

## SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

# Silicate-Substituted Carbonated Hydroxyapatite Powders Prepared by Precipitation from Aqueous Solutions

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**Abstract**—The powders of silicate-substituted carbonated hydroxyapatites were prepared by a precipitation method from aqueous alkaline solutions with a varied sodium silicate content. With the use of physicochemical techniques, it was established that the solid phase included to 7.36 wt % silicate ions and to 7.34 wt % carbonate ions under the test conditions. The nature of processes occurring on the thermal treatment of the samples depends on the Ca/P and Ca/(P + Si) molar ratios and the concentration of SiO<sub>4</sub> groups. A study of the behavior of solid phases on contact with a solution of NaCl (0.9 mol %) showed that the rates of dissolution of all of the silicon-containing samples were higher than that of unsubstituted hydroxyapatite species by a factor of 2–4 because of the active participation of silicates in the resorption of the materials.

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Hydroxyapatite (HA, Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) is a compound with labile crystal structure. Isovalent and heterovalent substitutions in both cation (CaI and CaII) and anion (PO<sub>4</sub><sup>3-</sup> and OH<sup>-</sup>) sublattices are plausible for this compound. Because of this, about a half of all of the elements of the periodic system can enter into the composition of the compound. Moreover, the introduction of even an insignificant amount of admixtures often leads to substantial changes in the physicochemical properties of the substance with the retention of its structure. This is especially important from a biochemical point of view. The doping of HA with essential substances by changing the composition stoichiometry, crystallinity, surface charge, dispersity, and particle morphology makes it possible to vary its physicochemical characteristics, in particular, solubility in biological fluids and their prototypes.

Currently, the compounds Ca<sub>10-x</sub>(Mg, Na, K)<sub>x</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> [1–6], Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH, F, Cl)<sub>2</sub> [4, 7–10], and Ca<sub>10</sub>(PO<sub>4</sub>, CO<sub>3</sub>)<sub>6</sub>(OH, CO<sub>3</sub>)<sub>2</sub> [4, 11–13] have received the most study because Mg, Na, K, F, Cl, and CO<sub>3</sub> are of interest as the natural components of bone tissue, dentine, and tooth enamel [4, 14]. The attention of researchers focuses on the silicate-substituted forms of HA due to the active role of silicon in regenerative processes in vivo [15]. The effectiveness of the use of materials containing SiO<sub>4</sub><sup>4-</sup> in bone tissue engineering was demonstrated based on an example of bioactive glasses and glass ceramics [16, 17]; however, they are essentially different from the mineral component of bone tissue in structure and composition. For this reason, new biomaterials should be developed based on

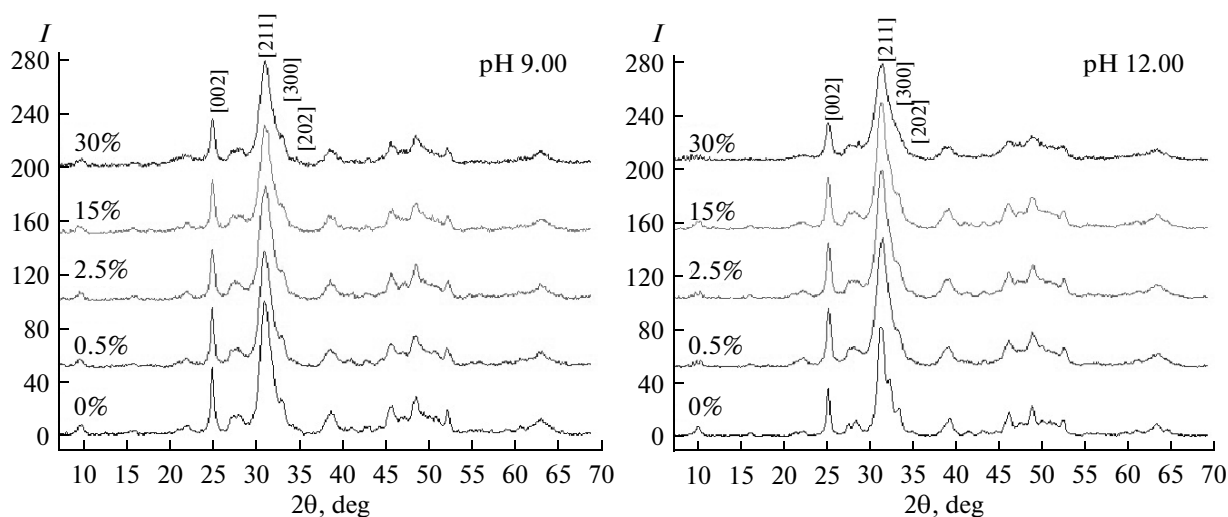
crystalline silicon-containing calcium phosphate compounds. In this context, approaches to the synthesis of silicate-substituted basic calcium phosphate have been developed.

Solid-phase [18–20], hydrothermal [21, 22] and wet methods [20, 23–25] were proposed for the preparation of HA containing silicon. Technically, the simplest methods are based on the precipitation of an insoluble compound from an aqueous solution. They make it possible to produce various substituted forms of basic calcium phosphate in a nanocrystalline state by choosing a medium and synthesis conditions. Thus, the use of Na<sub>2</sub>SiO<sub>3</sub>, Ca<sub>2</sub>SiO<sub>4</sub>, Mg<sub>2</sub>SiO<sub>4</sub>, Si(C<sub>2</sub>H<sub>5</sub>O)<sub>4</sub>, Si(C<sub>3</sub>H<sub>7</sub>O)<sub>4</sub>, Si(CH<sub>3</sub>COO)<sub>4</sub>, and colloidal or amorphous SiO<sub>2</sub> as silicon-containing reagents [18–26] makes it possible to obtain HA doped with silicate ions to different degrees. The admixture of carbonates can also be included into the composition of the phase as a result of the transfer of atmospheric CO<sub>2</sub> into an aqueous solution [4, 27]. For the suppression of this process, in a number of cases [4, 24], the reaction medium is blown with an inert gas (argon).

