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Synthesis of phosphorus- and arsenic-bearing framework silicates similar to feldspar

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The finds of phosphorus- and arsenic-bearing feldspars in natural complexes are described in literature [*London, et al.,* 1990; *Vergasova, et al.,* 2004]. Phosphorus-bearing feldspars synthesis has been successfully produced in the works [*Simpson,* 1977; *Bychkov, et al.,* 1989]. But the problems of isomorphic substitution and synthesis of solid solutions $(Na,K)(Al,Si,P)_4O_8$ и $(Na,K)(Al,Si, As)_4O_8$ remain insufficiently studied by experiment. So, we have carried out the synthesis of phosphorus- and arsenic-bearing sodium (potassium) feldspars in hydrothermal conditions at T=400÷600°C, P=1.5 kbar. The mixtures of salts and gels: $NaPO_3$ + Al_2SiO_5 (sillimanite gel); Na_3AsO_4 (or NaOH + As_2O_5) + Al_2SiO_5 (sillimanite gel) + SiO_2 were the initial mixtures. Sometimes glass of $NaAl_2SiPO_8$ composition obtained by melting of Al_2SiO_5 gel and sodium metaphosphate ($NaPO_3$) and water (10 wt %) at T=1200°C and pressure 2 kbar was used. The analyses of synthesized phases were produced by microanalysis and X-ray analysis. It is shown that synthesized phases may be related to feldspars based on the composition and X-ray properties. Isomorphism in synthesized feldspars exercises according to scheme of two silicon atoms substitution to aluminum and phosphorus (arsenic): $2Si^{4+} \leftrightarrow Al^{3+} + P^{5+}(As^{5+})$.

1. Phosphorus-bearing phases. Apparently, synthesized phases don't form continuous sequences of solid solutions in the $NaAlSi_3O_8$ – $NaAl_2SiPO_8$ systems. The figure 1 shows that in experiments of phosphorus-bearing feldspars synthesis practically pure albites coexist with phosphorus-bearing feldspars in which $NaAlSi_3O_8 \leftrightarrow NaAl_2SiPO_8$ substitution is up to 50 or more mol% of $NaAl_2SiPO_8$ minal. Moreover, in some experiments phosphorus practically entirely replaces silicon and phase $Na_{0.76}Al_{2.33}P_{1.65}O_8$ is formed. Substitution of $2Si^{4+} \leftrightarrow Al^{3+} + P^{5+}$ in synthesized phases is described by following regression equation: (Al+P)= 3.956 – 0.488*(2Si); (n=40; r=0.998; S_x=0.07; E_x=0.02).

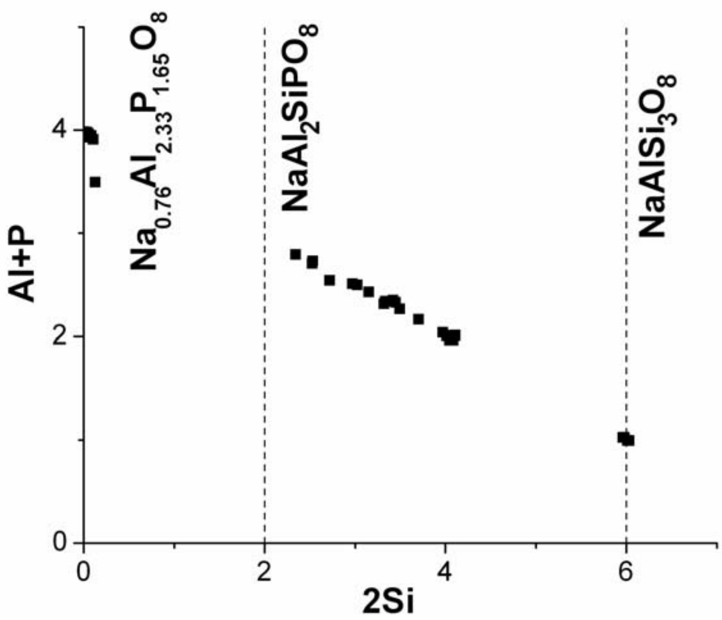

Fig. 1. Isomorphic interrelations in synthetic phosphorus-bearing feldspars

Table 1. Cell parameters of synthetic phosphorus-bearing feldspars

N	a, Å	b, [Å]	c, Å	α, °	β, °	γ, °	V, Å ^{3}
6378	8.179	12.992	7.168	94.39	116.67	89.47	677.9
6379	8.166	13.036	7.139	93.90	116.48	89.63	678.4
Sim*	8.164	13.019	7.139	94.00	116.61	89.85	676.4
l-*Ab***	8.135	12.785	7.158	94.27	116.60	87.68	663.8

* Cell parameters of synthetic phosphorus-bearing feldspar [*Simpson,* 1977].
** Cell parameters of low albite [*Kroll, Ribbe,* 1987].

X-ray study of synthesized phases has allowed correcting the cell parameters of phosphorus-bearing feldspars (tabl. 1). These data show that cell parameters of phosphorus-bearing feldspars are close to ones described in work [*Simpson,* 1977].

