

ISOMORPHOUS SUBSTITUTION IN NATURAL AND SYNTHETIC ALUNITE¹

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ABSTRACT

Seven synthetic alunites prepared at 100° C. differ from natural alunites in having slightly smaller unit cells at the potassium end of the alunite-natroalunite system and in containing lower percentages of alkalis and alumina and a higher percentage of water than natural alunite. These differences are attributed to the partial substitution of H_3O^+ for K^+ and Na^+ in the synthetic alunite structure. Heating of these synthetic alunites at 300° C. to eliminate the H_3O^+ gives synthetic alunites with cell dimensions nearly the same as those of natural alunite of corresponding composition. Both heat-treated and untreated synthetics form isomorphous series that conform to Vegard's law.

Plots of unit cell dimensions vs. composition for nineteen natural alunite samples outline a flat, reverse S-shaped curve for the alunite-natroalunite isomorphous series which deviates slightly from the straight-line curve outline by the heat-treated synthetic alunites.

INTRODUCTION

This paper is primarily concerned with the isomorphous substitution of K^+ , Na^+ , and H_3O^+ in synthetic and naturally occurring members of the alunite-natroalunite series, $(\text{K},\text{Na})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$. Conclusions on substitution are based on *x*-ray data derived from chemically analyzed alunite samples and from synthetic alunite prepared by the writer. When the work was begun, naturally occurring alunite in the mid-range of the alunite-natroalunite series was not available for study, so an attempt was made to bridge that gap with specially prepared synthetic specimens. These synthetic alunites, however, were found to form a separate series, and to differ sufficiently from the natural mineral to preclude their use in defining relations in the natural mineral. Recently samples in the mid-range of the natural series were acquired, and synthetic specimens that have unit cell dimensions nearly the same as natural alunites were produced by heating the previously studied synthetic alunites to 300° C.

SYNTHETIC ALUNITE SERIES

Alunite synthesis was patterned after that of Leonard (1927). Reagent grade K_2SO_4 and Na_2SO_4 were combined in different proportions and added to $3\frac{1}{3}$ to 4 times as much $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. The salts were then dissolved in 150 to 200 ml. of distilled water and boiled 2 to 4 days at atmospheric pressure. A reflux condenser was connected to the containing flask in order to maintain the boiling solution at a constant level. The precipitated synthetic alunite was washed and separated by centrifuging and decanting.

¹ Publication authorized by the Director, U. S. Geological Survey.

TABLE 1. DATA ON THE SYNTHESIS OF ALUNITE

Sample	K ₂ SO ₄	Na ₂ SO ₄	Al ₂ (SO ₄) ₃ ·18 H ₂ O	H ₂ O	Time	Calculated K	Na ¹
S-1	1.000 g	0.000 g	4.000 g	150 ml	2 days	100%	0%
S-2	.700	.400	4.000	150	2	58	42
S-3	.600	.490	4.000	150	2	50	50
S-4	.500	.700	4.000	150	2	37	63
S-5	.200	1.000	4.000	150	2 $\frac{3}{4}$	14	86
S-6	.150	1.500	6.000	200	4	7	93
S-7	0.000	1.500	6.000	200	4	0	100

¹ Computed relative atomic percentages of potassium and sodium in solution.

The pH of the sulfate solution prior to the precipitation of alunite was 3.0–3.5, but after complete precipitation, the pH had dropped to 1.5 to 2.

Data on the synthesis are summarized in Table 1, and chemical analyses of the synthetic alunite specimens are given in Table 2. A comparison of the relative atomic percentages of potassium and sodium calculated from the proportion of ingredients used in the alunite syntheses, and these percentages computed from the chemical analyses of the synthetic alunite precipitates, shows that potassium is preferentially taken into the lattice over sodium during crystallization of the alunite products (see Fig. 1). All the specimens intermediate in composition between the potassium and sodium end members crystallized richer in potassium, and both potassium and sodium end members crystallized with minor amounts of sodium and potassium, respectively, even though only one alkali was introduced into the solution in either synthesis. Presumably sodium and potassium contaminants in the end members came from the apparatus. Similarly, the specimens of intermediate composition may have been slightly contaminated.