Here, we report the results of a study of silicate-substituted carbonated hydroxyapatites obtained by precipitation in aqueous alkaline solutions. Sodium silicate, which is readily soluble in water unlike Si(C<sub>3</sub>H<sub>7</sub>O)<sub>4</sub> and Si(CH<sub>3</sub>COO)<sub>4</sub>, was chosen as a silicon agent.

## EXPERIMENTAL

The solid phases were obtained by a precipitation method in the Ca(NO<sub>3</sub>)<sub>2</sub>–(NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>–Na<sub>2</sub>SiO<sub>3</sub>–H<sub>2</sub>O systems. In this case, the concentration ratio



**Fig. 1.** Diffraction patterns of powders prepared from solutions with different concentrations of silicate ions (mol %) and with pH 9.00 and 12.00.

$C_{\text{Ca}^{2+}} / (C_{\text{PO}_4^{3-}} + C_{\text{SiO}_4^{4-}}) = 1.70$  ( $C_{\text{Ca}^{2+}} = 0.034$  mol/L) was specified, and the fraction of silicate ions in the total amount of precipitate-forming anions in the medium ( $X_{\text{SiO}_4^{4-}} = C_{\text{SiO}_4^{4-}} / (C_{\text{PO}_4^{3-}} + C_{\text{SiO}_4^{4-}})$ ) was varied in a range of 0.5–30 mol %. The synthesis was carried out at room temperature ( $T = 22\text{--}25^\circ\text{C}$ ). A silicate–phosphate solution was added to a solution of calcium nitrate at a rate of 4.5–5.0 mL/min with continuous stirring. The acidity of the medium was corrected to the values of pH 9.00 or 12.00 ( $\pm 0.05$ ) after the complete addition of the system components using HCl (1 : 1) or NaOH (20%). After 48 h, the precipitates were filtered off in a vacuum, dried at  $80^\circ\text{C}$ , ground into a powder, weighed, and studied by physicochemical techniques. For comparison, the synthesis of HA was carried out under analogous conditions but without the addition of a reagent containing silicon.

The X-ray diffraction (XRD) analysis of the samples was performed on a D8 Advance diffractometer (Bruker) with the interpretation of diffraction patterns using the EVA software (Bruker). The sizes of crystallites (coherent scattering regions, CSRs) were calculated using the TOPAS 3.0 software (Bruker). The IR absorption spectra of the precipitates were measured on an FT-801 Fourier transform IR spectrometer (SIMEKS); the test samples were prepared by pelletization with KBr. The concentrations of Ca, P, and Si in the solid phases were quantitatively determined by inductively coupled plasma atomic emission spectrometry (ICP AES) on a 710-ES spectrometer (Varian). The specific surface areas of powders were measured according to the BET method on a Sorbometr instrument. The thermal transformations of sample components were studied by thermogravimetry (STA-449C Jupiter, Netzsch). The process of sample dissolution in a 0.9% solution of NaCl was investi-

gated. The measurements were carried out in a thermostatically controlled cell at  $37.0 \pm 0.2^\circ\text{C}$  for 2 h at a constant liquid-phase volume with stirring. In the course of an experiment, the concentrations of  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{3-}$ , and  $\text{SiO}_4^{4-}$  were monitored. The morphological and functional-group compositions of a precipitate after dissolution were determined by optical microscopy and Fourier transform IR spectroscopy.

## RESULTS AND DISCUSSION

**Composition, dispersity, and morphology of powders.** According to the results of XRD analysis, all of the solid phases obtained upon varying the concentration of silicate ions and the pH of the reaction medium were single-phase HA. The weak resolution of the reflections of basic calcium phosphate in diffraction patterns indicates the weak degree of crystallization of HA and/or its highly dispersed state [22, 24, 25] (Fig. 1). The calculation of crystallite sizes in the directions of the crystallographic axes  $a$  and  $c$  ( $L_a$  and  $L_c$ , Table 1) based on the reflections [002] and [300] in the diffraction patterns of precipitates made it possible to determine that the particles were elongated along the axis  $c$ . The form factor  $F$  (the ratio  $L_c/L_a$ ) smoothly increased with the amount of  $\text{Na}_2\text{SiO}_3$  in solutions with pH 9.00 and 12.00; that is, the shape of particles gradually approaches a needlelike shape.

The Fourier transform IR-spectroscopic data indicate the dependence of the morphology and unit cell parameters of the samples on isomorphous admixtures in the structure of HA. The IR spectra of powders (Fig. 2) exhibit absorption bands due to  $\text{HPO}_4^{2-}$  ( $525$  and  $\sim 1225$   $\text{cm}^{-1}$ ) and  $\text{CO}_3^{2-}$  groups (pH 9.00: 877, 1420, 1460, and  $1550$   $\text{cm}^{-1}$ ; pH 12.00: 872, 1430, and  $1460$   $\text{cm}^{-1}$ ).

