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SHORT COMMUNICATIONS

Experimental Study of Silicate Phosphatization under Supergene Zone Conditions: Hornblende, Orthoclase, and Labradorite

A. V. Savenko*

Faculty of Geology, Moscow State University, Moscow, 119991 Russia

**e-mail: Alla_Savenko@rambler.ru*

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Abstract—The hypothesis of silicate phosphatization under supergene zone conditions was experimentally tested. To extend our previous experimental work on clay minerals (kaolinite and montmorillonite), we studied the phosphatization of aluminosilicates of other structural types (hornblende, orthoclase, and labradorite) interacting for nine months with 1.2–6.0 mM orthophosphate solutions over a wide range of solution acidity. Nearly linear dependence common for all minerals was found between variations in phosphorus and silicon concentrations in the solution: $\Delta[\mathrm{Si}] \approx -\Delta[\mathrm{P}]$. It was demonstrated that aluminosilicates can be replaced by phosphate minerals at relatively minor concentrations of dissolved phosphorus corresponding to phosphate abundances in soil solutions.

Keywords: silicates, phosphatization, supergene zone, experimental modeling

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INTRODUCTION

Savenko (2015) presented the results of long-term experiments on interaction between phosphate-bearing solutions and kaolinite or montmorillonite in a wide range of acidity (pH 1.8–8.8). It was shown that the amount of phosphates absorbed by clay minerals is significantly higher than their adsorption capacity, and a decrease in phosphate concentration is accompanied by the extraction of an equivalent amount of silicon into the solution. This allowed us to suggest that a major portion of phosphates was immobilized owing to a silicate phosphatization reaction localized in a thin surface layer of clay mineral particles. One intriguing result was that, despite the difference in the chemical composition of the samples, the parameters of the dependence between changes in the concentrations of dissolved phosphate and silica and between the amount of phosphates absorbed by clay minerals and equilibrium (final and time-independent) phosphate concentration were almost identical. The question addressed in this study is whether the established relations are valid for other major silicates or they are characteristic of clay minerals only.

EXPERIMENTAL METHODS

Monomineralic fractions of hornblende, orthoclase, and labradorite with a grain-size of less than 50 μm were used in experiments. The compositions of the samples are given in Table 1. The experimental procedure was the same as that described by Savenko (2015). Mineral aliquots (400 mg) were mixed with 160 mL of one of six background solutions with variable orthophosphate concentrations (1.2–6.0 mM) and acidity buffered by various systems at pH values from 1.6 to 8.8 (Table 2). The samples were mixed in a shaker for 6–8 h every day within the first six months and kept, then, with occasional stirring for three months. Then, the solutions were filtered through a 0.22 μm membrane filter, their pH values were determined, and silica and phosphate concentrations were

Table 1. Chemical compositions of minerals used in experiments, wt %

Component	Hornblende	Orthoclase	Labradorite
SiO_2	37.63	59.48	51.61
TiO_2	1.87	0.04	1.23
Al_2O_3	13.86	20.23	23.32
Fe_2O_3	19.57	0.59	5.85
MnO	0.16	0.03	0.06
MgO	11.93	0.02	1.36
CaO	10.68	0.19	9.59
Na_2O	2.12	4.34	4.26
K_2O	0.36	12.09	0.84
P_2O_5	0.02	0.17	0.29
LOI	1.34	3.00	0.96
Total	99.54	100.18	99.37

