in P-containing solutions of different concentrations are insufficiently understood. Phosphate solutions of relatively low concentrations (usually no higher than  $10^{-3}$ – $10^{-2}$  mol P/L) are usually used in experiments on the sorption of phosphate anions by acid soils and their components. Almost no information on the effect of more concentrated phosphate solutions is available. At the same time, the possible localization of microzones (loci) formed around the particles (granules) of water-soluble phosphoric fertilizers, where the phosphate load on the sorbents is anomalously high compared to the surrounding soil, should be taken into consideration [11].

The generalization of experimental data [10, 12] indicates that the binding of phosphate anions from solutions with increasing concentrations in the range  $10^{-6}$ – $10^{-2}$  mol P/L on the surface of sorbents results in the successive formation of different metal–phosphate complexes. At the low concentrations of phosphates typical for natural soil solutions ( $10^{-6}$ – $10^{-5}$  mol P/L), binuclear metal–phosphate complexes  $\text{Me-OPO-Me}$

(where *Me* denotes a metal), in which one phosphate anion serves as a bridge between two metal atoms, are formed on the surfaces [10]. The formation of such complexes proceeds in two stages. At the first stage,

$\text{H}_2\text{PO}_4^-$  (the major phosphate anion in acid soils), which has one electron-donating oxygen atom, is coordinated to a metal atom (electron acceptor) on the surface. This process involves the substitution/elimination of the most mobile ligand in the original complex. At the substitution of the hydroxyl ligand, the pH of the liquid phase in the sorbent–phosphate solution system increases [10].

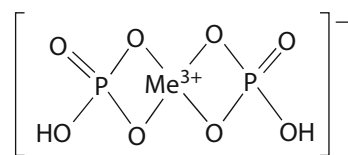
The coordination of the new ligand initiates the redistribution of electron density in the complex [4], which results in the deprotonation of the  $\text{H}_2\text{PO}_4$  ligand. The transformation of the monodentate<sup>1</sup>  $\text{H}_2\text{PO}_4$  ligand to the bidentate  $\text{HPO}_4$  ligand, the additional donating oxygen atom of which is capable of coordinating to the metal atom of the neighboring surface complex (second stage), results in the formation of a bridged binuclear complex strongly retained on the surface of the sorbent under the low concentration of phosphate solution [10]. The potential formation of binuclear complexes lies behind the concept of the strong binding of phosphate anions by Al- and Fe-containing sorbents.

When the concentration (and, hence, ligand activity) of phosphates in the solution increases, the binuclear metal–phosphate surface complexes are transformed to mononuclear complexes. The probability for the cleavage of the *Me*–OH–*Me* bonds in the binuclear hydroxo complexes of the sorbent itself increases [10]. As a result, separate structural fragments are detached from the sorbent polymer molecules, which favors the formation of mononuclear complexes with the general formula  $\text{Me}(X_n Z_m)$  (where *Me* =  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ; *X* =  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ; *Z* =  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ) corresponding to simple salts. These complexes containing water and hydroxyl ligands in the inner sphere are usually X-ray amorphous (i.e., they have unordered structure), which hampers their instrumental detection [28, 29, 35].

The mononuclear metal–phosphate complexes with two bidentate ligands in the inner coordination

<sup>1</sup> The ligand denticity is determined by the number of electron-donating atoms capable of coordination in the ligand. The  $\text{H}_2\text{PO}_4^-$  anion (which has one electron-donating O atom), the  $\text{HPO}_4^{2-}$  anion (which has two donating O atoms), and the anions of condensed phosphoric acids (which have more than two electron-donating O atoms) are referred to as mono-, bi-, and polydentate ligands, respectively. The bi- and polydentate ligands are chelating agents.

sphere have a negative charge [20, 21, 25, 31] and a cyclic (chelate) structure:



The charge of the anionic complexes is balanced by the binding of cations present in the solution [12, 20, 25, 31, 36]. The noted binding of cations from the solution suggests the potential formation of double (triple) phosphate salts with the general formula  $\text{Me}_b^1[\text{MeX}]$  (where  $\text{Me}^1 = \text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and other cations; *Me* =  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ; *X* =  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ) on the sorbent surface. However, no formation of such salts on the surface of soil sorbents was noted in model experiments with relatively low (less than  $10^{-2}$  mol P/L) concentrations of phosphate solutions.

However, the presence of double (triple) phosphate salts was observed in natural soils [30, 40], especially those formed on the rocks enriched with phosphates of lithogenic or biogenic origin [34, 37, 39]. Their formation in technogenically phosphatized soils was established [11, 14, 29, 36]. These data suggest that double (triple) phosphate salts are formed in soils with long-lasting high phosphate load on the sorbent compounds.

Minerals from the taranakite–leucophosphite series with the general (standardized) formula  $(\text{NH}_4^+, \text{K}^+, \text{Na}^+)_3(\text{Al}, \text{Fe}^{3+})_5(\text{HPO}_4)_6(\text{PO}_4)_2 \cdot 18\text{H}_2\text{O}$  [22, 24, 32, 39] are detected at the accumulation sites of biogenic products (in cavities). Theoretically, taranakite contains only aluminum, while leucophosphite contains only iron. Guano of birds and bats serves as a source of nitrogen and phosphorus for the formation of ammonium taranakite, and the underlying magmatic and sedimentary rocks are sources of metals [22, 24, 32, 39]. The standardized (conventional) formula of the ideal ammonium taranakite is that of the ammonium salt of complex aluminophosphoric acid  $(\text{NH}_4^+)_3[\text{Al}_5(\text{HPO}_4)_6(\text{PO}_4)_2]^{3-} \cdot 18\text{H}_2\text{O}$ .

According to the presented formula, the P/Al ratio in ammonium taranakite is 1.83, while it is 1.15 in the simple phosphate salt (aluminophosphate mineral variscite with the formula  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ). The high P/Al ratio indicates the involvement of phosphorus-enriched anionic aluminum-phosphate complexes in the formation of taranakite under high phosphate loads on Al-containing rocks.

The negatively charged  $\text{Al}(\text{Fe}^{3+})$ –phosphate complexes are anions of a higher order than the anions of common phosphoric acid. They should be considered as anions of metallophosphoric acids with peculiar properties and, hence, high reactivity, which also ensures the catalysis of reactions at the

interface [2, 3, 8, 15]. An important feature of complex anions is the ability to substitute the strongly bound ligands, including phosphate ligands. This property is related to the incongruent dissolution of phosphorus compounds in phosphate solutions, during which more and more complicated solid-phase and (most significantly) soluble P-containing compounds are successively formed [12, 13]. The ability of the formed metallophosphate anions to pass into the liquid phase increases with their charge [15]. This can be a reason for the higher solubilities of Al, Fe, Mn, Zn, Mg, and Ca compounds in the soil under the impact of polyphosphates than those of their orthophosphates [11, 23].