**Table 1.** Characteristics of the samples according to XRD analysis data

pH	$X_{\text{SiO}_4^{4-}}$ , mol %	Phase	$L_a$ , Å	$L_c$ , Å	$F$	$a$ , Å	$c$ , Å	$V$ , Å <sup>3</sup>
9.00	0	HA 100%	64	200	3.1	$9.442 \pm 0.003$	$6.868 \pm 0.003$	530.3
	0.5		61	238	3.9	$9.437 \pm 0.003$	$6.870 \pm 0.003$	529.9
	2.5		59	216	3.7	$9.428 \pm 0.003$	$6.874 \pm 0.003$	528.9
	15		51	209	4.1	$9.422 \pm 0.004$	$6.877 \pm 0.004$	528.7
	30		45	202	4.5	$9.415 \pm 0.004$	$6.883 \pm 0.004$	528.4
				$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (PDF 9-432)			9.418	6.884
12.00	0	HA 100%	112	230	2.1	$9.406 \pm 0.003$	$6.884 \pm 0.002$	527.5
	0.5		83	219	2.6	$9.402 \pm 0.004$	$6.877 \pm 0.004$	526.2
	2.5		72	193	2.7	$9.397 \pm 0.004$	$6.882 \pm 0.003$	526.3
	15		57	180	3.2	$9.411 \pm 0.003$	$6.890 \pm 0.003$	528.5
	30		51	167	3.3	$9.419 \pm 0.006$	$6.894 \pm 0.005$	529.7

This fact suggests the formation of a nonstoichiometric carbonate-containing form of HA.

According to Marchat et al. [24], the inclusion of impurity  $\text{SiO}_4^{4-}$  anions into the composition of a solid phase results in the appearance of a set of absorption bands due to the vibrations of Si–OH, Si–O–Si, and Si–O bonds in the IR spectra of the samples. However, because of the structural similarity of the tetrahedral anions  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$ , a number of absorption maximums manifested themselves at close frequencies.

The spectra of nonstoichiometric carbonated hydroxyapatites (nCHAs) obtained in the presence of silicates contain overlapped characteristic bands:

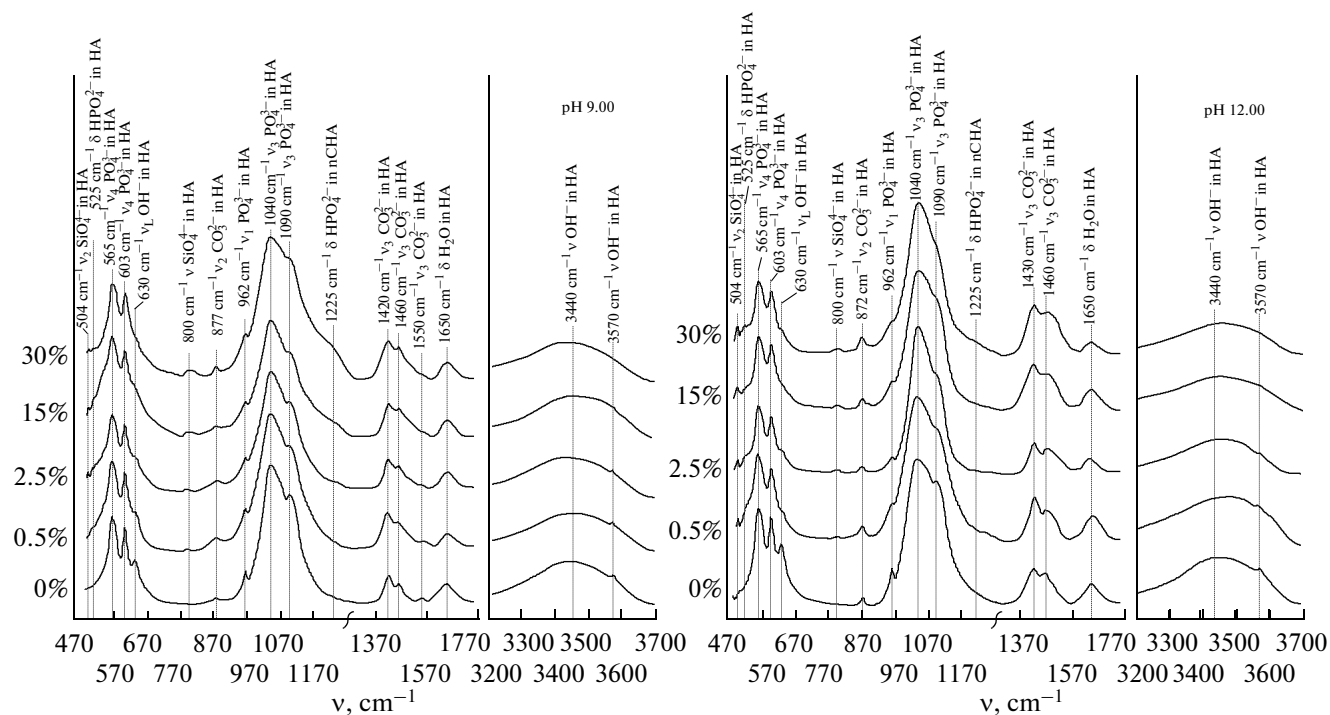
$$477\text{--}483\text{ cm}^{-1} \Rightarrow \nu_2(\text{P}\text{--}\text{O}) + \nu(\text{Si}\text{--}\text{O}\text{--}\text{Si}),$$

$$958\text{--}962\text{ cm}^{-1} \Rightarrow \nu_1(\text{P}\text{--}\text{O}) + \nu(\text{Si}\text{--}\text{O}),$$

$$1020\text{ cm}^{-1} \Rightarrow \nu_3(\text{P}\text{--}\text{O}) + \nu(\text{Si}\text{--}\text{OH}),$$

$$1089\text{--}1095\text{ cm}^{-1} \Rightarrow \nu_3(\text{P}\text{--}\text{O}) + \nu(\text{Si}\text{--}\text{O}),$$

$$2500\text{--}3700\text{ cm}^{-1} \Rightarrow \delta(\text{H}\text{--}\text{O}\text{--}\text{H}) + \nu(\text{Si}\text{--}\text{OH}).$$



**Fig. 2.** IR spectra of powders prepared from solutions with different concentrations of silicate ions at different pH values.