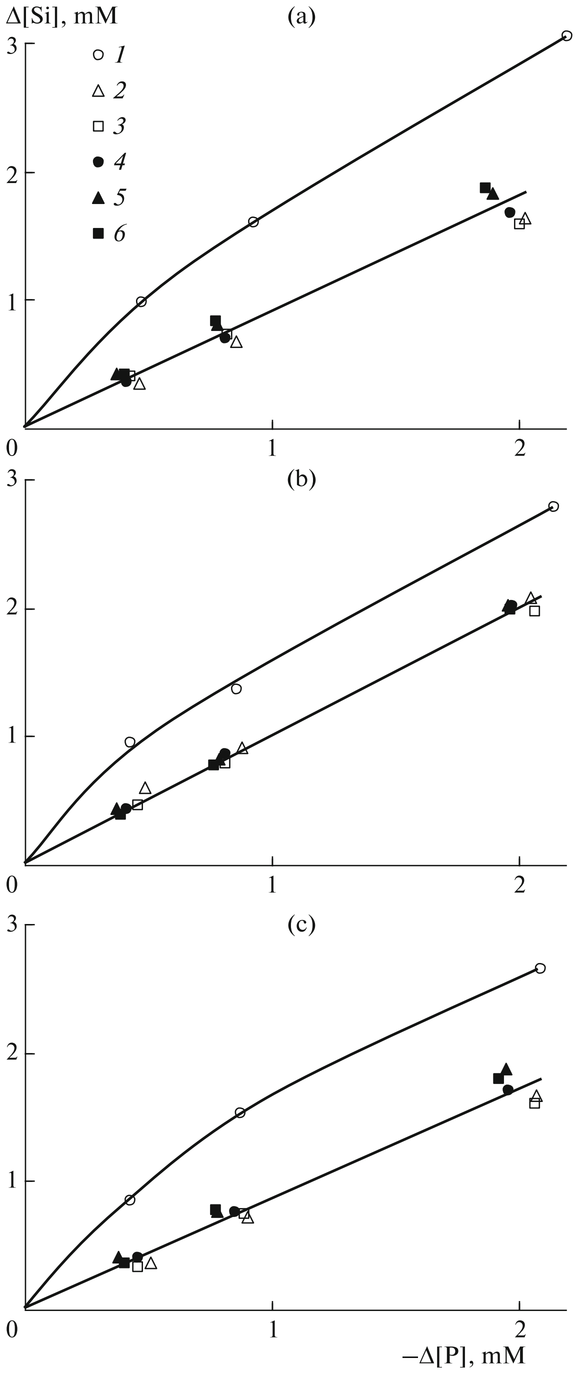

Fig. 1. Covariation of the concentrations of phosphorus and silicon in solution during the phosphatization of rock-forming aluminosilicates: (a) hornblende, (b) orthoclase, and (c) labradorite. Solution pH: (*1*) 1.6, (*2*) 3.7, (*3*) 4.9, (*4*) 6.7, (*5*) 7.9, and (*6*) 8.8.

Table 2. Compositions of background solutions used in experiments

pH in experiment	Concentration, mM			
	HCl	CH_3COOH	$NaCH_3COO$	Borax
1.61 ± 0.10	25.0	–	–	–
3.72 ± 0.04	–	175	25.0	–
4.89 ± 0.04	–	11.0	25.0	–
6.69 ± 0.06	–	0.6	25.0	–
7.92 ± 0.04	5.8	–	–	3.3
8.82 ± 0.06	1.8	–	–	5.4

measured by standard colorimetric methods (Lur'e, 1971). The uncertainty of measurements was no higher than ±0.005 for pH and ±3% for silica and phosphate.

RESULTS AND DISCUSSION

The experimental results are summarized in Table 3. All the relations established previously for kaolinite and montmorillonite were reproduced in the experiments with hornblende, orthoclase, and labradorite. Similar to the experiments with clay minerals, approximately equivalent changes in the concentrations of phosphorus and silicon were observed in all the samples at pH 3.7–8.8:

$$\Delta[\mathrm{Si}] \approx -\Delta[\mathrm{P}], \tag{1}$$

whereas at pH 1.6 ± 0.1 the extraction of silicon into the solution was 1.3–2.0 times higher than the removal of phosphorus (Fig. 1). The amount of absorbed phosphorus depends linearly on its final time-invariant concentration in the solution:

$$-\Delta[\mathrm{P}] = k[\mathrm{P}]_{\mathrm{final}} \tag{2}$$

and the proportionality factor k is almost identical for clay minerals, on the one hand, and hornblende, orthoclase, and labradorite, on the other hand (Fig. 2); the latter minerals show a weak tendency of k decrease at increasing pH (Table 4).

According to calculations (Table 5), at pH 3.7–8.8, the amount of silica extracted from the silicates and replaced by phosphate is 1.7–11.0% of the initial silica content in the minerals. A higher silica fraction (3.8–19.4%) is released into the solution at pH 1.6 ± 0.1, when phosphatization is probably accompanied by the acid leaching of silicates, which results in additional silica extraction and disturbance of Eq. (1). The considerable amounts of released silicon and absorbed phosphorus are much greater than the maximum magnitude of the sorption uptake of phosphates and provide compelling evidence for the occurrence of a chemical reaction resulting in silicate replacement by a phosphate mineral, which supports our previous conclusions on the phosphatization of kaolinite and montmorillonite.

