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Aluminum phosphate variants of feldspar

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Abstract

The compounds $NaAl_2PSiO_8$ and KAl_2PSiO_8 have been synthesized hydrothermally at 1 kbar and temperatures greater than 445°C. Both compounds are isostructural with high-temperature alkali feldspars and involve the coupled substitution of (Al + P) for (Si + Si). Cell parameters for both phases are (1) $NaAl_2PSiO_8$: $a = 8.164(6)$, $b = 13.019(17)$, $c = 7.139(3)$Å, $\alpha = 94.00(11)°$, $\beta = 116.61(5)°$, $\gamma = 89.85(10)°$; and (2) KAl_2PSiO_8: $a = 8.621(2)$, $b = 13.084(2)$, $c = 7.203(2)$Å, $\beta = 115.99(2)°$.

Introduction

Phosphorus ranks tenth in crustal abundance, and the dominant phosphorus-bearing mineral, apatite, is a common accessory in rocks. The behavior of phosphorus through the crystallization–differentiation process is complex and enigmatic. Euhedral apatite in gabbro, including some apatite enclosed by plagioclase, suggests that apatite is an early-crystallizing mineral. Common occurrences of acicular apatite crystals in micrographic intergrowths of potassium feldspar and quartz suggest that apatite is formed during the late stages of crystallization. Carmichael (1964) showed that phosphorus reaches a maximum in intermediate-composition rocks in eastern Iceland. He suggested that apatite becomes a stable phase on the liquidus surface, and the crystals are incorporated in the fractionated crystalline assemblage.

The crystallization of fluorapatite would result in a major reduction of phosphorus in the residual melt. Because fluorapatite requires fluorine, the behavior of phosphorus in the magmatic process is partly controlled by the activity of fluorine, an element ranking twelfth in crustal abundance. Thus, both elements must be considered in an appraisal of the behavior of phosphorus in magmatic processes.

Pentavalent phosphorus has an ionic radius nearly ideal for tetrahedral coordination with oxygen. Huttenlocher (1935) showed that berlinite ($AlPO_4$) is isostructural with α quartz, and Beck (1949) described polymorphs of aluminum phosphate as being isostructural with tridymite, cristobalite, and β-quartz. Thus, there is much similarity between the aluminum phosphate polymorphs and the polymorphs of silica.

This paper aims to show that there can be extensive substitution of aluminum and phosphorus in the alkali feldspars, and evaluates the significance of such substitution in regard to the distribution of phosphorus and apatite in magmatic processes.

Experimental method

Syntheses were by encapsulation of mixtures in gold tubes, which were then reacted in standard cold-seal hydrothermal vessels. Runs ranged from a day to several weeks, and the total pressure for all syntheses was 1 kbar. The general scheme involved raising the temperature of the charge to greater than 900°C for at least four hours and then cooling to the desired temperature. Most mixes melted at the high temperatures.

The following are the reactions involved for the synthesis of the feldspar analogs:

$$(1)\ NaH_2PO_4 \cdot H_2O + Al_2O_3 + SiO_2 \rightarrow NaAl_2PSiO_8 + 2H_2O$$

$$(2)\ KH_2PO_4 + Al_2O_3 + SiO_2 \rightarrow KAl_2PSiO_8 + H_2O$$

The potassium and sodium phosphates and the alumina were analytical reagents, and the silica was finely-divided quartz. Mixtures were prepared by grinding under alcohol and then regrinding dry.

Results

$NaAl_2PSiO_8$

A mixture of equal molar amounts of $NaH_2PO_4 \cdot H_2O$, Al_2O_3, and SiO_2 is dominantly glass

Table 1. Cell dimension for aluminum phosphate variants of feldspar

	NPF	High Albite*	KPF	High Sanidine*	Ab-NPF
a(Å)	8.164(6)	8.149	8.621(2)	8.564	8.171(7)
b(Å)	13.019(17)	12.880	13.084(2)	13.030	12.940
c(Å)	7.139(3)	7.106	7.203(2)	7.175	7.131(4)
α	94.00(11)°	93.37°	90.00	90.00°	93.62(13)°
β	116.61(5)°	116.30°	115.99(2)	115.99°	116.55(5)°
γ	89.85(10)°	90.28°	90.00	90.00°	90.11(10)°

**Data from Borg and Smith (1969)*
(6) indicates an esd of 0.006Å or 0.06°

after heating to 900°C under 1 kbar total pressure. The refractive index of the glass is 1.498 ± 0.002, and X-ray diffraction shows the included crystalline material to be berlinite. Under the microscope some minute corundum crystals were found sparsely distributed in the products from all syntheses.