\*Numbers at the curves specify the fraction of silicate ions in the total amount of silicates and phosphates in the initial reaction medium (mol %).

**Table 2.** Mechanisms of substitution reactions occurring under synthesis conditions

Substitution reaction	Changes in unit cell parameters*	Reaction conditions
$\frac{1}{2}\text{Ca}^{2+} + \text{PO}_4^{3-} \leftarrow \frac{1}{2}\square_{\text{Ca}} + \text{HPO}_4^{2-}$	$\uparrow a, \downarrow c$	9.00, 12.00 ( $X_{\text{SiO}_4^{4-}} > 2.5\%$ )
$\frac{1}{2}\text{Ca}^{2+} + \text{OH}^- \leftarrow \frac{1}{2}\square_{\text{Ca}} + (\square_{\text{OH}}, \text{H}_2\text{O})$		9.00, 12.00 ( $X_{\text{SiO}_4^{4-}} > 2.5\%$ )
$2\text{OH}^- \leftarrow \square_{\text{OH}} + \text{CO}_3^{2-}$		9.00
$\frac{1}{2}\text{Ca}^{2+} + \text{PO}_4^{3-} \leftarrow \frac{1}{2}\square_{\text{Ca}} + \text{CO}_3^{2-}$	$\downarrow a, \uparrow c$	12.00
$\text{PO}_4^{3-} + \text{OH}^- \leftarrow \text{SiO}_4^{4-} + \square_{\text{OH}}$		9.00, 12.00

( $\square_{\text{OH}}, \text{H}_2\text{O}$ ) refers to vacancies in the positions of  $\text{OH}^-$  ions occupied by water molecules.

\* As compared with the unit cell parameters of stoichiometric HA (PDF 9-432).

The superposition of the above strong bands does not make it possible to estimate the presence of silicates in the samples based on these absorption bands.

A conclusion on the incorporation of  $\text{SiO}_4^{4-}$  into the composition of the solid phases can be made based on weak peaks at 504 and 800  $\text{cm}^{-1}$ . A small increase in their intensity was observed with increasing silicon content of the initial reaction media. The simultaneous extinction of the vibration modes of  $\text{OH}^-$  ions (630 and 3570  $\text{cm}^{-1}$ ) is indicative of the replacement of phosphates by silicates with the participation of hydroxyl groups. Table 2 summarizes the reaction schemes of the above substitution types and the reaction conditions. A change in the unit cell parameters of HA correlates with variation in the parameters  $a$  and  $c$  (Table 1).

The inclusion of isomorphous admixtures into the composition of the samples led to a decrease in the weight fractions of calcium and phosphorus in the solid phases as the initial concentration of  $\text{Na}_2\text{SiO}_3$  in the reaction medium was increased. In this case, the amount of Si ( $\text{SiO}_4^{4-}$ ) in the precipitates of each series increased (Table 3). Greater weight fractions of silicon (silicates) were obtained in a highly alkaline medium (pH 12.00). A decrease in the fraction of calcium in the samples upon phosphate–silicate replacement suggests an indirect relationship between the amounts of  $\text{Ca}^{2+}$  and  $\text{Si}/\text{SiO}_4^{4-}$  in the composition of precipitates. According to the commonly accepted ideas (Table 2), the Ca cations do not participate in ionic substitutions. However, based on the experimental results, we can hypothesize that the introduction of  $\text{SiO}_4^{4-}$  groups with a greater charge and more bulky than the  $\text{PO}_4^{3-}$  tetrahedrons due to an increase in the structure imperfection of HA facilitates the inclusion of other impurity species into the positions of phos-

phate and hydroxyl ions, which leads to the appearance/strengthening of calcium deficiency. This dependence occurs in a wide range of acidity (in the stability region of basic calcium phosphate); in this case, the value of pH determines the intensity rather than the possibility of coupled reactions.

Differences in the values of Ca/P for silicon-containing nCHA obtained at pH 9.00 were not reliably established. The average value (1.50) indicates that all of the samples consisted of apatite with a deficiency in calcium. The Ca/(P + Si) ratio in them decreased from 1.51 to 1.35 (Table 3). Other tendencies toward changes in molar coefficients were observed in solid phases from solutions with pH 12.00: the Ca/P ratio increased grows from 1.67 to 1.95 (excessive calcium HA), and the Ca/(P + Si) ratios remained close to 1.67. At  $X_{\text{SiO}_4^{4-}} \geq 10\%$ , a small decrease in Ca/(P + Si) (to  $1.62 \pm 0.04$  and  $1.64 \pm 0.04$ ) was observed; this was likely due to the fact that an (excess) amount of  $\text{SiO}_4^{4-}$  was polymerized on the surface of particles rather than incorporated into the positions of  $\text{PO}_4$  tetrahedrons [22, 25]. Experimental data suggest that the formation of  $-\text{[Si-O-Si]}_n$  groups comes into play under the conditions when the fraction of silicon in the precipitate reaches  $\sim 1.6$  wt %.