Thus, the preliminary results of studies indicate the ability of anionic metallophosphate complexes formed at the binding of phosphate anions by iron and aluminum compounds (sorbents in acid soils) to pass into the liquid phase. However, the formation conditions of anionic  $Me^{3+}$ -phosphate complexes and their behavior in the soil-P-containing solution system are insufficiently understood; therefore, a more thorough study of changes in the structure of particular sorbents under the impact of different phosphate loads is advisable. Of primary importance is study of the effect of anomalously high phosphate loads on the sorbents, because a long-lasting localization of sites with the phosphate load exceeding the typical load for the bulk soil mass by several orders of magnitude is possible in the technogenically phosphatized soils [11].

The aim of this work was to study the structural changes of the mineral gibbsite under the impact of phosphate solutions, whose concentrations are close to those of natural soil solutions and the solutions localized in the reaction zones of phosphoric fertilizer granules.

## METHODOLOGY

Aluminum hydroxide with the formula  $Al(OH)_3$  was used in the work. Its X-ray diffraction pattern corresponded to the mineral gibbsite [16]. The gibbsite crystals usually have a pseudo-hexagonal section; hydrogen bonds play an important role in their formation. Atoms of  $Al^{3+}$  in the crystal have a coordination number of 6 and are in the octahedral surrounding of OH ligands, which act as bridges to the neighboring aluminum atoms. The surface complexes of defective crystal surfaces (along with bridged OH ligands) also have aqua and hydroxo ligands (bound to the Al atom of a separate complex) in the coordination sphere.

Powder of  $Al(OH)_3$  was treated with distilled water (control) or an  $NH_4H_2PO_4$  solution of the corresponding concentration ( $10^{-6}$ ,  $10^{-5}$ ,  $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$ ,  $10^{-1}$ , 1, and 2 mol P/L) at a ratio of 1 g : 100 mL. The pH values of the initial solutions before the preparation of the  $Al(OH)_3-H_2O$  and  $Al(OH)_3-NH_4H_2PO_4-H_2O$  systems varied in the range 4.56–4.61. The pH values

of all solutions (including water) were brought to the same level using 0.05 N HCl and 0.05 N NaOH solutions. Gibbsite suspensions were shaken for 2 h and left to stand at room temperature for 1 day, 10 days, and 2 months with daily shaking for 1 min. In suspension filtrates (the liquid phases of the systems), pH was determined with a glass electrode, and the contents of phosphorus and aluminum were determined by the atomic emission method on a Perkin Elmer Optima 5300 DV spectrometer. Before the analysis, the filtrates with high phosphorus concentrations were diluted with distilled water to a concentration of  $10^{-3}$  mol P/L. The contents of P and Al in the filtrates were determined after the thermal acid hydrolysis of aliquots (treatment with  $HCl_{1,19}$  for 10 min) to split aluminum-phosphate complexes [1]. The contents of phosphates bound to gibbsite were calculated from the difference between the P contents in the initial solutions and in the liquid phases of the  $Al(OH)_3-NH_4H_2PO_4-H_2O$  systems. The presented analytical data were obtained from three replicates. The deviations from the mean values did not exceed 4% for phosphorus and 6% for aluminum.

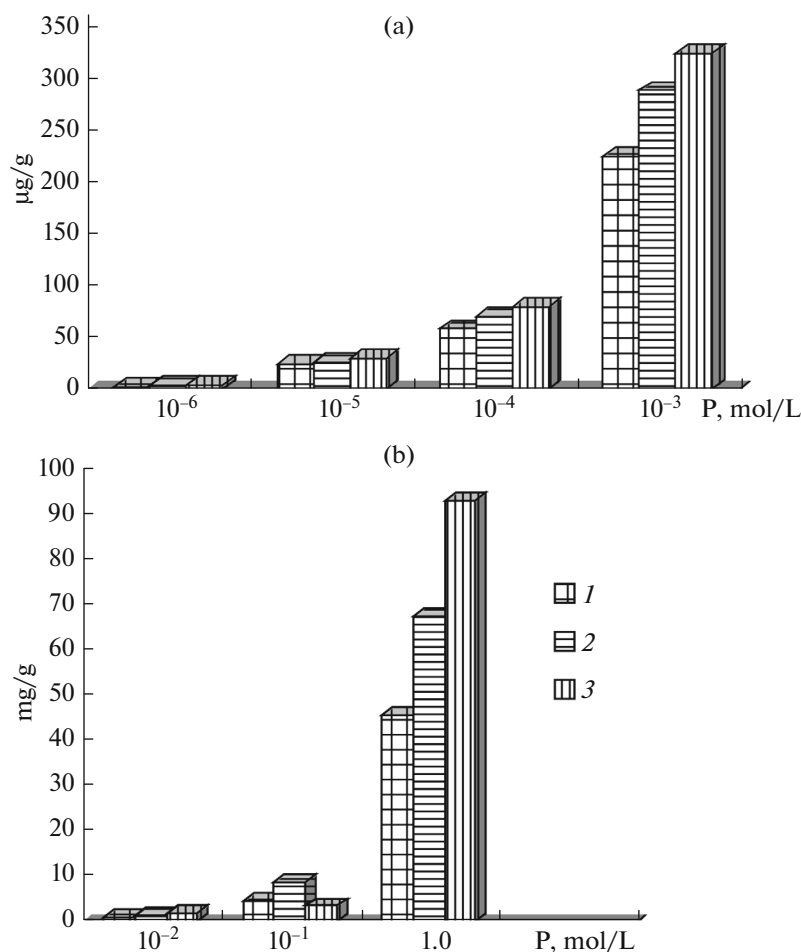
The electron absorption spectra of the liquid phases from the  $Al(OH)_3-H_2O$  and  $Al(OH)_3-NH_4H_2PO_4-H_2O$  systems were recorded on a Hitachi-557 spectrophotometer with a 20-mm cell. Water and the liquid phase of the  $Al(OH)_3-H_2O$  control system, respectively, were used as comparison standards.

Solid products of the phosphate treatment of aluminum hydroxide were separated, washed with water, air-dried, and subjected to instrumental analysis. The X-ray diffractometric study was performed on a DRON-3 instrument (with a Co anode). The structural transformation of gibbsite in phosphate solutions was observed using a Tescan Vega-3 LMU scanning electron microscope with an INCA Energy 350 microanalysis system.

## RESULTS AND DISCUSSION

Direct relationships between the content of phosphate anions bound to gibbsite and the concentration of phosphate solution are shown in Fig. 1. When solutions with concentrations in the range  $10^{-6}$ – $10^{-4}$  mol P/L (typical for natural soil solutions) were used, their phosphates were completely bound to gibbsite during the treatment for two months. The sufficiently slow binding of phosphate anions could be due to the crystalline structure of gibbsite. It is believed that only the ligands in aluminum complexes on the defective crystal surfaces can be substituted by phosphate anions in this case [10, 35]. In the water environment, mixed-ligand complexes occur on such surfaces because they contain water molecules, along with OH groups.

