

## AMMONIUM IN ALKALI FELDSPARS

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## ABSTRACT

Ammonium can substitute for potassium and sodium in alkali feldspars. Some "zeolitic" water is apparently necessary to stabilize the structure of ammonium feldspar. Hydrothermal synthesis of  $\text{NH}_4\text{AlSi}_3\text{O}_8 \cdot \frac{1}{2}\text{H}_2\text{O}$  yields a product very similar to the mineral buddingtonite (Erd *et al.*, 1964); a stability field has not been determined. The small amount of available ammonium restricts the terrestrial occurrence of buddingtonite.

## INTRODUCTION

On the basis of its suitable ionic radius (approximately 1.43 Å, intermediate between those of potassium and rubidium) and its unit charge, several workers have suggested that ammonium might substitute for alkali metals in minerals, including feldspars (Rankama and Sahama, 1950, p. 577; Wlotzka, 1961; Stevenson, 1962). Ammonium substitution in synthetic silicates was experimentally demonstrated long ago. Exchange of ammonium for alkali metals in reactions between silicates and  $\text{NH}_4\text{Cl}$  was reported by Schneider and Clarke (1893), and discussed in a later series of papers by Clarke and Steiger (1899, 1900a, 1900b). All or nearly all the sodium and potassium in analcime, leucite, and natrolite is replaced by ammonium if the mineral is heated with dry ammonium chloride in a closed tube for six hours at 350° C. Clarke and Steiger (1902) tried the same ionic exchange technique on feldspars, with less spectacular results. Judging from their analyses of the soluble and insoluble products, they may have forced up to 20 per cent of the ammonium feldspar end-member into solid solution at 350° C. and a few atmospheres pressure, but they did not demonstrate that the ammonium-bearing insoluble product was actually a feldspar.

Schachtschabel (1940), in a series of ionic exchange experiments involving silicates and ammonium chloride solutions at room temperature and one atmosphere pressure, observed some exchange of  $\text{NH}_4$  for K in adularia. He used the name " $\text{NH}_4$ -Feldspat," but interpreted the ammonium as adsorbed in hydrolyzation products on the surfaces of feldspar grains. "Die Bezeichnung ' $\text{NH}_4$ -Feldspat' soll zudem nur aussagen, dass Feldspat mit  $\text{NH}_4$  gesättigt wurde und nicht, dass das Kali ohne Veränderung des Kristallgitters durch  $\text{NH}_4$  ersetzt wurde" (Schachtschabel, 1940, p. 217).

The small and nearly constant amount of nitrogen in igneous rocks argues against any significant amount of  $\text{NH}_4^+$  in feldspars. The total nitrogen content of rocks ranging from granite to dunite is about  $20 \pm 10$  ppm, and appears to be independent of rock type (Wlotzka, 1961).

The nitrogen occurs as  $\text{NH}_3$  or  $\text{NH}_4^+$ , and about half is leachable with water, suggesting that the soluble portion is dissolved in intergranular fluid or in fluid inclusions. The unleachable or "fixed" nitrogen apparently occupies sites in the crystal structures of the minerals.

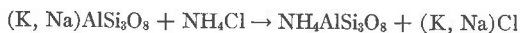
The nitrogen content of feldspars is generally higher than that of co-existing quartz, and a higher proportion in feldspars is "fixed" nitrogen (Wlotzka, 1961). Alkali feldspars average about 20 ppm N, but values range from 3 ppm to 125 ppm. Natural alkali feldspars, therefore, should rarely contain more than 0.10 mole per cent of an ammonium feldspar endmember,  $\text{NH}_4\text{AlSi}_3\text{O}_8$ .