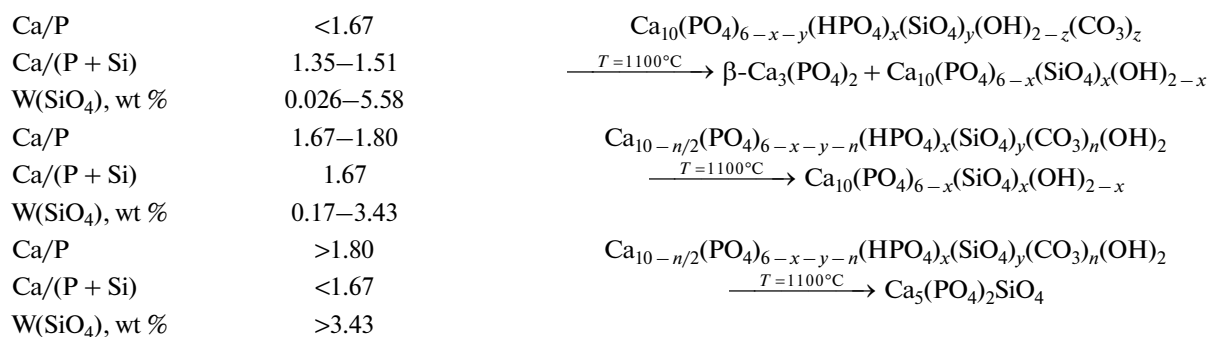
**A study of the thermal behavior of powders** by thermogravimetry and Fourier transform IR spectroscopy showed that the chemical transformations of silicon-containing nCHAs crystallized at pH 9.00 and 12.00 include the removal of adsorbed water ( $T_1 = 25\text{--}200^\circ\text{C}$ ) and carbonates ( $T_2 > 500^\circ\text{C}$ ). In this case, losses in a range of 3.67–7.34 wt % occurred at the stage of the release of  $\text{CO}_3$  groups from the composition of samples (Table 3). The results of the Fourier transform IR-spectroscopic and XRD analysis of the calcined powders allowed us to establish that the reac-

**Table 3.** Chemical compositions of the powders

pH	$X_{\text{SiO}_4^{4-}}$ , mol %	$W$ , wt %			Ca/P	Ca/(P+Si)
		Si	SiO <sub>4</sub>	CO <sub>3</sub>		
9.00	0	—	—	3.67	1.51 ± 0.02	1.51 ± 0.02
	0.5	0.0079	0.026	3.79	1.49 ± 0.05	1.49 ± 0.05
	1.0	0.012	0.039	—	1.50 ± 0.06	1.50 ± 0.02
	1.5	0.015	0.049	—	1.51 ± 0.05	1.51 ± 0.05
	2.5	0.043	0.14	4.31	1.48 ± 0.04	1.47 ± 0.05
	5.0	0.088	0.29	—	1.50 ± 0.02	1.49 ± 0.04
	10	0.43	1.41	—	1.48 ± 0.02	1.44 ± 0.02
	15	1.03	3.38	5.17	1.50 ± 0.05	1.40 ± 0.02
12.00	30	1.70	5.58	5.19	1.51 ± 0.03	1.35 ± 0.04
	0	—	—	3.83	1.67 ± 0.01	1.67 ± 0.01
	0.5	0.052	0.17	4.61	1.67 ± 0.02	1.67 ± 0.02
	1.0	0.11	0.37	—	1.66 ± 0.02	1.65 ± 0.03
	1.5	0.16	0.52	—	1.72 ± 0.02	1.70 ± 0.02
	2.5	0.27	0.88	5.16	1.69 ± 0.02	1.66 ± 0.04
	5.0	0.49	1.62	—	1.75 ± 0.03	1.69 ± 0.02
	10	1.04	3.43	—	1.80 ± 0.04	1.69 ± 0.05
	15	1.45	4.75	5.96	1.83 ± 0.03	1.62 ± 0.04
	30	2.24	7.36	7.34	1.95 ± 0.06	1.64 ± 0.04

tion path of the thermal conversion of a calcium phosphate component of the samples depends on the Ca/P

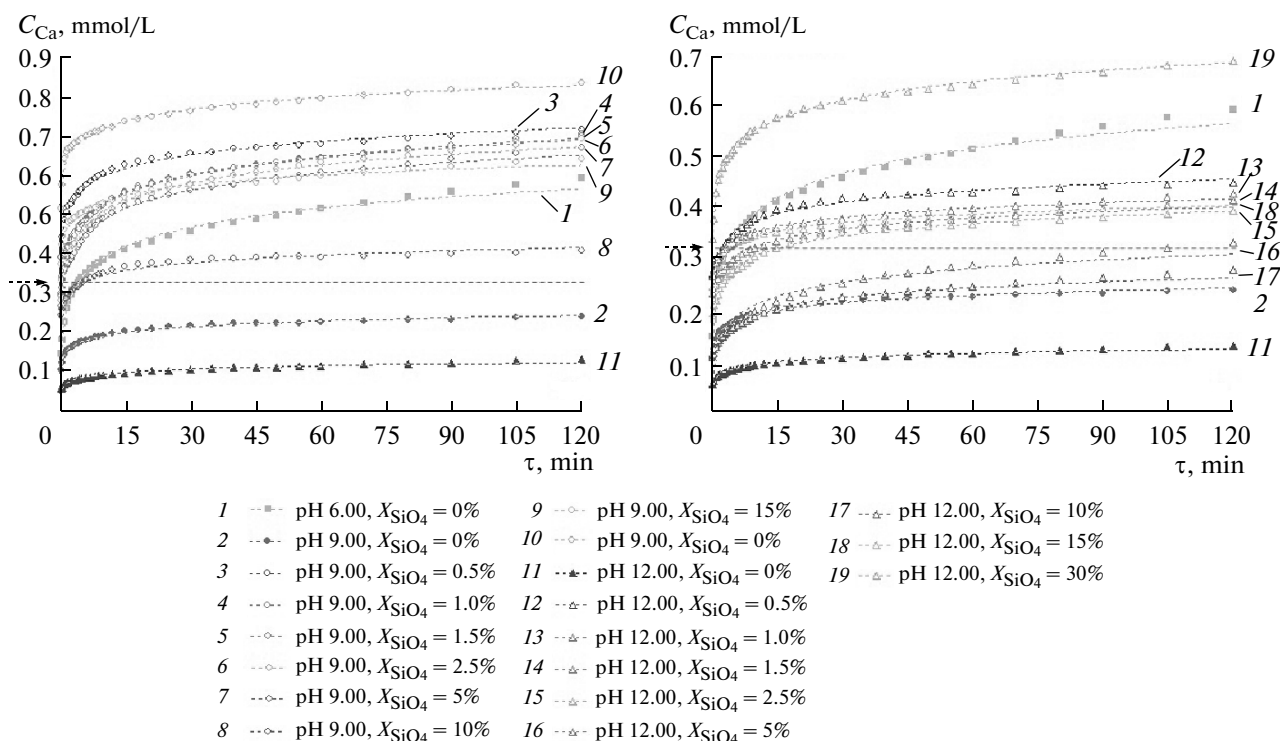
and Ca/(P + Si) molar ratios and the concentration of silicate ions in the samples:



The mixtures of  $\beta\text{-Ca}_3(\text{PO}_4)_2$  and silicate-substituted HA are formed as a result of the calcination of samples based on apatite with calcium deficiency (Ca/P < 1.67). The calcium silicate phosphate phase ( $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ ) is the decomposition product of basic calcium phosphate with excess calcium (Ca/P > 1.80) and a high silicon content. The samples of silicate-substituted nCHA in which the concentration of  $\text{SiO}_4^{4-}$  anions was no higher than 3.5 wt % and the Ca/P ratio varied in a range of 1.67–1.80 were characterized by the greatest thermal stability. As a result of the release of carbonates from their structure upon

thermal treatment, a basic salt containing only silicate admixtures was formed.

**The dissolution of silicate-substituted nCHA in a 0.9% solution of NaCl** was studied with the monitoring of the concentrations of  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{3-}$ , and  $\text{SiO}_4^{4-}$  in time. According to the results of the experiments, it was established that interactions with ions in solution caused the degradation of samples and the gradual transfer of ions from their structure into the solution. The measured kinetic curves of  $C_{\text{Ca}} = f(\tau)$  (Fig. 3) showed that the concentration of cations in the solution increased in the course of the entire experiment. The functions were adequately approximated by a log-



**Fig. 3.** Dependence of the concentration of  $\text{Ca}^{2+}$  ions in solution on the time of dissolution of the powders prepared at pH 9.00 and 12.00.

arithmic trend ( $r^2 = 0.98\text{--}0.99$ ). The rate of accumulation of  $\text{Ca}^{2+}$  reached a maximum at the initial stage of the experiment ( $\tau < 20$  min). Then, the intensity of the release of metal ions into a liquid phase gradually decreased for all of the samples as the  $\text{Ca}^{2+}$  concentration gradient decreased. In this case, during the entire period of measurements, the concentration of calcium ions in the solution and the specific rates of sample dissolution for powders containing silicon were higher

by a factor of 2–4 than those for reference samples (Table 4).

Along with calcium, the  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$  anions passed into the liquid phase in the course of dissolution. Table 4 indicates that their amounts in the solution at the end of experiment monotonically increased and the concentration of phosphates considerably decreased as the  $\text{SiO}_4^{4-}$  content of the powder was increased.

**Table 4.** Characteristics of the dissolution of silicate-substituted nCHA

$W(\text{SiO}_4)$ , wt %	Ca/P in the sample	Concentration in solution after completion of measurements, mmol/L				$\text{Ca}^{2+} : \text{PO}_4^{3-} : \text{SiO}_4^{4-}$	$v_{\text{sp}}$ , $\mu\text{mol g}/(\text{L min m}^2)$	$\Delta m$ , %
		$\text{Ca}^{2+}$	$\text{PO}_4^{3-}$	$\text{SiO}_4^{4-}$	Ca/P			
0	1.51	0.24	0.34	0	0.71	5 : 7	2.3	29.1
0.026	1.49	0.72	0.67	0.064	1.07	11 : 11 : 1	8.3	24.6
0.14	1.48	0.69	0.57	0.069	1.21	10 : 8 : 1	6.1	28.2
3.38	1.50	0.64	0.41	0.31	1.56	2 : 1 : 1	8.2	34.9
5.58	1.51	0.84	0.38	0.42	2.21	2 : 1 : 1	10.5	29.6
0	1.67	0.13	0.090	0	1.44	7 : 5	0.91	26.9
0.17	1.67	0.45	0.47	0.075	0.96	6 : 6 : 1	3.6	24.5
0.88	1.69	0.39	0.076	0.11	7.50	5 : 1 : 2	2.2	19.4
4.75	1.83	0.41	0.030	0.35	13.7	14 : 1 : 12	3.2	23.1
7.36	1.95	0.69	0.027	0.48	25.6	26 : 1 : 18	5.4	26.5