Water molecules are coordinated to Al atoms on the defective surface due to the presence of unshared electron pairs on the O atom.



**Fig. 1.** Binding of phosphate anions by gibbsite from  $\text{NH}_4\text{H}_2\text{PO}_4$  solutions of different concentrations: (a)  $\mu\text{g P/g}$  gibbsite; (b)  $\text{mg P/g}$  gibbsite; time of interaction: (1) 24 h; (2) 10 days; (3) 2 months.

The ideal surface aqua (hydroxo) complex  $[\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3]^0$  formed Al with a coordination number of 6 has a zero charge. If the substitution/elimination of the OH group by the water molecule occurs during the coordination, which is reflected in the increase in the pH of the liquid phase of the gibbsite–water control system to 4.91 compared to the water pH of 4.56 (Table 1), an  $[\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2]^+$  surface complex with positive charge is formed.

Water molecules in the coordinated state are capable of dissociation with the release of  $\text{H}^+$  ions. In the presence of more than three OH ligands in the inner

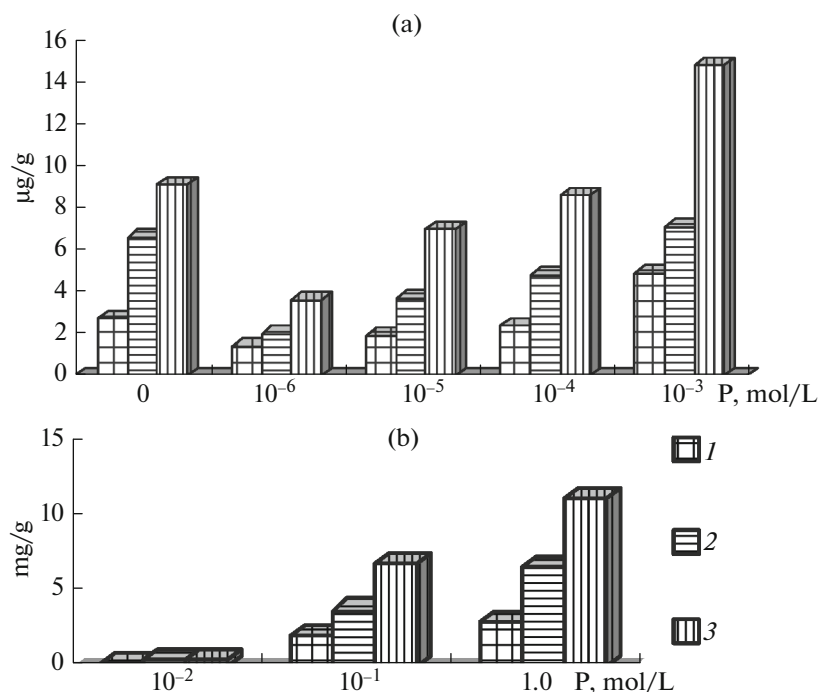
sphere, the surface complex<sup>2</sup> acquires a negative charge:  $[\text{Al}(\text{OH})_4(\text{H}_2\text{O})_2]^-$ . The ability of the anionic complex to pass into the liquid phase is proved by data on the increase in the content of Al in the control (P-free) system with increasing contact time between water and gibbsite (Fig. 2). The electron spectrum (Fig. 3, curve 1) revealed absorption in the region of 265 nm, which can be assigned to the anionic

<sup>2</sup> To simplify the formulas of complexes with  $\text{H}_2\text{O}$  ligands, the latter are usually omitted, because they do not affect the charge of the complex:  $[\text{Al}(\text{OH})_4(\text{H}_2\text{O})_2]^- = [\text{Al}(\text{OH})_4]^-$ .

**Table 1.** Liquid phase pH values in the gibbsite–P solution systems

Initial concentration, mol P/L	0	10 <sup>-6</sup>	10 <sup>-5</sup>	10 <sup>-4</sup>	10 <sup>-3</sup>	10 <sup>-2</sup>	10 <sup>-1</sup>	1.0
pH	4.91	5.52	5.69	5.61	5.47	5.03	4.54	4.23

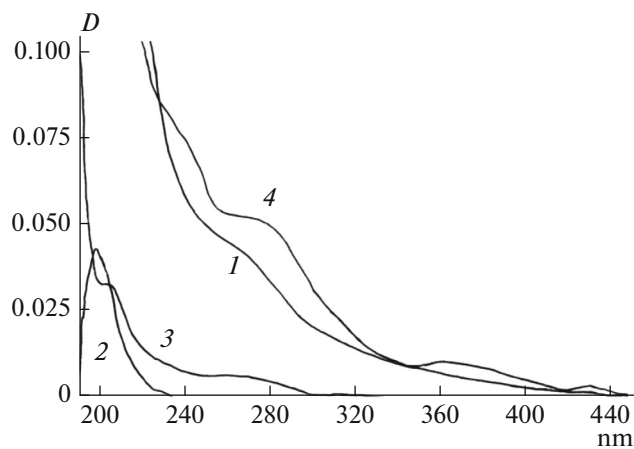
Initial water pH was 4.56.



**Fig. 2.** Release of aluminum into the liquid phase of the gibbsite–P solution systems; the amount: (a)  $\mu\text{g Al/g gibbsite}$ ; (b)  $\text{mg Al/g gibbsite}$ ; time of interaction: (1) 24 h; (2) 10 days; (3) 2 months.

complex because the absorption of the  $\text{OH}^-$  anions is manifested in the region of 190–200 nm.

The binding of phosphate anions by surface aqua (hydroxo) complexes proceeds via the substitution of water and hydroxo ligands. The substitution of OH groups is confirmed by an increase in the pH of liquid phases in the systems containing  $10^{-6}$ – $10^{-5}$  mol P/L compared to the control P-free system (Table 1).



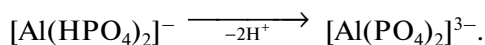
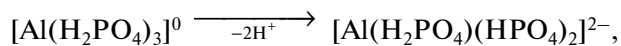
**Fig. 3.** Electron absorption spectra of the liquid phase of the daily gibbsite–P solution systems; the solution concentrations (P, mol/L): (1) without P, control (standard–water); (2)  $10^{-6}$ ; (3)  $10^{-4}$ ; (4) 1.0; the liquid phase of the control system was used as a standard in treatments 2, 3, and 4.