NATURAL ALUNITE

Alunite samples from Marysvale, Utah, Summitville, Colorado, and Comerio, Puerto Rico, are used to represent a wide range in composition of potassium- and sodium-bearing alunites. Chemical analyses of these are given in Table 3. All except the natroalunite end member (Table 3, no. 19) were studied by the author; data on the natroalunite end member are from the literature (Moss, 1958).

Though some specimens contain admixtures of quartz, kaolinite and halloysite, hematite, and possibly gibbsite, the presence of these minerals neither interferes with α -ray analysis of the alunite fraction nor prevents computation of the alunite from the chemical analyses. The relative pro-

TABLE 2. CHEMICAL ANALYSES AND UNIT CELL DIMENSIONS OF SYNTHETIC ALUNITE SPECIMENS AND THEORETICAL COMPOSITIONS OF ALUNITES

	S-1	S-2	S-3	S-4	S-5	S-6	S-7	Alunite ³	Natro- alunite ³	(H ₂ O)Al ₃ (SO ₄) ₂ (OH) ₆ ³
K ₂ O	9.79	9.31	9.00	8.78	7.33	5.70	.11 K ₂ O	11.35	—	—
Na ₂ O	.12	.47	.58	.75	1.64	2.74	6.03 Na ₂ O	—	7.79	—
Al ₂ O ₃	32.1	32.8	32.6	33.7	34.0	34.7	36.6 Al ₂ O ₃	36.96	38.44	38.83
SO ₃	39.2	38.9	38.6	38.6	38.3	39.2	40.0 SO ₃	38.65	40.20	40.61
Rem ¹	18.79	18.52	19.22	18.17	18.73	17.66	17.26 H ₂ O	13.04	13.56	20.56
K ²	98	93	91	89	75	58	1			
Na ²	2	7	9	11	25	42	99			
a ⁴	7.013	7.012	7.006	7.012	7.007	7.006	6.998			
c ⁵	17.14	17.10	17.10	17.08	17.02	16.96	16.71			
a ⁶	6.982	6.978	6.979	6.972	6.974	6.982	6.974			
c ⁷	17.32	17.26	17.27	17.26	17.14	17.07	16.69			

W. W. Brannock and Leonard Shapiro, analysts. Specimens S-1 to S-7 are the same as in Table 1.

¹ Rem. includes H₂O-, H₂O+ and any impurities, computed by difference.

² Relative atomic percentages in the alunite formula computed from chemical analyses, the total alkalis having been summed to 100 per cent.

³ Theoretical composition.

⁴ In Å computed from (2240).

⁵ In Å computed from (0006).

⁶ In Å computed from (2240); heated at 300° C. for 1 hour.

⁷ In Å computed from (0006); heated at 300° C. for 1 hour.

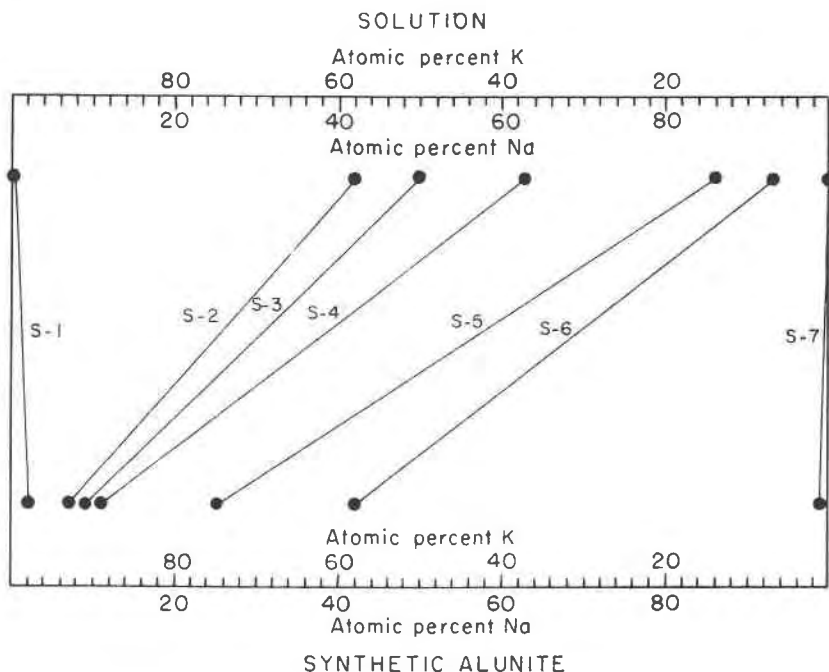


FIG. 1. Relative atomic percentages of potassium and sodium in synthetic alunite and in solution prior to the precipitation of alunite.