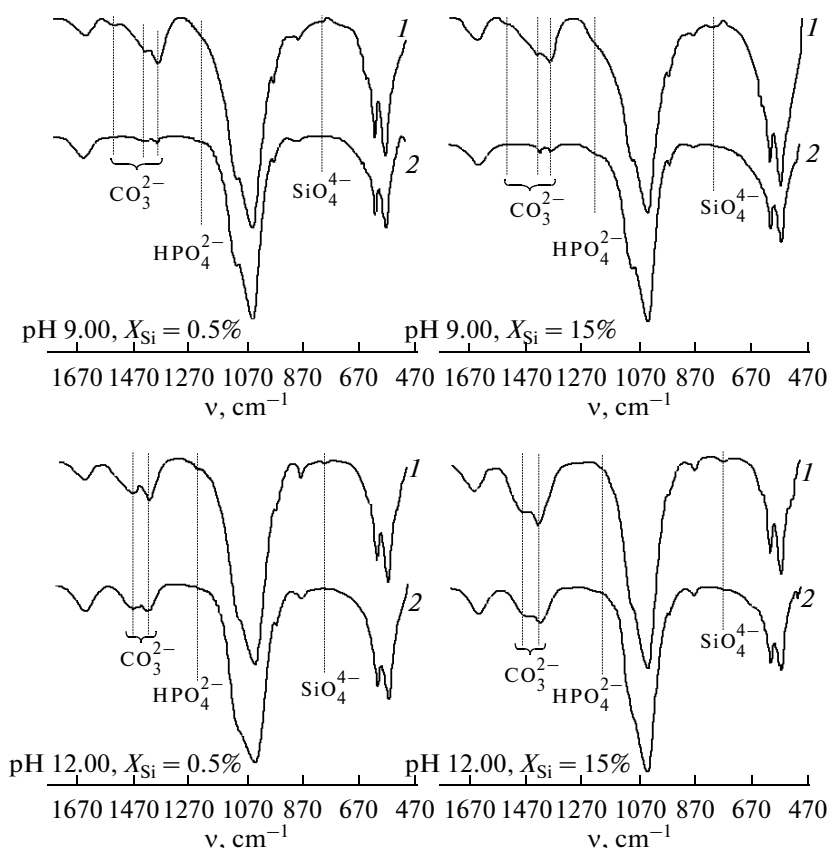


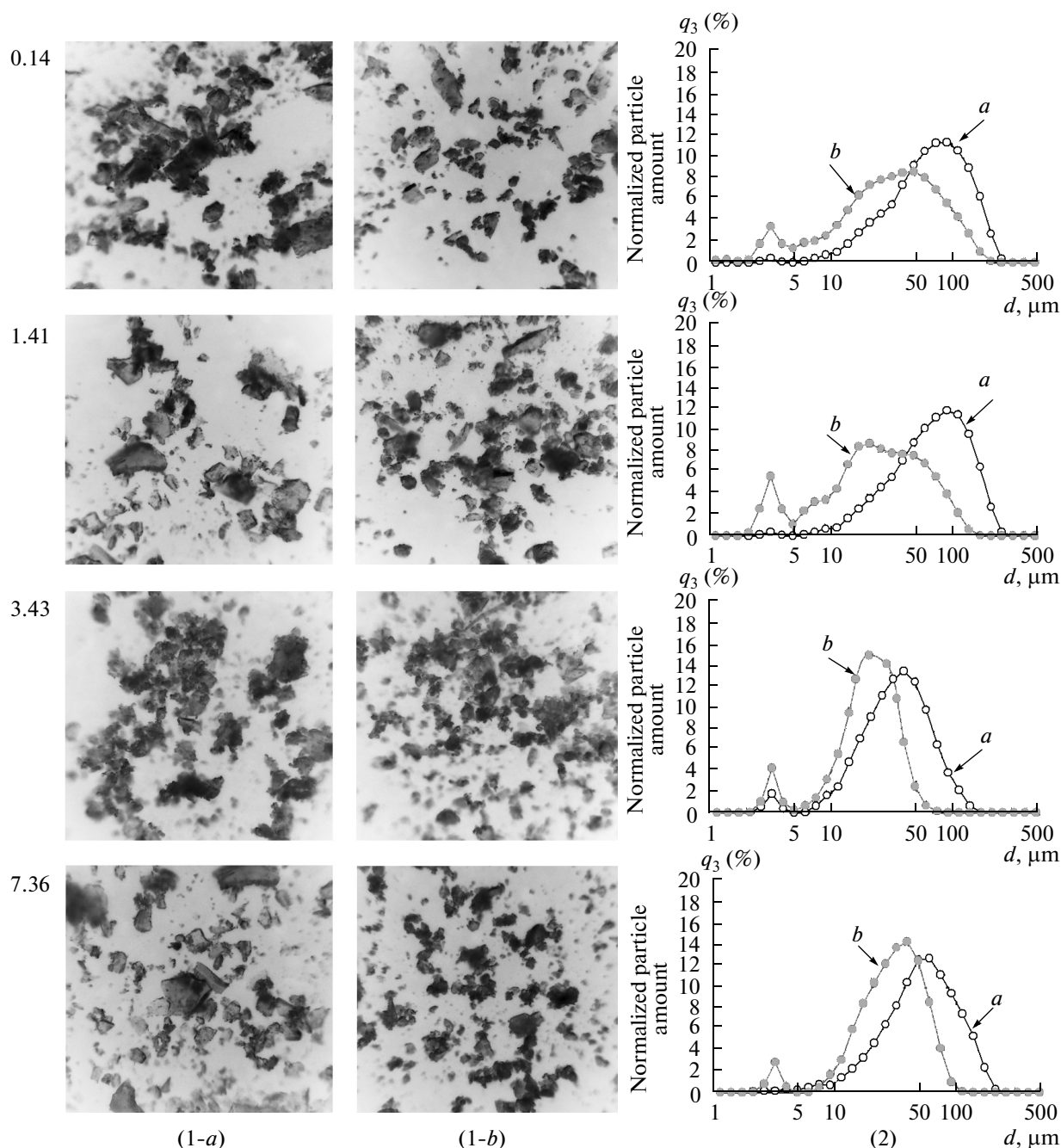
Fig. 4. IR spectra of the samples (1) before and (2) after dissolution in a 0.9% solution of NaCl.

The Ca/P molar ratios were calculated based on data on the concentrations of ions in the final solutions (Table 4). The resulting values indicate that the dissolution of all of the samples occurred incongruently. In this case, the concentration of  $\text{SiO}_4^{4-}$  in the solution increased relatively to the concentrations of calcium ions and phosphates as the silicon content of the precipitates obtained at pH 9.00 and 12.00 was increased.