In the electron spectrum of the liquid phase of the system containing  $10^{-6}$  mol P/L (Fig. 3, curve 2), the absorption at 265 nm disappeared, but the absorption intensity in the region of 200 nm slightly increased (compared to the control system) because of the release of OH groups. Because no new absorption was spectrally recorded, it may be concluded that the formed aluminum–phosphate complexes were almost insoluble in water; i.e., they were strongly bound to the sorbent. This was also indicated by trace Al amounts in the liquid phase, which were lower than in the gibbsite–water control system (Fig. 2). Binuclear aluminum–phosphate complexes were apparently formed in the system containing  $10^{-6}$  mol P/L and retained by the gibbsite surface.

When the concentration of phosphate solution increased, new absorption bands appeared in the electron spectra of the liquid phases of the systems containing  $10^{-4}$  and 1 mol P/L (Fig. 3, curves 3, 4), which could be assigned to phosphate anions (260–330 nm) and anionic aluminum–phosphate complexes (230–255 nm). Absorption in the regions of 350–420 and 420–440 nm (Fig. 3, curve 4) can be assigned to excitations in the inner sphere of the newly formed aluminum–phosphate complexes, which point to the incompleteness of processes in the sphere initiated by the coordination of phosphate ligands.

The binding of phosphate anions from the solutions containing  $10^{-4}$ –1 mol P/L was accompanied by the successive decrease in the pH of the liquid phases

of the systems. The most significant decrease of pH against the gibbsite–water control system was observed in the systems containing  $10^{-1}$  and 1.0 mol P/L (to 4.54 and 4.23, respectively), which indicated the deprotonation of the coordinated  $\text{H}_2\text{PO}_4$  groups with the release of  $\text{H}^+$  ions. The deprotonation was due to the redistribution of electron density in the complex initiated by the coordination of the phosphate ligand [4]. This resulted in an increase in the denticity (number of donating O atoms) of the phosphate ligands and the negative charges of the corresponding complexes:



The X-ray diffraction patterns (not given) of the products of gibbsite treatments with the solutions at concentrations lower than 1 mol P/L revealed no new peaks compared to the control gibbsite, probably because of the amorphicity or the relatively low content of the new phase. The revelation of aluminum in the liquid phase (Fig. 2b) can be indicative of the dissolution of aluminophosphate product in the phosphate solution. The dissolution of the phosphatized gibbsite layer points to a decrease in the content of phosphorus in the solid phase (Fig. 1b) at the increase in the time of treatment with a  $10^{-1}$  mol P/L solution from ten days to two months. This means that a significant part of phosphorus bound by gibbsite in the first ten days passed into the liquid phase under the continuing impact of the P-containing solution. Consequently, the structure and properties of the aluminum–phosphate complexes formed during ten days changed with time, probably because of the introduction of additional phosphate ligands increasing the negative charge of the complexes and their ability to pass into the solution.

It may be supposed that the anionic complexes in the two-month system containing  $10^{-1}$  mol P/L were intermediate products with catalytic properties, because their formation significantly accelerated the transformation of gibbsite. The highest rate of the process was observed in the systems containing 1 and 2 mol P/L. In the two-month systems, the formation of new solid phases was noted (Figs. 4b, 4c) having structures that differed from those of gibbsite (Fig. 4a). The diffraction patterns of the products of gibbsite treatment with 1 and 2 mol P/L solutions for two months (Figs. 4b, 4c) are characterized by the absence of peaks typical for this mineral [16], except two remained peaks with reduced intensities (at 4.889 and 4.395 Å).

The peaks present in the diffraction pattern of the product of gibbsite treatment with a 1 mol P/L solution at 16.289, 8.030, 7.560, 3.180, and 2.649 Å with intensities of 99.9, 100.0, 9.4, 16.7, and 10.2%, respectively

(Fig. 4b), are characteristic for ammonium taranakite with the formula  $(\text{NH}_4)_3[\text{Al}_5(\text{HPO}_4)_6(\text{PO}_4)_2] \cdot 18\text{H}_2\text{O}$  [27].

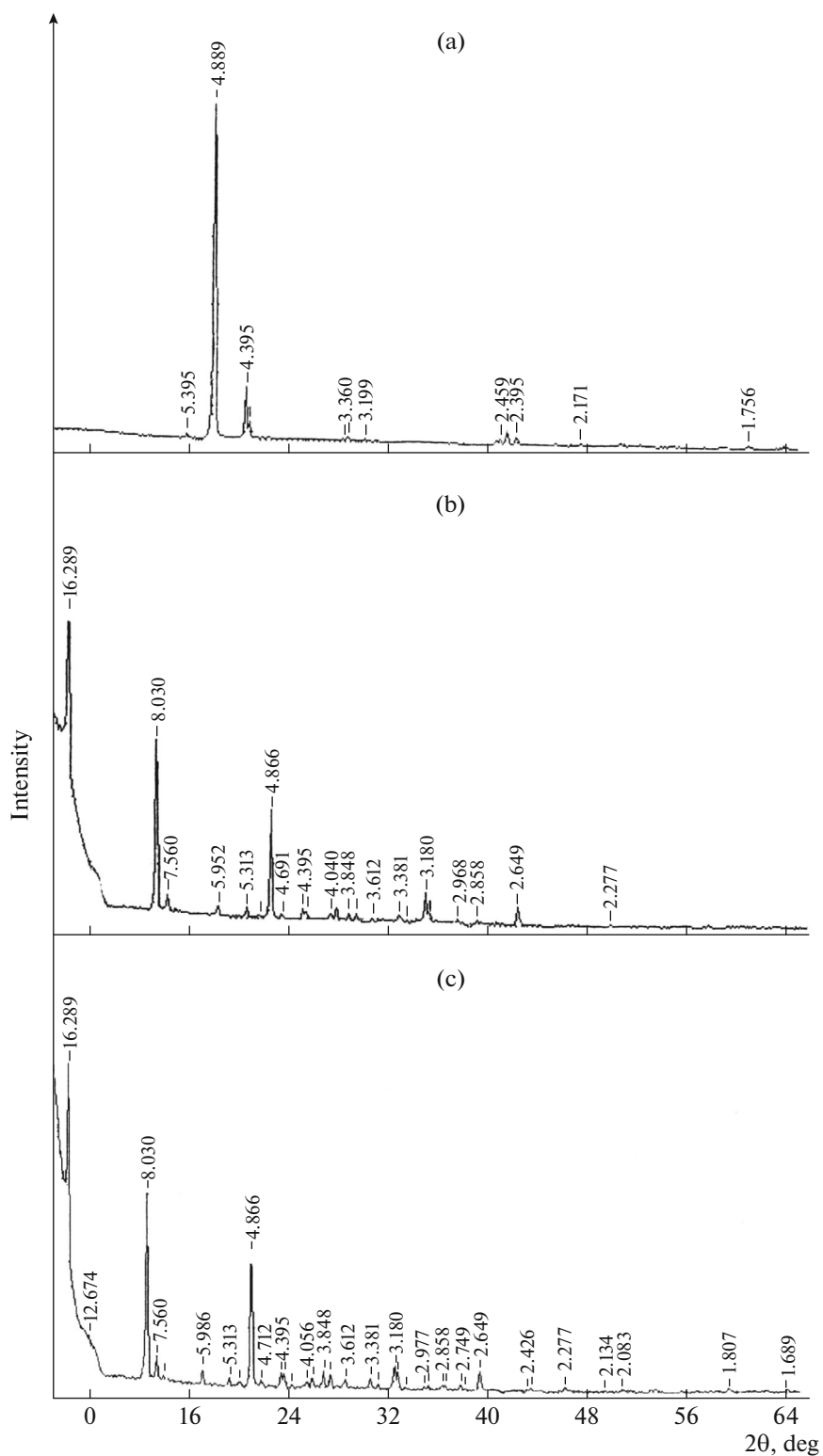
The diffraction pattern of the product of gibbsite treatment with 2 mol P/L solution (Fig. 4c) contains the same peaks as the diffraction pattern of the product of gibbsite treatment with 1 mol P/L solution (Fig. 4b), as well as additional peaks at 5.986, 5.313, 4.712, 4.253, 3.848, 3.779, and 3.381 Å, which are not related to taranakite but are typical for salts of pyro(poly)phosphoric acids (Fig. 4c). The mentioned peaks (some of them are also present in the diffraction pattern of the product formed in the system containing 1 mol P/L) are typical for the pyrophosphate salt  $(\text{NH}_4)_3\text{HP}_2\text{O}_7$  and long-chained polyphosphates with the common formula  $(\text{NH}_4)_{n+2}\text{P}_n\text{O}_{3n+1}$  [27].