Many minerals, including silicates precipitated from aqueous solutions at low temperatures, are dominated by X-ray amorphous material, which strongly limits the use of traditional physical methods of solid phase identification. To overcome this difficulty, Savenko and Savenko (2009) proposed the method of variable mineral : solution mass ratios, which provides insight into the stoichiometry of the replacement reac-

Table 3. Variations in the concentrations of phosphorus and silicon in solution during the phosphatization of rock-forming aluminosilicates

Final pH	[P], mM			[Si], mM		
	initial	final	$-\Delta$[P]	initial	final	Δ[Si]
Hornblende						
1.51 ± 0.08	1.20	0.72	0.48	1.30	2.27	0.97
	2.40	1.46	0.94	1.30	2.89	1.59
	6.00	3.80	2.20	1.30	4.34	3.04
3.69 ± 0.01	1.20	0.74	0.46	0.23	0.58	0.35
	2.40	1.54	0.86	0.23	0.91	0.68
	6.00	3.98	2.02	0.23	1.87	1.64
4.86 ± 0.01	1.20	0.77	0.43	0.10	0.50	0.40
	2.40	1.57	0.83	0.10	0.83	0.73
	6.00	3.99	2.01	0.10	1.68	1.58
6.70 ± 0.04	1.20	0.79	0.41	0.08	0.43	0.35
	2.40	1.59	0.81	0.08	0.77	0.69
	6.00	4.03	1.97	0.08	1.74	1.66
7.88 ± 0.01	1.20	0.83	0.37	0.07	0.51	0.44
	2.40	1.62	0.78	0.07	0.89	0.82
	6.00	4.10	1.90	0.07	1.91	1.84
8.78 ± 0.06	1.20	0.79	0.41	0.06	0.48	0.42
	2.40	1.62	0.78	0.06	0.89	0.83
	6.00	4.13	1.87	0.06	1.92	1.86
Orthoclase						
1.70 ± 0.06	1.20	0.77	0.43	4.64	5.58	0.94
	2.40	1.53	0.87	4.64	5.99	1.35
	6.00	3.85	2.15	4.64	7.42	2.78
3.76 ± 0.03	1.20	0.72	0.48	2.65	3.25	0.60
	2.40	1.52	0.88	2.65	3.56	0.91
	6.00	3.95	2.05	2.65	4.73	2.08
4.94 ± 0.02	1.20	0.74	0.46	0.43	0.89	0.46
	2.40	1.58	0.82	0.43	1.22	0.79
	6.00	3.93	2.07	0.43	2.39	1.96
6.67 ± 0.06	1.20	0.78	0.42	0.14	0.57	0.43
	2.40	1.58	0.82	0.14	1.00	0.86
	6.00	4.02	1.98	0.14	2.15	2.01
7.94 ± 0.03	1.20	0.83	0.37	0.10	0.54	0.44
	2.40	1.62	0.78	0.10	0.92	0.82
	6.00	4.04	1.96	0.10	2.12	2.02
8.86 ± 0.04	1.20	0.81	0.39	0.12	0.50	0.38
	2.40	1.63	0.77	0.12	0.89	0.77
	6.00	4.03	1.97	0.12	2.10	1.98

Table 3. (Contd.)

Final pH	[P], mM			[Si], mM		
	initial	final	−Δ[P]	initial	final	Δ[Si]
Labradorite						
1.61 ± 0.04	1.20	0.77	0.43	2.16	3.00	0.84
	2.40	1.52	0.88	2.16	3.68	1.52
	6.00	3.90	2.10	2.16	4.80	2.64
3.71 ± 0.01	1.20	0.69	0.51	0.29	0.66	0.37
	2.40	1.49	0.91	0.29	1.02	0.73
	6.00	3.93	2.07	0.29	1.96	1.67
4.88 ± 0.02	1.20	0.74	0.46	0.15	0.48	0.33
	2.40	1.51	0.89	0.15	0.89	0.74
	6.00	3.92	2.08	0.15	1.75	1.60
6.69 ± 0.05	1.20	0.73	0.47	0.11	0.50	0.39
	2.40	1.54	0.86	0.11	0.87	0.76
	6.00	4.03	1.97	0.11	1.80	1.69
7.94 ± 0.02	1.20	0.83	0.37	0.10	0.52	0.42
	2.40	1.62	0.78	0.10	0.87	0.77
	6.00	4.05	1.95	0.10	1.97	1.87
8.82 ± 0.06	1.20	0.79	0.41	0.13	0.49	0.36
	2.40	1.62	0.78	0.13	0.90	0.77
	6.00	4.07	1.93	0.13	1.92	1.79