According to Dorozhkin [28], on the dissolution of stoichiometric HA in acidic and weakly acidic media, the  $\text{OH}^-$  ions are removed from its surface (as the constituents of water molecules) at the initial stage. The resulting local positive charge is compensated due to the replacement of the nearest  $\text{Ca}^{2+}$  ion by the  $\text{H}^+$  ion from the solution. The addition of hydrogen ions to phosphate groups leads to the formation of a thin surface layer of acid calcium phosphate ( $\text{CaHPO}_4$ ). In the case of the dissolution of silicon-containing nCHA; the formation of silanol groups ( $\text{Si-OH}$ ) because of the strong basic properties of silicate ions is more probable at this stage.<sup>1</sup> The protonation of these

<sup>1</sup>  $\text{H}_4\text{SiO}_4$ :  $\text{pK}_1 = 9.9$ ,  $\text{pK}_2 = 11.8$ , and  $\text{pK}_3 = 13.7$ ;  $\text{H}_3\text{PO}_4$ :  $\text{pK}_1 = 2.15$ ,  $\text{pK}_2 = 7.21$ , and  $\text{pK}_3 = 12.3$ ;  $\text{H}_2\text{CO}_3$ :  $\text{pK}_1 = 6.35$  and  $\text{pK}_2 = 10.32$  [29].

groups under the conditions of an unsaturated solution in terms of  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{3-}$ , and  $\text{SiO}_4^{4-}$  will occur up to the formation of  $\text{H}_4\text{SiO}_4$  with the subsequent diffusion of the product into the bulk of solution. Following the removal of silicates, the interaction of crystal structure elements with less basic properties, namely  $\text{PO}_4^{3-}/\text{HPO}_4^{2-}$  and  $\text{CO}_3^{2-}$ , with protons becomes possible. Thus, based on the Fourier transform IR-spectroscopic data, the almost complete disappearance of a shoulder at  $1225\text{ cm}^{-1}$ , which characterizes the presence of  $\text{HPO}_4^{2-}$  groups in the HA structure, from the spectra of the undissolved part of the powders was observed (Fig. 4); that is, the hydrogen phosphate ions left the composition of the solid phases upon the treatment of the powder in a 0.9% solution of the NaCl. The intensity of absorption bands due to carbonates in the spectra of the samples prepared at pH 9.00 also considerably decreased. The degradation of the solid phases crystallized at pH 12.00 occurred with smaller losses of the anions of this type. This gives grounds to assume that the intensity of the release of carbonates is determined by their position in the structure of basic calcium phosphate: the  $\text{CO}_3^{2-}$  groups more easily leave the positions of OH ions than those of  $\text{PO}_4$  tetrahedrons. Thus, it is believed that the passage of ions from



**Fig. 5.** (1) Micrographs ( $\times 120$ ) and (2) differential particle-size distribution curves of the powders containing 0.14, 1.41, 3.43, and 7.36 wt % silicate ions (a) before and (b) after dissolution.

the composition of silicon-containing nCHA into a liquid phase occurs in the following sequence: (1)  $\text{OH}^-$ , (2)  $\text{Ca}^{2+}$ , (3)  $\text{SiO}_4^{4-}$ , (4)  $\text{PO}_4^{3-}/\text{HPO}_4^{2-}$ , and (5)  $\text{CO}_3^{2-}$ .

Further, as the values of  $C_{\text{Ca}} > 0.32$  mmol/L (Fig. 3), which correspond to a solution saturated with  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , were reached, the polycondensation of Si–OH groups became probable in the individual sections of the solid phase surface with the formation of a thin layer of hydrated silica gel. By analogy with

glass ceramics [16, 30], the formation of crystallization nuclei can occur due to the adsorption of  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  ions from the solution on it to afford the bioactivity of the material.

Data on changes in the weights of powders and the results of their characterization by optical microscopy and Fourier transform IR spectroscopy suggest the occurrence of secondary precipitation reactions on the dissolution of synthetic silicon-containing pow-



ders. It is likely that similar weight losses for all of the test samples (Table 4) can be explained by the fact that  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  began to crystallize at a certain point in time along with the dissolution of a solid phase in the systems with silicate-substituted nCHA, whereas the formation of a solid phase was not observed in reference samples, which were characterized by smaller specific rates of dissolution. In this case, the particle size of the silicon-containing powders decreased in the course of dissolution (Fig. 5), and a fraction with sizes of  $\sim 3 \mu\text{m}$  appeared; it is likely that this fraction consisted of newly crystallized aggregates.

Thus, we found that nCHA, in which the  $\text{PO}_4$  tetrahedrons were partially replaced by silicate ions, precipitated in the alkaline calcium phosphate systems on varying the fraction of a silicon agent from 0.5 to 30 mol %. The admixture anion content of the precipitates varied from 0.026 to 7.36 wt % (in a range of 0.008–2.24 wt % in terms of silicon). Against the background of an increase in the relative amount of  $\text{SiO}_4^{4-}$  in the solid phase, the crystallinity decreased, and the dispersity of the basic salt and a deficiency in calcium and phosphates increased. Because metal cations do not participate in a phosphate–silicate substitution process (according to currently accepted concepts), it is believed that there is an indirect relationship between the concentrations of  $\text{Ca}^{2+}$  and  $\text{SiO}_4^{4-}$  in a wide range of acidity in the stability region of HA; in this case, the value of pH determines the intensity rather than the possibility of coupled reactions. The processes occurring on the thermal treatment of the powders depend on the Ca/P and Ca/(P + Si) molar ratios and the concentration of silicate ions in the solid phase. As a result of thermal destruction,  $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x(\text{OH})_{2-x}$ , its mixture with  $\beta\text{-Ca}_3(\text{PO}_4)_2$ , or pure  $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$  can be obtained. The rates of dissolution of all of the silicon-containing phases were higher by a factor of 2–4 than the rate of dissolution of reference samples as a result of the active participation of silicate ions in the sample dissolution processes.

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