### EXPERIMENTS

If more ammonium were readily available, would it freely substitute for alkali metals in feldspars? To answer this question, ionic exchange experiments were successfully performed (Barker, 1963). Several months later, the experimental demonstration of  $\text{NH}_4^+$  substitution was amply confirmed by the discovery of the mineral buddingtonite,  $\text{NH}_4\text{AlSi}_3\text{O}_8 \cdot \frac{1}{2} \text{H}_2\text{O}$  (Erd *et al.*, 1964).

Synthetic alkali feldspars and crystalline  $\text{NH}_4\text{Cl}$ , with or without  $\text{H}_2\text{O}$ , were sealed in platinum capsules. All runs were made in Tuttle cold seal pressure vessels, using water as the confining pressure medium. Pressures were maintained to within a few per cent by an air-operated high pressure pump and measured by a Bourdon-type gauge. Temperatures were controlled and continuously measured to  $\pm 2^\circ \text{C}$ .

In the anhydrous runs, the reaction



takes place rapidly above  $600^\circ \text{C}$ . and at 2000 bars confining pressure, but a further reaction, for which a likely equation is



also takes place above  $600^\circ \text{C}$ .

In anhydrous runs longer than 24 hours at  $700^\circ \text{C}$ ., or 120 hours at  $600^\circ \text{C}$ .,  $\text{NH}_4\text{AlSi}_3\text{O}_8$  initially forms, but is metastable and breaks down to silica, mullite, ammonia, and water (all four products of the decomposition were positively identified, and the equation given, yielding 16 moles of silica and one mole of mullite from 6 moles of ammonium feldspar, seems the most likely in view of the much greater amount of tridymite than mullite inferred from *x*-ray diffraction powder patterns). Data for runs in the anhydrous system are presented in Table 1. The persistence of ammonium feldspar, without decomposition, in a few runs was probably caused by the insufficient time allowed for the breakdown reaction to occur, or possibly by unintentional incorporation of suffi-

cient H<sub>2</sub>O in the charge, from atmospheric humidity or incomplete drying of the starting materials, before the platinum capsule was welded.

Runs with alkali feldspars and NH<sub>4</sub>Cl aqueous solutions are listed in Table 2. The importance of H<sub>2</sub>O in stabilizing the ammonium aluminosilicate is clear from a comparison of the two tables. Even in runs of 72 hours in the hydrous system under 700° C., silica and mullite did not

TABLE 1. EXPERIMENTS INVOLVING ALKALI FELDSPARS AND DRY NH<sub>4</sub>CL.  
T = TRIDYMITÉ, M = MULLITE, F = FELDSPAR

Run	Starting feldspar	T, °C	P, bars	Time, hrs.	Products	Remarks
77-62	Or <sub>100</sub>	700	2000	48	T+M+F	decomposed
85-62	Or <sub>100</sub>	675	2000	48	T+M+F	decomposed
99-62	Or <sub>100</sub>	650	2000	48	T+M+F	decomposed
82-62	Or <sub>100</sub>	650	2000	24	F	no reaction
78-62	Or <sub>100</sub>	600	2000	22	F	no reaction
104-62	Or <sub>100</sub>	600	2000	120	F+T+M	decomposed
98-62	Or <sub>95</sub> Ab <sub>5</sub>	650	2000	48	F+T+M	decomposed
81-62	Or <sub>95</sub> Ab <sub>5</sub>	650	2000	26	F	exchanged
103-62	Or <sub>95</sub> Ab <sub>5</sub>	600	2000	120	F+T+M	decomposed
93-62	Or <sub>65</sub> Ab <sub>35</sub>	700	350	48	T+M	decomposed
86-62	Or <sub>65</sub> Ab <sub>35</sub>	700	2000	48	T+M	decomposed
97-62	Or <sub>65</sub> Ab <sub>35</sub>	650	2000	48	F+T+M	decomposed
80-62	Or <sub>65</sub> Ab <sub>35</sub>	650	2000	26	F	exchanged
102-62	Or <sub>65</sub> Ab <sub>35</sub>	600	2000	120	F	exchanged
94-62	Or <sub>30</sub> Ab <sub>70</sub>	700	350	48	T+M	decomposed
87-62	Or <sub>30</sub> Ab <sub>70</sub>	700	2000	48	T+M+F	decomposed
75-62	Ab <sub>100</sub>	706	2000	24	T+M	decomposed
92-62	Ab <sub>100</sub>	700	350	48	T+M	decomposed
84-62	Ab <sub>100</sub>	675	2000	48	T+M+F	decomposed
83-62	Ab <sub>100</sub>	650	2000	24	T+M+F	decomposed
100-62	Ab <sub>100</sub>	600	2000	120	T+M+F	decomposed
70-62	Ab <sub>100</sub>	600	2000	22	F	no reaction