Synthesis at 800°C for one day yielded more than 95 percent feldspar-like material with the remainder of the charge consisting of several percent glass. Optics and X-ray diffraction patterns show that this material is similar to high-albite. Albite twins are common, and pericline and, rarely, Carlsbad twins are also present. The larger crystals are about 0.3 mm in length and 0.15 mm in width, and some occur as thin platelets. Considering the composition of the initial charge and the high degree of crystallinity, the composition of these crystals should be $NaAl_2PSiO_8$. This composition is related to albite by the coupled substitution of (Al + P) for (Si + Si), and this compound will hereafter be referred to as a sodium aluminum phosphorus feldspar and abbreviated as NPF.

The refractive indices of NPF are $\alpha = 1.516$, $\beta = 1.520$, and $\gamma = 1.522$, all ± 0.002. The crystals are negative with a moderate $2V$. Dispersion is moderate to strong with $v > r$. Extinction by the method of Michel-Lévy is 12°. The orientation is similar to albite. Some of the polysynthetic twins have diffuse boundaries; however, most are distinct. Most composition planes are parallel to cleavages and crystal faces, but some are inclined roughly 6° from a crystal face, a value consistent with σ for the rhombic section of high-albite. The optical properties are closely related to high-albite; however, the diffuse nature of some twins suggests that there has been strain, or change in triclinicity, during the cooling or quench.

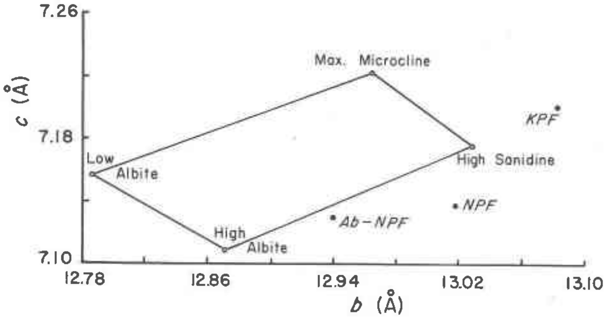

Fig. 1. Aluminum phosphate variants of feldspar compared to alkali feldspar. NPF = $NaAl_2PSiO_8$, KPF = KAl_2PSiO_8, and Ab-NPF is intermediate in bulk composition. The two end-members are splits from the entire ground charge. Alkali feldspar data from Stewart (1972).

Other NPF was synthesized over the temperature range of 800° to 445°C. Although NPF synthesized by cooling from 900° to 445°C commonly occurred in crystals with radial extinction, no material appeared as spherulites. Some samples contained a minor or trace amount of glass.

X-ray diffractograms were indexed by analogy to high-albite, as listed by Borg and Smith (1969). Cell parameters determined using the program of Appleman and Evans (1973) are given in Table 1. The b and c parameters are shown (Fig. 1) on a plot for the alkali feldspars as developed by Wright (1968), Wright and Stewart (1968), and Stewart (1972, 1975). In comparison of high-albite, the NPF has a nearly identical a parameter but slightly enlarged b and c parameters. This increase in the cell volume of 1.4 percent is consistent with the cell volume of berlinite being 2.6 percent greater than that of quartz.

Because of the similarity of high-albite and NPF, syntheses of the NPF analog of low-albite was attempted. Even though several charges were heated to 900°C and then cooled over several hours to temperatures as low as 445°C, there was no optical or X-ray evidence of a low-temperature polymorph of the NPF feldspar. The longest synthesis at low temperatures was a week, and perhaps a still longer period would produce a low-temperature polymorph.

KAl_2PSiO_8

A mixture of KH_2PO_4, Al_2O_3, and SiO_2 was used to synthesize the analog of sanidine. The only water present during the synthesis was released from the potassium phosphate. Consequently, these potassium charges contained only half the water of the sodium charges. Charges treated at 900°C lacked glass. The crystals have X-ray and optical properties closely related to sanidine, and this product will hereafter be called KPF.

Crystals of KPF are commonly 10–20μm, euhedral, and lack twins. The indices are: $\alpha = 1.512$ and $\gamma = 1.518 \pm 0.002$. Lattice parameters are given in Table 1, and *b* and *c* are shown relative to the alkali feldspars in Figure 1. The cell volume of KPF is slightly greater than that of sanidine.