The series of changes in gibbsite structure during the treatment with phosphate solutions for two months was studied using a scanning electron microscope (Figs. 5–7). It is shown in Fig. 5a that the gibbsite crystals from the control system (with water but without P) were initially grouped in global conglomerates about 170 μm in size. Separate crystals (Fig. 5b) differed in the degree of peripheral damage (shears, cleavages, and pits in the form of pores or grooves, etc.) and size (from 25 to 15 μm and smaller). Slightly larger pits in gibbsite crystals (at the retention of the conglomerate shape) in the two-month system containing  $10^{-3}$  mol P/L (Figs. 5c, 5d) can be due to some enhancement of dissolution, which was confirmed by the increase in the content of Al in the liquid phase compared to the control (Fig. 2).

The treatment of gibbsite with a 1 mol P/L solution for two months strongly changed the shapes of conglomerates of gibbsite crystals (Figs. 6a, 6b). According to the sizes of conglomerates, they remained intact (no cleavage into component crystals occurred), but their flattened and laminated surface suggests that the phosphatized top layer was subjected to dissolution. The dissolution is clearly visible for a separate conglomerate (Fig. 6c), whose lower part has a clear lamination (Fig. 6d). The dissolution of the phosphatized gibbsite surface is confirmed by the high content of aluminum in the liquid phase of the corresponding system. The dissolution was accompanied by the formation of coatings on conglomerates and their cleavage fragments (Figs. 6a–6d), as well as tridimensional neoformations in the form of rosettes on coating cracks (Figs. 6e, 6f).

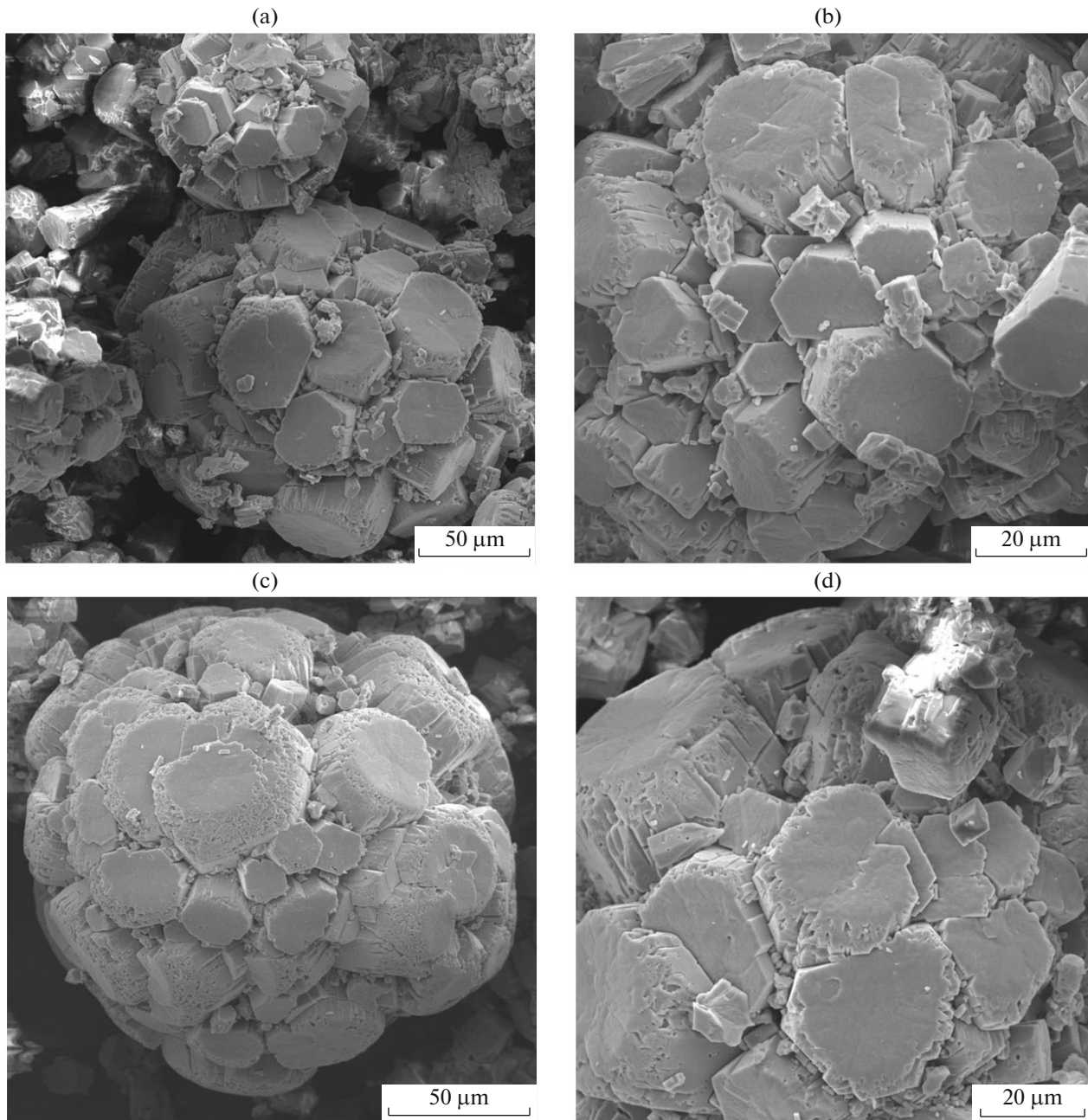
The spectral microanalysis of surface formations (Table 2) showed that their chemical composition was not identical: the highest differences were observed for the content of phosphorus. Along with P and Al, nitrogen was also present which had content directly related to the content of phosphorus.