tion and the composition of the newly formed phase. This approach is only partly applicable for the experiments described here, because silicate phosphatization occurred at constant pH imposed by buffer solutions, and the balance of H^+ ions, which very probably take part in the reaction, cannot be calculated.

Nevertheless, let us attempt to explain the relation established in the previous work and in the present experiments that the equivalence of changes in the silica and phosphate concentrations and the proportionality between the final time-invariant phosphorus concentration and the change of phosphate content during phosphatization have identical quantitative characteristics for all the silicates considered, despite the difference in their structural type and chemical composition. Such a relation can exist, if only one silicate phase is stable within a certain pH range, and it is formed on the surface of different silicate minerals and replaced by a phosphate mineral in contact with a phosphate-bearing solution. Phosphatization affects the secondary silicate phase appearing owing to silicate–water interaction, rather than the silicate minerals themselves. This results in identical parameters of the phosphatization reaction for different silicates, and the changes of the parameters at pH 1.6–1.8

Table 4. Proportionality factor *k* in Eq. (2) as a function of solution pH

Mineral	pH					
	1.6–1.8	3.7	4.9	6.7	7.9	8.8
Kaolinite, montmorillonite	0.58	0.58	0.54	0.50	0.44	0.44
Hornblende, orthoclase, labradorite	0.56	0.56	0.54	0.52	0.48	0.48
Mean	0.57	0.57	0.54	0.51	0.46	0.46

Table 5. Amount of silica extracted into solution in experiments on silicate phosphatization, percent of the initial content in the mineral*

pH	Mineral		
	hornblende	orthoclase	labradorite
1.6 ± 0.1	6.2–19.4	3.8–11.2	3.9–12.3
3.7–8.8	2.5–11.0	1.9–8.1	1.7–8.0

* The minimum value corresponds to the initial concentration of dissolved phosphates (1.2 mM), and the maximum value is 6.0 mM.