Table 2. Composition of KPF

	Weight Percent		Moles	Ideal
Al_2O_3	36.5 ± 0.5	Al	1.96	2
P_2O_5	21.4 ± 0.5	P	0.82	1
SiO_2	26.8 ± 0.5	Si	1.22	1

$NaAlPSi_3O_8$–$NaAl_2PSiO_8$

Two experiments were conducted to determine the extent of solid solution between albite and NPF. For this, Ramona albite (Ab_{99}) was mixed in equal molar amounts with the components of NPF. Two samples were heated to 900°C. Then one was cooled to 800°C and held for three days, and the other was cooled over 12 hours to 665°C. All samples gave X-ray patterns closely related to high-albite, and lattice pa-

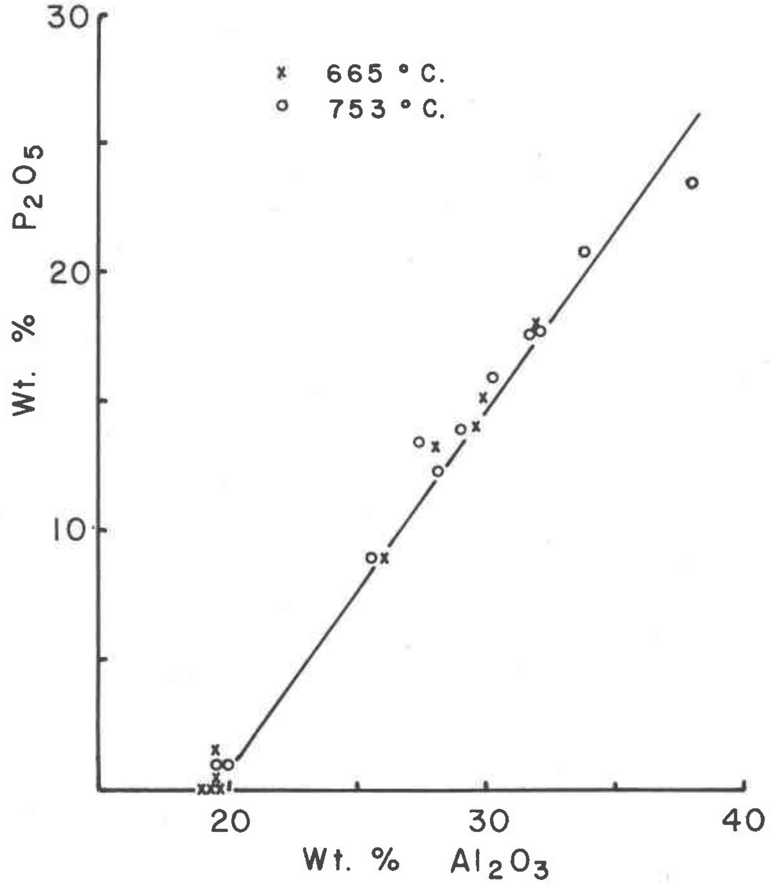

Fig. 2. Microprobe data on various crystals of $NaAl_2PSiO_8$ and solid-solution variants of albite. The line shows the ideal 1 : 1 molar ratio for the substitution of Al and P for 2Si.

rameters are between those of NPF and albite (Fig. 1, Table 1). Optically, the material appeared as a single phase, except for the inclusions of corundum.

Microprobe data

An ARL electron microprobe operated at 15kV accelerating voltage and 0.05 mA beam current was used on carbon-coated specimens of KPF and NPF to determine aluminum, phosphorus, and silicon contents. Ramona albite and fluorapatite were used as standards. The analysis of KPF is shown in Table 2. Conversion of the oxides to mole fractions based on four tetrahedral sites illustrates that the crystals are slightly enriched in silicon and diminished in aluminum and phosphorus. Thus, the crystals are a varient of KPF with solid solution toward sanidine.

Two samples of NPF were analyzed. Both were heterogenous, with solid solution toward albite. In fact, one sample was synthesized from a mixture of NPF and Ramona albite. During microprobe analysis some crystals were observed to be zoned with albitic cores and NPF rims. The results of the analyses of areas within and among crystals for both samples are shown in Figures 2 and 3. There is a direct linear relation between aluminum and phosphorus and an inverse relation between aluminum and silicon. Both support the model of coupled substitution of aluminum and phosphorus for two silicons, and extensive or complete solid solution between albite and NPF.

Discussion

This study indicates that aluminum and phosphorus readily substitute for two silicons in the alkali