Similar contents of these chemical elements were noted on the surface of the conglomerate shown in



**Fig. 4.** X-ray diffraction patterns of gibbsite and products of its 2-month-long treatments with (a) water (control) and P solutions: (b) 1 mol/L; (c) 2 mol/L.



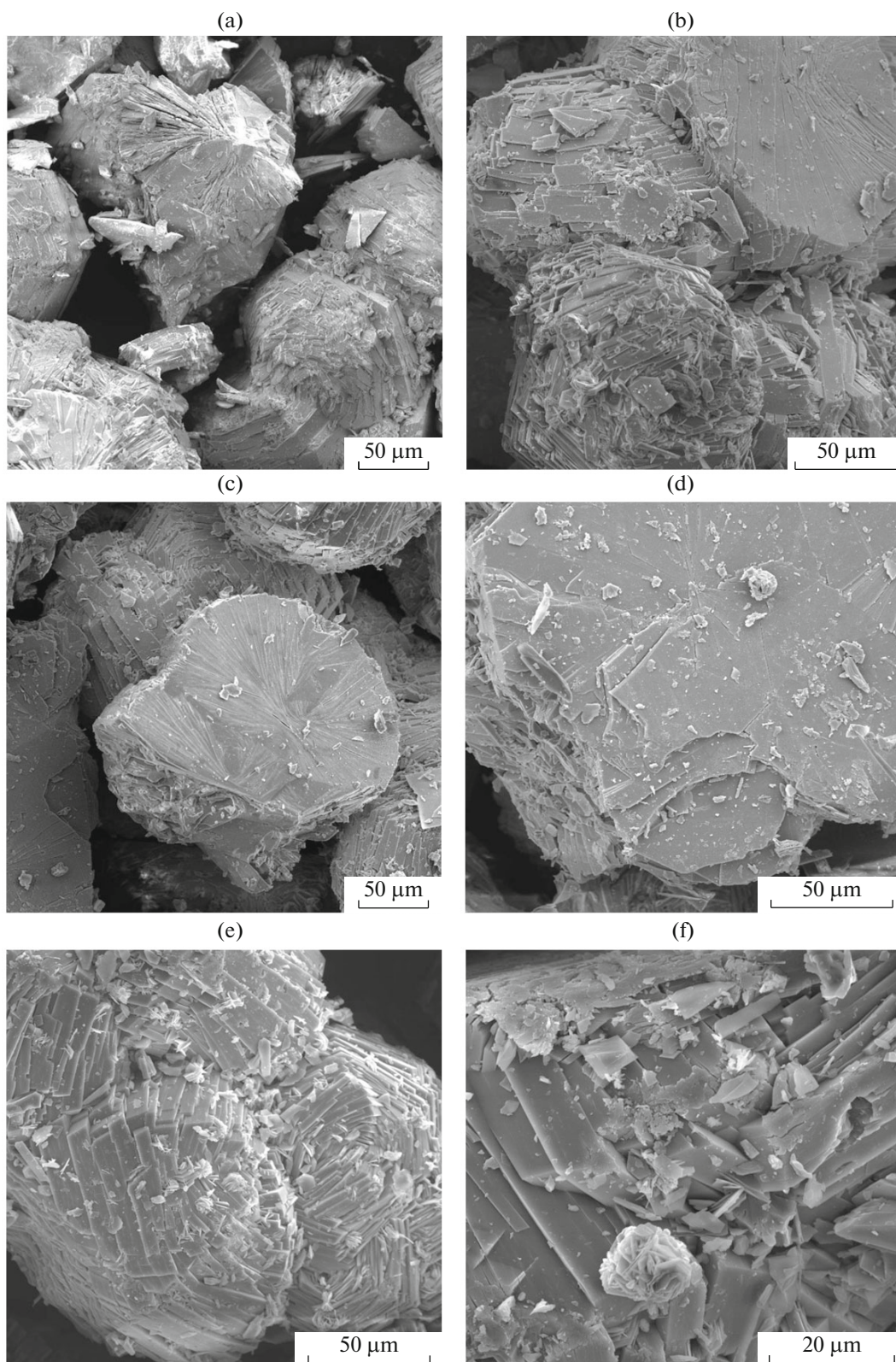


**Fig. 5.** Electron micrographs of gibbsite after 2-month-long treatments with water (a) magnification 874 $\times$ ; (b) magnification 2210 $\times$ ) and a  $10^{-3}$  mol P/L solution (c) magnification 1110 $\times$ ; (d) magnification 2130 $\times$ .

Fig. 6a (top, center), as well as on the surfaces of detached flakes (Fig. 6b, left). According to the P/Al ratio of 1.86 and the content of nitrogen, the composition of these surface coatings was close to that of ammonium taranakite with the formula  $(\text{NH}_4)_3[\text{Al}_5(\text{HPO}_4)_6(\text{PO}_4)_2] \cdot 18\text{H}_2\text{O}$  (Table 3). The P/Al ratios of 1.96 and 2.11 (Table 2), which exceeded the value for taranakite (1.83), corresponded to the surface coatings of the conglomerate shown in Fig. 6c and its dissolving part (Fig. 6d). The highest P/Al ratio (2.23) was noted for the phase of rosettes (Figs. 6e, 6f).

This phase contained more phosphorus (22.72%) and nitrogen (5.30%) than the surface coatings. The higher contents of these elements than the theoretical values for ammonium taranakite with the standardized formula (19.39% P and 3.28% N) indicate a higher negative charge of aluminophosphate anions entering in the composition of the tridimensional phase of rosettes on the cracks of phosphatized surface coatings (Figs. 6e, 6f) and, hence, their capacity to bind  $\text{NH}_4^+$  cations from the solution.





**Fig. 6.** Electron micrographs of the product of gibbsite treatment with a 1 mol P/L solution under magnification,  $\times$ : (a) 609; (b) 959; (c) 705; (d) 1150; (e) 1200; (f) 3010.