2. Arsenic-bearing phases. Synthesis of arsenic-bearing feldspars has allowed obtaining As-substituted phases with compositions: $NaAl_{1.5}Si_2As_{0.5}O_8$ and $NaAl_2SiAsO_8$. $2Si^{4+} \leftrightarrow Al^{3+} + As^{5+}$ substitution in synthesized phases is described by following regression equation:

$$(Al+As)= 3.754 - 0.448*(2Si); (n=40; r=0.989; S_x=0.12; E_x=0.04).$$

Moreover, in some experiments the phase corresponding to composition of entirely silicon substitution to aluminum and arsenic $2Si^{4+} \rightarrow Al^{3+} + As^{5+}$ has been synthesized. The composition of this phase is following: $(Na,K)_{1.64}Al_{1.89}As_{1.74}O_8$. The comparison of this phase with the phase of phosphorus feldspar (entirely substituted by aluminum and phosphorus) is presented in tabl. 2. From tabl. 2 it follows that entirely substituted phosphorus and arsenic phases differ in interrelation of isomorphic elements; it seems to connect with geometric, dimension factors. Isomorphic interrelations in arsenic-bearing feldspars are presented by fig. 1. It is shown that solid solutions from albite to $(Na,K)Al_2SiAsO_8$ exist. Fig. 2 demonstrate the entirely substituted by arsenic and aluminum phase $(Na,K)_{1.64}Al_{1.89}As_{1.74}O_8$, too.

Isomorphic interrelations in natural P, As-bearing feldspars are presented in fig. 3. All natural As-bearing feldspars are shown to correspond to solid solutions of $(Na,K)AlSi_3O_8$–$(Na,K)Al_2Si(As,P)O_8$ system. $2Si^{4+} \leftrightarrow Al^{3+} + (P^{5+}, As^{5+})$ substitution in synthesized phases is described by following regression equation:

$$[Al+(As,P)]= 4.057 - 0.508*(2Si); (n=40; r=0.996; S_x=0.05; E_x=0.02).$$

Extrapolation of this equation to entirely silicon substitution by aluminum, phosphorus and arsenic ($2Si^{4+} = 0$) contributes that aluminum, phosphorus and arsenic sum must be 4. If accept that phosphorus and arsenic enter the structure in pentavalent form we can calculate the formula of hypothetic feldspar (for calculation to 8 oxygen atoms: $(Na,K)_{1.0}Al_{2.5}(P,As)_{1.5}O_8$). The synthetic phase – sodium aluminophosphate $Na_{0.76}Al_{2.33}P_{1.65}O_8$ is nearest to this one.

Table 2. Formula and atomic interrelations in phosphorus- and arsenic substituted feldspars

Formula to 8 atoms (O)	(Na+K)/Al	[Al+P(As)]	Al/[P(As)]
$Na_{0.76}Al_{2.33}P_{1.65}O_8$	0.326	3.98	1.412
$(Na,K)_{1.64}Al_{1.89}As_{1.74}O_8$	0.868	3.63	1.104
$(Na,K)Al_2SiP(As)O_8$	0.5	4.00	1.00

The existence of phases with entirely silicon substitution to aluminum, phosphorus and arsenic in natural phosphorus- and arsenic-bearing feldspars is not noted. In natural conditions the chemical activity of phosphorus and arsenic is likely to be less than in our experiments.

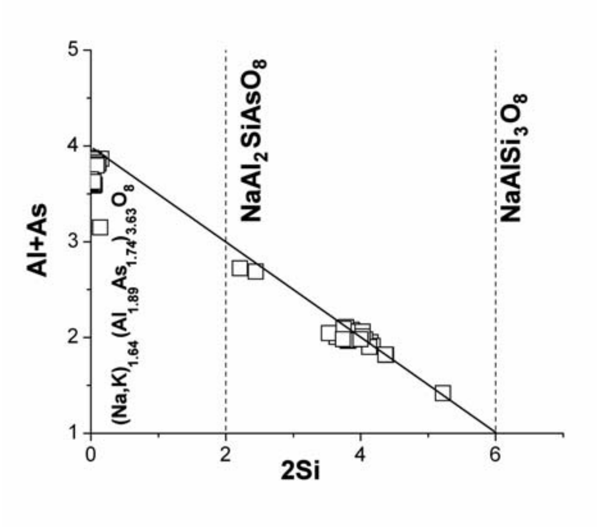

Fig. 2. Isomorphic interrelations in synthetic arsenic-bearing feldspars

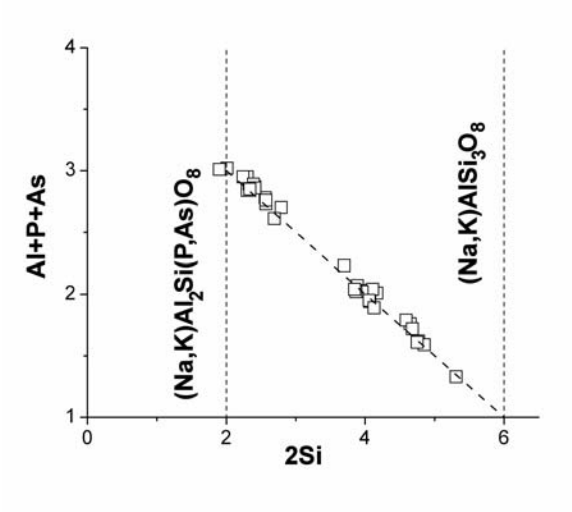

Fig. 3. Isomorphic interrelations in natural P, As-bearing feldspars (volcano Tolbachik)

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