appear at temperatures at which they were the dominant insoluble phases in the dry system.

The "wet" runs in Table 2 are more significant than the "dry" runs in Table 1. For one thing, ionic exchange was demonstrated easily by *x*-ray diffraction powder patterns. In all but one case (that at 700° C.), the water-insoluble material remained a feldspar, but the positions of the diffraction peaks shifted to lower *2θ* values, showing the slight expansion of the feldspar crystal structure to accommodate the larger ammonium ions.

In the hydrous runs, the crystalline and fluid materials were completely

recovered, separated, and analyzed for Na and K with a Perkin-Elmer model 146 flame photometer using Li as an internal standard.  $\text{NH}_4$  was then obtained by difference. The validity and precision of this technique are best evaluated by referring to the small differences in Na and K values between bulk composition of the starting assemblage and the values in the final fluid in run 47-63, Table 2, the only experiment in the wet system which yielded quartz plus mullite as the crystalline phases.

As indicated in Table 2, sodium is replaced more readily than potassium, and, in alkali feldspars containing both Na and K, the Na is almost entirely removed. Substitution is more rapid in alkali feldspars of intermediate composition than in either pure sodium or potassium endmem-

TABLE 2. HYDROTHERMAL RUNS, ALKALI FELDSPARS+ $\text{NH}_4\text{Cl}$ + $\text{H}_2\text{O}$ 

Run	Temp., °C	Bulk Composition			Final Fluid			Final Feldspar			Original Feldspar (Weight Per Cent)	Original Normality of $\text{NH}_4\text{Cl}$ Solution
		K	Na	$\text{NH}_4$	K	Na	$\text{NH}_4$	K	Na	$\text{NH}_4$		
112-62	600	49.0	2.9	48.1	36.1	2.2	61.7	60.9	3.3	35.8	$\text{Or}_{95}\text{Ab}_5$	2
113-62	600	22.8	13.1	64.1	23.1	21.0	55.9	22.2	0	77.8	$\text{Or}_{65}\text{Ab}_{35}$	2
114-62	650	46.9	2.7	50.4	46.6	2.7	50.7	47.3	2.7	50.0	$\text{Or}_{85}\text{Ab}_{15}$	2
115-62	650	26.0	14.8	59.2	27.2	23.6	49.2	24.2	2.2	73.6	$\text{Or}_{65}\text{Ab}_{35}$	2
21-63	560	8.0	0.9	91.1	4.5	0.9	94.6	44.0	1.4	54.6	$\text{Or}_{90}\text{Ab}_{10}$	38.6
66-63	550	39.6	4.7	55.7	33.5	7.5	59.0	47.4	1.1	51.5	$\text{Or}_{90}\text{Ab}_{10}$	4.9
67-63	550	5.0	10.9	84.1	3.8	12.6	83.6	10.9	4.7	84.4	$\text{Or}_{30}\text{Ab}_{70}$	24.7
68-63	550	0.8	20.0	79.2	1.0	26.2	72.8	2.7	0	97.3	$\text{Or}_5\text{Ab}_{95}$	14.0
69-63	550	11.5	12.1	76.4	7.4	15.4	77.2	24.6	1.5	73.9	$\text{Or}_{50}\text{Ab}_{50}$	9.8
70-63	550	16.5	21.3	62.2	9.9	33.8	56.3	27.2	0.7	72.1	$\text{Or}_{45}\text{Ab}_{55}$	5.9
71-63	550	12.7	31.1	56.2	8.0	54.6	37.4	18.8	0.8	80.4	$\text{Or}_{30}\text{Ab}_{70}$	5.2
47-63	700	0.8	15.3	83.9	0.9	16.5	82.6	Quartz and Mullite			$\text{Or}_5\text{Ab}_{95}$	9.7