**Table 2.** Composition of gibbsite transformation products in 1 M (Fig. 6) and 2 M (Fig. 7) phosphate solutions

Figure	Element	Content, %	Ratios		Figure	Element	Content, %	Ratios	
			P/Al	P/N				P/Al	P/N
6a	P	18.41	1.86	5.51	—	—	—	—	—
	Al	9.91							
	N	3.34							
6b	P	18.30	1.86	4.93	7b	P	19.03	1.83	5.60
	Al	9.84				Al	10.39		
	N	3.71				N	3.40		
6c	P	20.89	1.96	4.88	7c	P	22.02	2.15	4.88
	Al	10.68				Al	10.25		
	N	4.28				N	4.51		
6d	P	22.20	2.11	4.41	7d	P	25.80	2.29	4.27
	Al	10.52				Al	11.26		
	N	5.03				N	6.04		
6e, 6f (rosettes)	P	22.72	2.23	4.29	7e, 7f (rosettes)	P	28.91	2.69	4.18
	Al	10.21				Al	10.75		
	N	5.30				N	6.92		

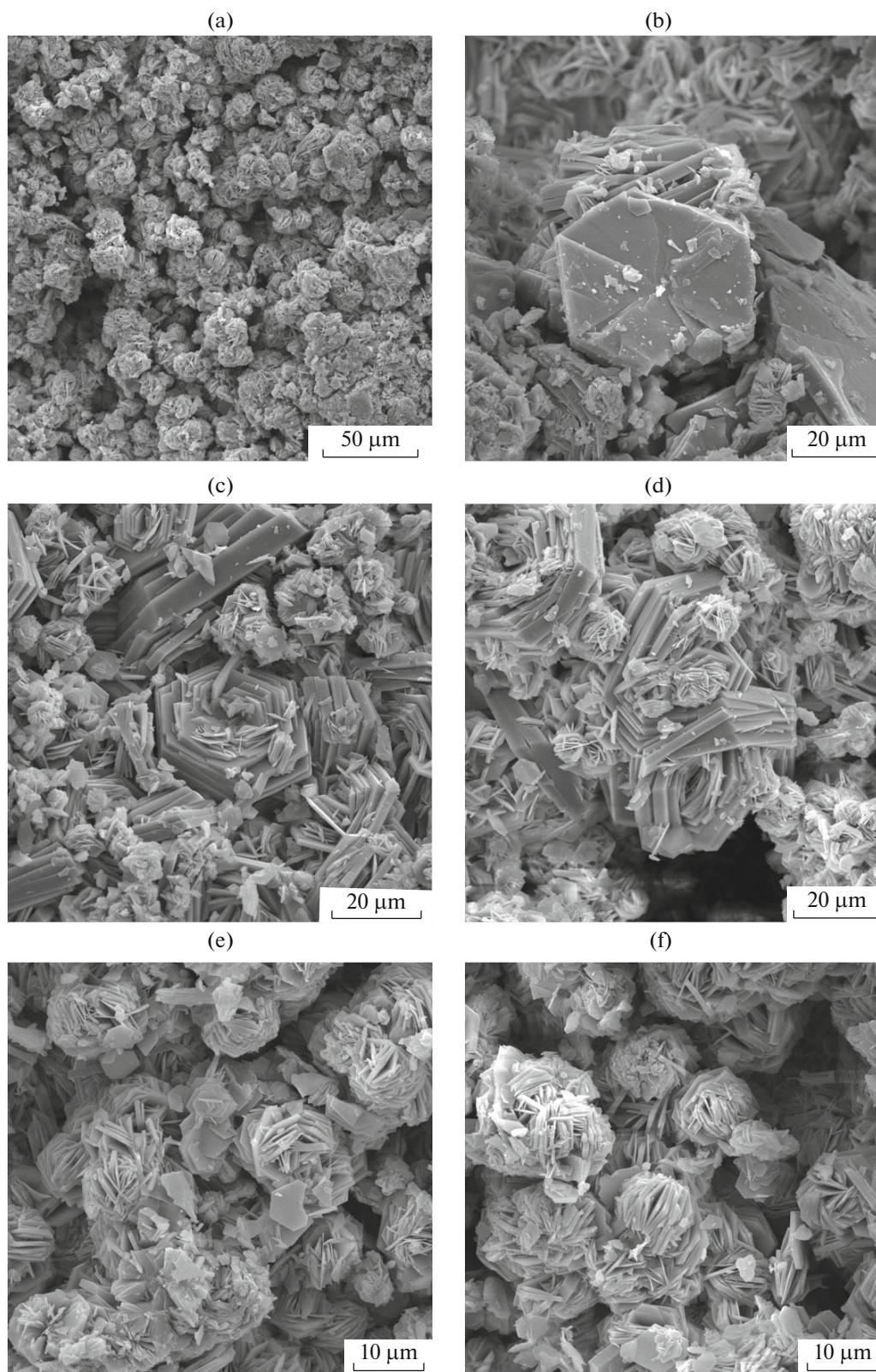
**Table 3.** Composition of some aluminum-ortho(pyro)phosphate anions and ammonium phosphate salts

Anion, salt	Element	Content, %	Ratios	
			P/Al	P/N
[Al(HPO <sub>4</sub> ) <sub>2</sub> ] <sup>-</sup>	P	29.22	2.37	
	Al	12.32		
[Al(HPO <sub>4</sub> )(PO <sub>4</sub> ) <sub>2</sub> ] <sup>2-</sup>	P	28.44	2.30	
	Al	12.38		
[Al(PO <sub>4</sub> ) <sub>2</sub> ] <sup>3-</sup>	P	28.57	2.29	
	Al	12.44		
[Al(HPO <sub>4</sub> )(P <sub>2</sub> O <sub>7</sub> )] <sup>3-</sup>	P	31.31	3.44	
	Al	9.09		
(NH <sub>4</sub> ) <sub>3</sub> [Al <sub>5</sub> (HPO <sub>4</sub> ) <sub>6</sub> (PO <sub>4</sub> ) <sub>2</sub> ] · 18H <sub>2</sub> O (ammonium taranakite)	P	19.39	1.83	5.91
	Al	10.60		
	N	3.28		
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	P	26.96		2.22
	N	12.17		
(NH <sub>4</sub> ) <sub>3</sub> HP <sub>2</sub> O <sub>7</sub>	P	27.07		1.43
	N	18.34		
(NH <sub>4</sub> ) <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	P	25.20		1.11
	N	22.76		

It can be seen (Fig. 7a) that the two-month-long treatment with a 2 mol P/L solution resulted in the decomposition of the conglomerates of gibbsite crystals and the formation of discrete structures of different shape and mainly small size: from 5 μm and smaller to about 15 μm. A hexagonal formation is visible in the partially decomposed fragment of the treat-

ment product (Fig. 7a, bottom, right). In the high power field (Fig. 7b), it can be seen that this is a discrete crystal with cracks in the surface layer and rosettes on the crack edges. The contents of phosphorus, aluminum, and nitrogen, as well as the P/Al ratio in the surface crystal layer (Table 2), correspond to their theoretical values for ammonium taranakite. The





**Fig. 7.** Electron micrographs of the product of gibbsite treatment with a 2 mol P/L solution under magnification,  $\times$ : (a) 945; (b) 2190; (c) 2200; (d) 2170; (e) 3440; (f) 3440.

crystal is about 42  $\mu\text{m}$  in diameter (Fig. 7b); i.e., it is significantly larger than the gibbsite crystals of similar shape (Fig. 5b). The crystal of taranakite (Fig. 7b) is apparently a transformation product of the entire conglomerate of gibbsite crystals (common integrity). Therefore, it may be considered as a primary product formed in the system with a 2 mol P/L solution. It should be noted that an ammonium taranakite crystal of analogous shape and size with tridimensional formations on the surface was obtained from a reaction mixture with an  $\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : \text{NH}_4 : \text{H}_2\text{O}$  molar ratio of 1 : 1.4 : 0.7 : 62 under heating to 70°C [33].

