

## Regularities in Low-Temperature Phosphatization of Silicates

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**Abstract**—The regularities in low-temperature phosphatization of silicates are defined from long-term experiments on the interaction between different silicate minerals and phosphate-bearing solutions in a wide range of medium acidity. It is shown that the parameters of the reaction of phosphatization of hornblende, orthoclase, and labradorite have the same values as for clayey minerals (kaolinite and montmorillonite). This effect may appear, if phosphatization proceeds, not after silicate minerals with a different structure and composition, but after a secondary silicate phase formed upon interaction between silicates and water and stable in a certain pH range. Variation in the parameters of the reaction of phosphatization at  $\text{pH} \approx 1.8$  is due to the stability of the silicate phase different from that at higher pH values.

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As is known, the process of carbonation of silicates (replacement of salts of silicic acid with salts of stronger carbonic acid) is widely abundant in the zone of hypergenesis. An analogous process of phosphatization of silicates accompanied by replacement of free silica from them and by the formation of poorly soluble Ca, Al, and Fe phosphates may occur in the same area. Thermodynamic calculations [1–3] supporting the probability of phosphatization of silicates under the conditions of the hypergenesis zone are not sufficiently reliable, because they used the values of free energy determined with a low accuracy. The results of experimental modeling of the interaction between dissolved phosphates and silicates ([4–8] and others) do not provide unambiguous conclusions as well, since the experiments were short, which limited the participation of the bulk mineral phase in the reaction. In this study, based on the results of long experiments, we established regularities in low-temperature phosphatization of silicates of different structural types upon their interaction with phosphate-bearing solutions in a wide pH range.

Phosphatization of silicates was studied using the example of rock-forming minerals of different structural types: hornblende, orthoclase, labradorite, kaolinite, and montmorillonite with the chemical composition reported in Table 1. To the weights of minerals ground to a powdered state (400 mg), 160 ml of one of six background solutions with a variable concentration of orthophosphates (0.25–6.0 mM) were added. The acidity of these solutions was supported by the different buffer systems (Table 2) in the range of  $\text{pH} = 1.8$ –8.8. The samples were mixed on a shaker daily for 6–8 h for 6 months; after that, they were kept for several months with periodic single stirrings. Then, the solutions were filtered through a 0.22- $\mu\text{m}$  membrane filter with measurement of the pH, as well as of the concentration of silicon and phosphates by the standard colorimetric methods [9].

The results of experiments allowed us to register the following regularities. First, all samples are characterized by almost equivalent variation in the concentrations of phosphorus and silicon in the solution in the pH range of 3.7–8.8:

$$\Delta[\text{Si}] \approx -\Delta[\text{P}], \quad (1)$$

where as at  $\text{pH} \approx 1.8$  the introduction of dissolved silicon exceeds the removal of phosphates by a factor of 1.3–2 (Fig. 1). This is likely explained by the change in the stoichiometry of the phosphatization reaction.

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**Table 1.** Chemical composition of the minerals used in the experiments, wt %

Component	Hornblende	Orthoclase	Labradorite	Kaolinite		Montmorillonite, Askania	
				Glukhovetsk	Podol'sk	Sample 1	Sample 2
SiO <sub>2</sub>	37.63	59.48	51.61	50.16	45.42	57.54	56.78
TiO <sub>2</sub>	1.87	0.04	1.23	1.22	0.95	0.33	0.30
Al <sub>2</sub> O <sub>3</sub>	13.86	20.23	23.32	34.29	36.35	14.39	16.73
Fe <sub>2</sub> O <sub>3</sub>	19.57	0.59	5.85	0.35	0.97	2.53	3.19
MnO	0.16	0.03	0.06	0.01	0.01	0.04	0.20
MgO	11.93	0.02	1.36	0.04	0.13	2.89	3.46
CaO	10.68	0.19	9.59	0.07	0.13	0.37	0.91
Na <sub>2</sub> O	2.12	4.34	4.26	0.02	0.14	2.35	2.68
K <sub>2</sub> O	0.36	12.09	0.84	0.35	0.39	0.86	4.30
P <sub>2</sub> O <sub>5</sub>	0.02	0.17	0.29	0.09	0.06	0.02	0.12
L.O.I.	1.34	3.00	0.96	13.02	14.71	18.02	11.07
Total	99.54	100.18	99.37	99.61	99.25	99.34	99.74

Second, the content of phosphorus absorbed by silicates has a linear dependence on its equilibrium concentration in the solution

$$-\Delta[\text{P}] = k[\text{P}]_{\text{eq}}$$

with almost the same values of the coefficient of proportionality  $k$  for different minerals decreasing slightly with decreasing pH of the medium:

**Table 2.** Composition of background solutions

pH in experiments	Concentrations, mM			
	HCl	CH <sub>3</sub> COOH	NaCH <sub>3</sub> COO	Borax
1.76 ± 0.13	25.0	—	—	—
3.73 ± 0.02	—	175	25.0	—
4.89 ± 0.02	—	11.0	25.0	—
6.75 ± 0.08	—	0.6	25.0	—
7.84 ± 0.09	5.8	—	—	3.3
8.79 ± 0.06	1.8	—	—	5.4

pH	1.8	3.7	4.9	6.8	7.8	8.8
$k$	0.57	0.57	0.54	0.51	0.46	0.46

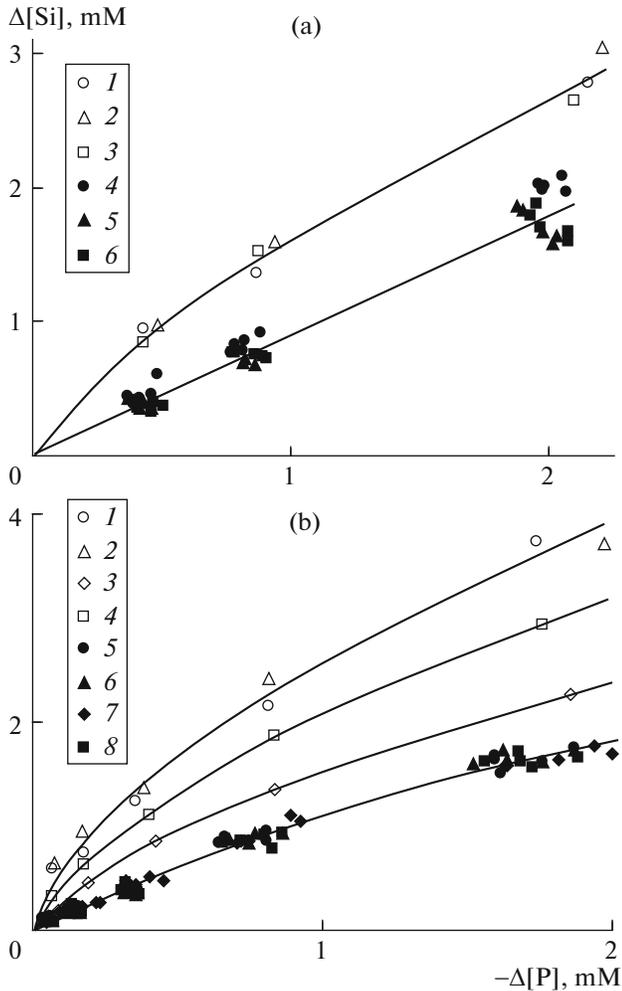
**Table 3.** Content of Si transformed into solution in the runs on phosphatization of silicates at the maximal initial concentration of phosphates \*, % of the initial concentration in the mineral

Mineral	pH	
	1.8	3.7–8.8
Hornblende	19.4	11.0
Orthoclase	11.2	8.1
Labradorite	12.3	8.0
Kaolinite, Glukhovetsk	18.0	7.8
The same, Podol'sk	19.9	8.6
Montmorillonite, Askania, Sample 1	9.4	6.5
The same, Sample 2	12.4	6.9

\* 5 mM for hornblende, orthoclase, and labradorite; 6 mM for kaolinite and montmorillonite.

The content of silicon removed from the silicates studied and replaced with phosphates at pH = 3.7–8.8 reaches 6.5–11.0% of the initial silicon concentration in the minerals (Table 3). A higher content of silicon (up to 9.4–19.9%) is introduced in the solution at pH ≈ 1.8, when the process of phosphatization is accompanied by acid leaching of silicates, which results in extra release of silicon and violation of equivalence (1). Such high concentrations of removed silicon and absorbed phosphorus, which are much higher than the limiting values of sorption removal of phosphates, definitely indicate the chemical reaction of the replacement of silicate with a phosphate mineral.

A likely reason for the differences between the results obtained and the data of the papers [4–8], in which the negative correlation between variation in the concentrations of phosphates and silicon has been interpreted as the result of adsorption exchange of phosphate ions and silica on the surface of silicates, is that the run durations in these studies did not exceed several days. This time was sufficient to establish the adsorption equilibrium, but was not enough for noticeable progress in the reaction of phosphatization of the bulk silicate phase. Our runs proceeded for more than one year; after that, the chemical reaction of phosphatization resulted in a change in the composition of solutions interacting with the solid phase.



**Fig. 1.** Correlation between variations in the concentrations of phosphorus and silicon in the solution upon phosphatization of phosphates. (a) pH = 1.8: (1) hornblende, (2) orthoclase, (3) labradorite; pH = 3.7-8.8: (4) hornblende, (5) orthoclase, (6) labradorite; (b) pH = 1.8: (1) kaolinite, Glukhovetsk, (2) the same, Podol'sk, (3) montmorillonite, Askania, Sample 1, (4) the same, Sample 2; pH = 3.7-8.8: (5) kaolinite, Glukhovetsk, (6) the same, Podol'sk; (7) montmorillonite, Askania, Sample 1, (8) the same, Sample 2.

The same quantitative characteristics of the process of phosphatization for all silicates studied corresponding to different structural types and with different chemical compositions were an unusual result. This regularity may occur if not the silicate minerals, but rather the secondary silicate phase formed upon the interaction of silicates with water and stable under a certain pH range is subjected to phosphatization. The parameters of the reaction of phosphatization at pH  $\approx$  1.8 vary due to the stability of the surface silicate phase, which is different from that in the area of higher pH values.

Thus, the data obtained allow us to substantiate the probability of the reaction of phosphatization of silicates in the zone of hypergenesis. This reaction should play an important role in regulation of the phosphate potential of soils and, therefore, influence the biological productivity of land cover.

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