P=2000 bars; time for all runs was 72 hours, with the exception of 47-63 (168 hours).

K, Na, and  $\text{NH}_4$  values are in mole per cent, with  $\text{K}+\text{Na}+\text{NH}_4=100$  per cent.

bers.  $\text{Or}_{100}$  and  $\text{Ab}_{100}$  gave no convincing sign of ammonium substitution under the experimental conditions. Equilibrium is not claimed for any runs.

An x-ray diffraction powder pattern of the synthetic product of run 68-63 is compared with that of natural buddingtonite in Table 3. Correspondence between the two is good; incipient breakdown of ammonium feldspar, releasing silica, may account for the more intense peak at 3.3 Å. Quartz is not a major phase, however, so the compositions of feldspar products in Table 2, assumed to be pure feldspar, are not far from the actual values for K, Na, and  $\text{NH}_4$ .

#### THE WATER PROBLEM

The ammonium feldspar is definitely a hydrous phase, probably with the formula  $\text{NH}_4\text{AlSi}_3\text{O}_8 \cdot \frac{1}{2}\text{H}_2\text{O}$  (Erd *et al.*, 1964). The x-ray diffraction

pattern is that of an alkali feldspar, and the water, which is reversibly driven off at about 300° C., is probably zeolitic, occupying few or no fixed sites and not changing the crystal structure by its presence or absence (Eitel, 1954, p. 986-987).

In many, but not all, aluminosilicates, substitution of  $\text{NH}_4^+$  causes a change in the water content of the silicate. The ammonium analogues of the hydrous alkali aluminosilicates analcime, natrolite, and scolecite are

TABLE 3. X-RAY DIFFRACTION POWDER PATTERNS, NATURAL AND SYNTHETIC AMMONIUM ALUMINOSILICATES

(1)		(2)	
$d_{hkl}$ Å.	I	$d_{hkl}$ Å.	I
—	—	6.75	16
6.52	75	6.52	96
5.92	25	5.91	33
4.33	50	4.33	65
3.98	25	3.98	33
3.81	80	3.81	100
3.63	10	3.63	12
3.57	10	3.60	5
3.459	20	3.462	23
3.383	25	3.381	72
3.342	100	3.314	34
3.262	25	3.258	62
3.225	50	3.225	69
—	—	3.129	3
3.012	10	3.014	39
2.947	10	2.954	13
2.910	20	2.910	20

(1). Product of run 68-63 ( $\text{Or}_{2.7}\text{Ab}_{0.3}\text{Bd}_{97.3}$ ). Cu/Ni radiation. Scanned at  $\frac{1}{4}^\circ 2\theta$  per minute with Norelco high-angle diffractometer; silicon powder as internal standard.

(2). Natural buddingonite. Data from Table 1, Erd *et al.*, 1964.

anhydrous (Barrer, Baynham, and McCallum, 1953; Hey and Bannister, 1932). The Li, K, Ag and Tl analogues of natrolite are hydrous, however.

Eitel (1954, p. 1010) offers an explanation: "If in natrolite the ammonium is introduced to replace sodium, its tetrahedral constitution brings about a saturation of the bindings by four surrounding oxygen ions and no more bindings are available for water. Therefore anhydrous natrolite is stable."