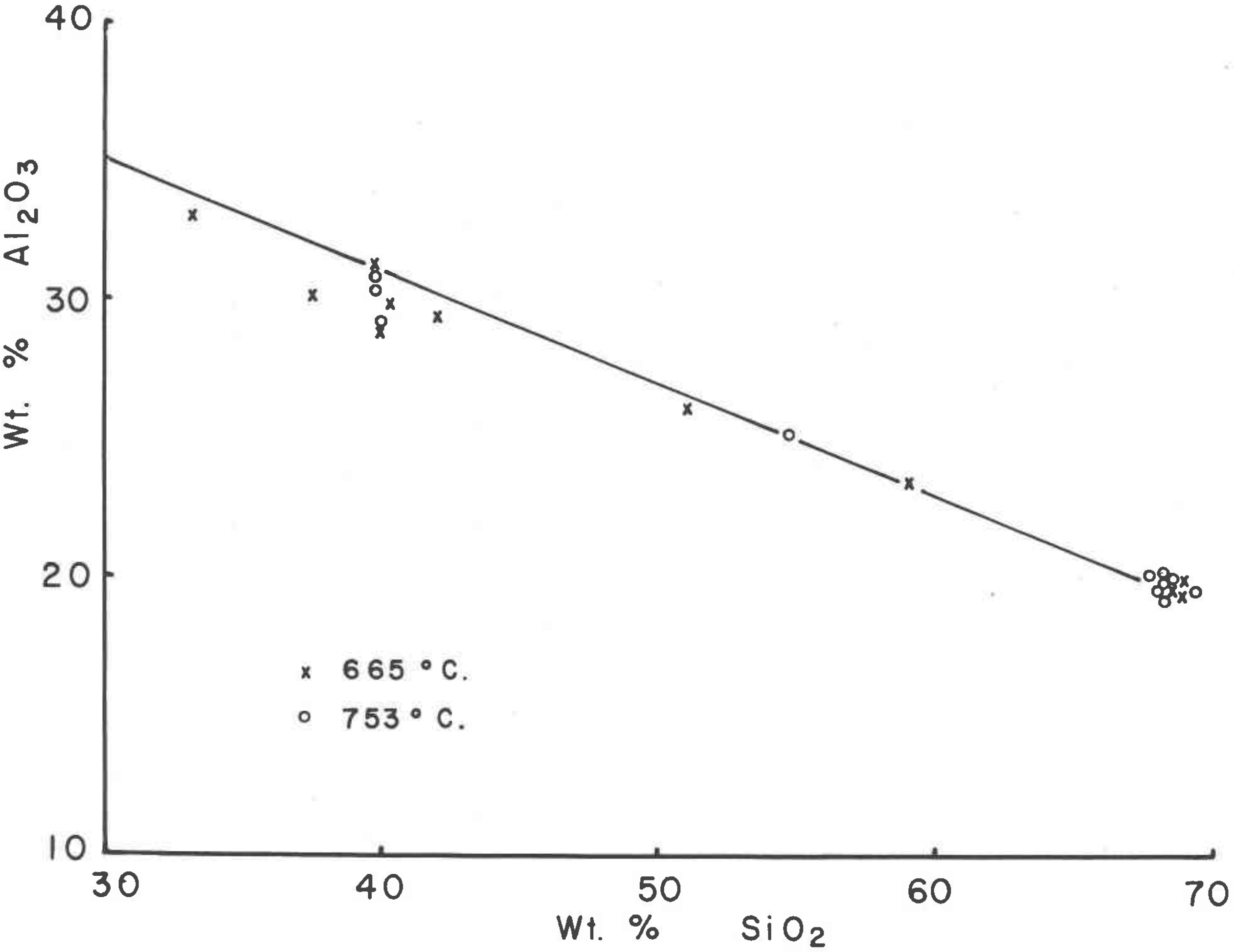

Fig. 3. Relation of aluminum and silicon for $NaAl_2PSiO_8$ and solid-solution variants of $NaAlSi_3O_8$. The line shows the 1:1 molar decrease of the silicon with increase of aluminum.

feldspars. Smith and Ribbe (1966) show that phosphorus occurs in alkali feldspar to the 0.0*x* percent level. Their highest value was 0.1 percent phosphorus for Spencer H. This would correspond to roughly 0.2 percent P_2O_5 in the chemical analysis. The absence of feldspars rich in phosphorus suggests that availability of phosphorus and not the crystal-chemical nature of feldspar limits this substitution.

The average crustal abundance of phosphorus is roughly 0.1 percent, and in most rocks this can be accounted for by fluorapatite. In some rocks fluorapatite has paragenetic relations indicative of an early crystallization, and in others it appears late. The occurrence of fluorapatite may be controlled by the availability of any of its constituents; calcium, phosphorus, or fluorine. If fluorapatite is absent, perhaps as a result of insufficient fluorine in the system, the phosphorus may remain in the residual melt.

Phosphorus concentrated in a residual melt may be removed by an increase in fluorine to some critical value, resulting in the precipitation of apatite. In the absence of this critical amount of fluorine, the phosphorus may be incorporated in crystallizing feldspars. Because phosphorus and aluminum form a coupled substitution, the occurrence of phosphorus in feldspar is favored in peraluminous magmas. Nepheline syenites and mica-bearing granites are rock types most likely to have appreciable phosphorus in the feldspar.

Commonly acicular crystals of fluorapatite are found enclosed by alkali feldspar, or lying athwart intergrowths of alkali feldspar and quartz. Some occurrences of this type may result from a fluoride-bearing late-stage vapor, or a deuteric solution, reacting with a phosphorus-bearing feldspar to precipitate apatite. In this light, a role of the feldspars may be one of a transient repository for phosphorus.

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