The presence of smaller formations around the large taranakite crystal (Figs. 7a, 7b) indicates its susceptibility to further transformation in a 2 mol P/L solution. The images in Figs. 7b–7d make it possible to trace the series of transformations manifested in the lamination of the crystal and the thinning of its layers because of dissolution. During the dissolution, the contents of phosphorus and nitrogen in the solid products increased, but the content of aluminum remained almost constant, which indicated the bi(poly)denticity of phosphate ligands in aluminum complexes.

The anionic bi(poly)dentate aluminum–phosphate complexes, being strong electron-donating (nucleophilic) agents, are capable of easily cleaving bonds in bi(poly)nuclear hydroxo complexes ( $\text{Me}-\text{OH}-\text{Me}$ ). This property can be a reason for the deep dissolution of gibbsite in a phosphate solution of high concentration resulting in the formation of small structures in the form of coils (Figs. 7c, 7d), which are transformed to rosettes, as is well seen in the high power field (Figs. 7e, 7f).

According to the data in Table 2, the rosette-shaped structures were characterized by especially high contents of phosphorus and nitrogen (28.91 and 6.92%, respectively). The P/Al ratio in the rosettes (2.69) was higher than that in taranakite with the standardized formula (1.83), the anionic component of which represents a polynuclear aluminum–phosphate complex with a charge of 3<sup>-</sup>, which includes two kinds of orthophosphate ligands ( $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$ ), and in mononuclear complexes with the same ligands  $[\text{Al}(\text{HPO}_4)_2]^-$ ,  $[\text{Al}(\text{HPO}_4)(\text{PO}_4)]^{2-}$ , and  $[\text{Al}(\text{PO}_4)_2]^{3-}$  (2.37, 2.30, and 2.30, respectively) (Table 3).

It may be supposed that the transformation of a large taranakite crystal in the system with 2 mol P/L to rosette-shaped structures (Figs. 7e, 7f) is related to the appearance of aluminum–phosphate complexes with pyro(poly)phosphate ligands, as, e.g., in the complex  $[\text{Al}(\text{HPO}_4)(\text{P}_2\text{O}_7)]^{3-}$  (P/Al = 3.44). This is proved by the X-ray diffraction pattern of the product of gibbsite treatment with a 2 mol P/L solution for two months (Fig. 4c), which includes peaks at 5.986, 5.313, 4.712, 4.253, 3.848, 3.779, and 3.381 Å assigned to condensed phosphates [27].

It can be seen in electron micrographs that the rosette-shaped structures were also instable in the phosphate solution. This is confirmed by the release of small (about 8  $\mu\text{m}$  in diameter) hexagonal plates (Fig. 7e) and their accumulation in the system with a 2 mol P/L solution (Fig. 7f, bottom). Crystals of analogous shape and size, considered as ammonium taranakite, were obtained at the heating of a mixture of  $\text{Al}(\text{H}_2\text{PO}_4)_3$  and  $\text{NH}_4\text{OH}$  water solutions to 90°C [38].

The heating of reaction mixtures is widely used in the synthesis of taranakites [27]. The effect of heating can be explained by the dehydration of phosphate tetrahedrons and their condensation with the formation of pyro(poly)phosphates containing P–O–P bonds [8]. Our data indicate that the synthesis of ammonium taranakite can also proceed at room temperature, if the content of phosphorus in the gibbsite system is 1 mol P/L and higher. Under these conditions, the formation of taranakite is favored by the high release rate of aluminum into the liquid phase in the form of complexes with high negative charge.

The appearance of P–O–P group(s) can be explained by the addition of phosphate anions from the solution to the P atoms with effective positive charges in the groups coordinated by Al atoms. The shift of electron density in these groups from the O atoms to the Al atoms increased the deficit of electrons (positive charge) on the P atoms. Possibility of reactions at the positively polarized P atoms in the ligands of aluminum–phosphate complexes is a mechanism of key importance (not considered in the special literature) for binding phosphate anions on the phosphatized surfaces of gibbsite crystals.

The groups with the P–O–P bonds typical for pyro(poly)phosphates are detected in the structure of natural phosphate minerals (of lithogenic and biogenic origin) [5–7, 19, 26], which indicates their specific role in the formation of minerals. It may be supposed that this role implies the ability of the corresponding ligands to acquire a configuration suitable for cyclization, which is important for the formation of crystalline structures [17].

## CONCLUSIONS

The obtained data significantly expand the concepts of the nature of processes occurring on the surface of the mineral gibbsite with the participation of phosphate anions from  $\text{NH}_4\text{H}_2\text{PO}_4$  solutions. The study showed that the complete binding of phosphate anions in the aluminum–phosphate complexes retained by the sorbent surface occurred only from the solutions with concentrations similar to those in the natural soils ( $10^{-6}$ – $10^{-5}$  mol P/L). At the higher concentrations typical for technogenically phosphatized soils ( $10^{-3}$ –1 mol P/L), the binding of phosphate anions occurred in the form of anionic aluminum–phosphate complexes capable of passing into the liq-

uid phase. The negative charge of the complex anions increased with increasing phosphate load on the sorbent, as was indicated by the data on the content of  $\text{NH}_4^+$  ions bound to the phosphatized surface. The dissolution of gibbsite significantly increased with the increase in the denticity of ligands in the aluminum–phosphate complexes, which ensured the conditions for the formation of ammonium taranakite.

In the system with a 1 M phosphate solution, ammonium taranakite with the corresponding contents of phosphorus, aluminum, and nitrogen was formed on the surfaces of conglomerates of gibbsite crystals subjected to destruction. In the system with a 2 M phosphate solution, successive transformations of taranakite crystals to secondary crystalline structures of different shapes and sizes were observed. The increased contents of phosphorus and nitrogen suggest that the formation of secondary phases was due to the transformation of bidentate orthophosphate ligands to polyphosphate (polydentate) ligands.

Thus, ammonium taranakite is not a stable phase in the presence of free phosphate anions (potential ligands) in the system. It is transformed to small crystals more enriched with phosphorus and nitrogen.

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