In some silicates (stilbite, chabazite, laumontite, thomsonite), exchange of  $\text{NH}_4^+$  for  $\text{Ca}^{2+}$  and  $\text{Na}^+$  causes no change in the amount of zeolitic water (Hey, 1962).

The ammonium analogues of alkali feldspar, muscovite, and at least one artificial permutite contain more water than the corresponding ammonium-free forms. Barrer and Denny (1961) synthesized a dioctahedral mica with the approximate formula  $(\text{NH}_4)_{0.85}\text{Al}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 \cdot (\text{H}_2\text{O})_{0.25}$ . E. Gruner (1931) noted a coupled substitution of  $\text{NH}_4^+$  and  $\text{H}^+$  for two alkalis in a permutite, according to the exchange reaction



According to a hypothesis reminiscent of that quoted above from Eitel, for water-poor ammonium silicates, structural imbalance could explain the "zeolitic" water in ammonium feldspar. The imbalance may be caused by the geometry of the  $\text{NH}_4^+$  group; hydrogen at the tetrahedral apices of the ammonium unit may polarize adjacent oxygen ions, requiring the presence of zeolitic water in the feldspar structure. The complexity of the problem, particularly of the caution necessary in using "ionic radii" of ions in various coordinations, is pointed out by Smith and Schreyer (1962) with reference to the sites occupied by Ar and  $\text{H}_2\text{O}$  in cordierite; the "cation" is not necessarily placed *symmetrically* within the available space in the crystal structure. Instead it may cling to one side of the "hole" available for it. MacKenzie (1957, p. 487) has synthesized an analcime which is apparently of albite composition ( $\text{Al}/\text{Si} = \frac{1}{3}$ ). Further, Smith and Rinaldi (1962, p. 211) have predicted zeolite analogues of feldspars.

#### SIGNIFICANCE OF AMMONIUM SUBSTITUTION

The substitution of ammonium for alkalis in most natural feldspars must be very small. If, however, an alkali feldspar analysis is recast in terms of Ab, An and Or as the only endmembers, the presence of ammonium or other univalent cations will cause an apparent excess of Al and Si, enough to account for the excesses actually observed. There has been discussion of the meaning of excess silica in feldspars (for example, see Chayes and Zies, 1962, p. 116). Should a feldspar in a nepheline syenite, for example, have less silica than another feldspar, with the same proportions of univalent and divalent cations, in a granite? At present it is impossible to distinguish nonstoichiometry in feldspars from analytical errors or omissions. Further, Carman and Tuttle (1963) report solid solution between  $\text{NaAlSi}_3\text{O}_8$ ,  $\text{KAlSi}_3\text{O}_8$ , and Schwantke's molecule,  $\text{CaAl}_2\text{Si}_6\text{O}_{16}$ . Such solid solution may provide the best single explanation of excess silica in feldspars.

The Sulphur Bank occurrence of the ammonium feldspar buddingtonite (White and Roberson, 1962; Erd *et al.*, 1964) corroborates the experimental results. Buddingtonite formed as a replacement of plagioclase,

just as K-feldspar may also replace plagioclase hydrothermally (Orville, 1963, p. 224). Buddingtonite is rare simply because a suitable ammonium-rich environment is rare in the crust of the earth. In comets, the major planets, and possibly on a primordial accreting earth, silicates containing ammonium or other complexes, such as methyl or ethyl radicals, may be important phases. Buddingtonite should be sought in carbonaceous chondrites.

The temperature and pressure conditions used in the experimental synthesis of buddingtonite have little bearing upon the conditions of natural formation. The high temperature and pressure made the exchange *easier*, but indicate nothing about a stability field for buddingtonite. This particular ammonium aluminosilicate is not stable in the hydrous system at a temperature of 700° C. and a total pressure of 2000 bars, but even at the lowest temperatures at which synthesis was achieved in limited time (550° C.), buddingtonite may well be metastable with respect to silica, mullite, ammonia and water.

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