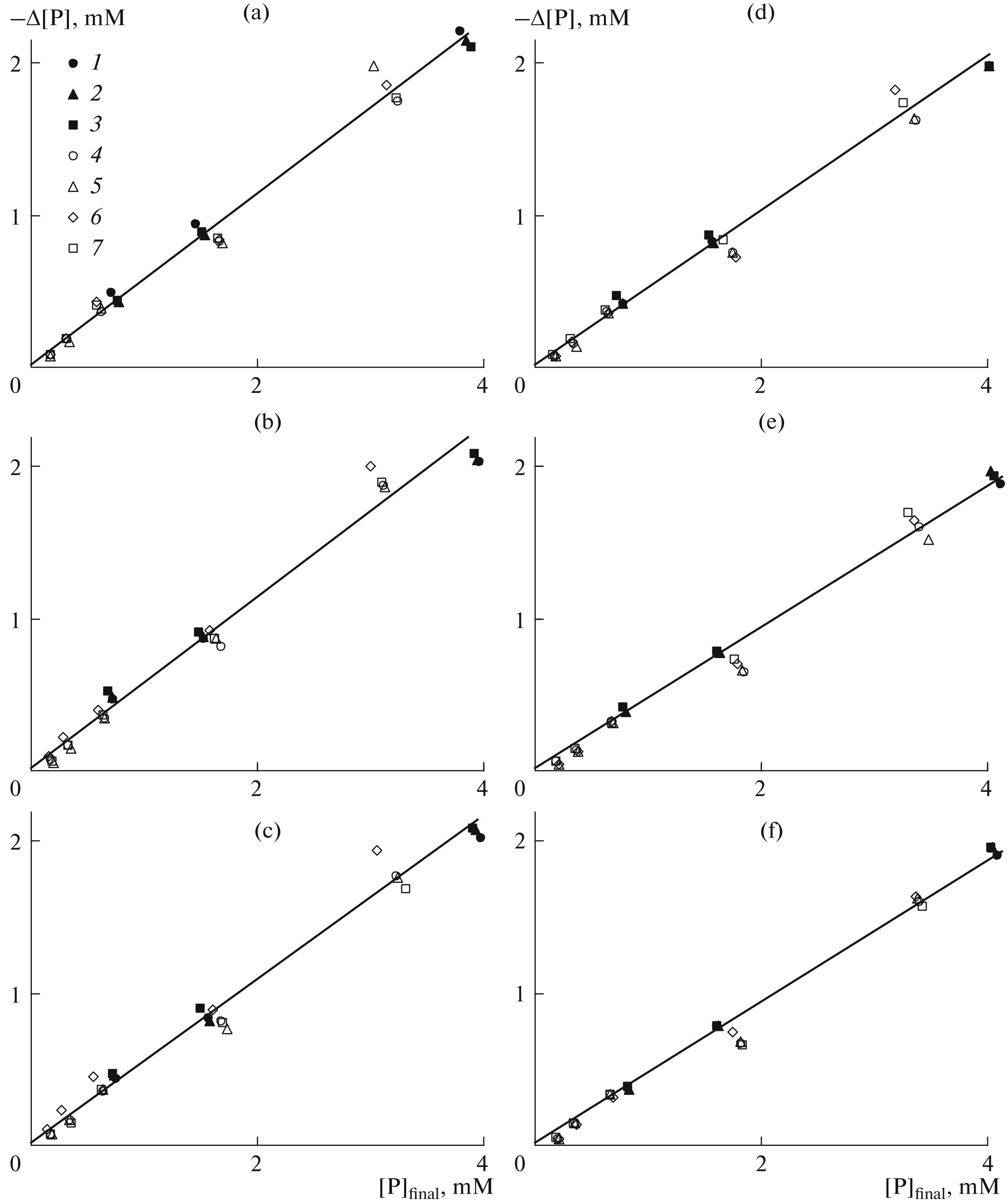

Fig. 2. Amount of phosphorus absorbed by aluminosilicates as a function of the final time-invariant concentration of phosphorus in the solution: (*1*) hornblende, (*2*) orthoclase, (*3*) labradorite (this study), (*4*) Glukhovetsk kaolinite, (*5*) Podolsk kaolinite, (*6*) Askania montmorillonite, sample 1, and (*7*) Askania montmorillonite, sample 2 (Savenko, 2015). Solution pH: (a) 1.6–1.8, (b) 3.7, (c) 4.9, (d) 6.7; (e) 7.9, and (f) 8.8.

should be interpreted as a consequence of the stability of a different surface silicate phase under such conditions compared with the pH range 3.7–8.8.

CONCLUSIONS

(1) Interaction of hornblende, orthoclase, and labradorite with aqueous solutions containing 1.2–6.0 mM phosphates at pH 3.7–8.8 is accompanied by approximately equivalent changes in the concentrations of phosphorus and silicon in the solution: $\Delta[\mathrm{Si}] \approx -\Delta[\mathrm{P}]$, whereas the release of silica into the solution at pH 1.6 ± 0.1 is 1.3–2.0 times higher than the removal of phosphates, which is probably related to a change in the stoichiometry of the phosphatization reaction.

(2) The amount of phosphorus absorbed by the silicates is linearly dependent on its final time-invariant concentration in the solution: $-\Delta[\mathrm{P}] = k[\mathrm{P}]_{\mathrm{final}}$. The proportionality factor k is practically identical for all the minerals considered and decreases slightly at a decrease in solution acidity: from 0.56 at pH 1.6 ± 0.1 to 0.48 at pH 8.8.

(3) The quantitative parameters of the phosphatization reaction for hornblende, orthoclase, and labradorite are identical to those for clay minerals (kaolinite and montmorillonite). This effect could appear, if a secondary silicate phase that is formed owing to silicate–water interaction and remains stable within a certain range of pH is affected by phosphatization, rather than the silicate minerals with different structures and compositions. The changes of the parameters of the phosphatization reaction at pH 1.6 ± 0.1 is a consequence of the stabilization of a different surface silicate phase under such conditions compared with higher pH conditions.

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