portions of potassium and sodium as determined from the chemical analyses provide a basis for comparing unit cell dimensions of the different specimens and for establishing the nature of the alunite-natroalunite isomorphous series.

X-RAY DATA

All samples were examined with a Norelco *x*-ray diffractometer set to traverse at the rate of one-fourth degree (2θ) per minute. Using a chart speed of 15 inches per hour, diffraction patterns were produced with a scale of one inch equal to one degree (2θ) which can be conveniently measured to within 0.01° (2θ). The instrument was standardized using silicon powder furnished by the manufacturer, and the observed interplanar spacings agreed within 0.01° (2θ) of the standard values. The deviation from standard values is nearly the same as the error of measurement at the above-mentioned instrument settings and hence is due mostly to the measuring error. Copper radiation was used exclusively. Computations are based on $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) for reflec-

TABLE 3. CHEMICAL ANALYSES AND UNIT CELL DIMENSIONS OF ALUNITE AND NATROALUNITE

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
SiO ₂	31.72	.22	10.85	30.04	27.10	—	2.20	10.95	34.80	4.65	—	39.00	10.7	4.4	42.1	49.0	34.6	43.78	—
Al ₂ O ₃	25.14	37.18	38.50	23.98	28.70	—	39.45	35.35	24.40	37.70	—	23.21	32.9	36.2	22.1	20.3	25.5	24.80	36.8
Fe ₂ O ₃	.57	—	—	4.32	—	—	—	.24	—	—	—	.16	4.97	—	—	—	—	.81	0.4
K ₂ O	7.15	10.46	7.90	6.90	6.75	6.6	7.67	7.00	6.49	8.25	7.8	6.4	4.53	6.4	3.7	3.4	2.8	1.04	0.1
Na ₂ O	.14	.33	.26	.23	.38	—	.61	.67	.67	1.12	2.0	1.10	2.1	2.4	1.5	1.4	2.6	3.11	7.0
TiO ₂	.86	—	—	.78	—	—	—	.35	—	—	—	.05	.14	—	—	—	—	.62	—
P ₂ O ₅	—	.58	—	—	—	—	—	—	—	—	—	—	.97	—	—	—	—	—	—
SO ₃	24.62	38.34	29.30	23.67	26.20	—	36.10	31.50	23.41	34.00	—	23.36	33.3	36.0	21.2	19.2	24.3	16.86	38.3
H ₂ O+	9.81	12.90	13.33	9.11	9.50	—	13.33	12.50	8.28	13.00	—	7.92	11.8	12.1	7.5	8.6	8.1	8.1	14.9
H ₂ O-	.06	.09	.10	.22	.10	—	.15	.16	.10	.10	—	.07	.00	—	—	—	—	.34	—
BaO	—	—	—	—	—	—	—	—	—	—	—	—	.22	—	—	—	—	—	0.1
CaO	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.9
SrO	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.6
PbO	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
K ^a	100.07	100.10	100.24	99.27	98.73	—	99.58	98.12	98.80	98.82	—	99.49	98.3	97.5	98.1	100.2	98.4	99.97	99.7
Na ^a	97	96	96	95	92	88	88	87	86	87	72	72	67	64	62	62	42	18	1
d ^b	3	4	4	5	8	12	12	13	14	17	28	28	33	30	38	38	58	82	99
c ^c	6.981	6.982	6.975	6.977	6.977	6.983	6.974	6.981	6.982	6.977	6.981	6.976	6.981	6.981	6.970	6.978	6.976	6.977	6.983
	17.34	17.32	17.30	17.32	17.30	17.30	17.32	17.31	17.32	17.30	17.18	17.16	17.16	17.11	17.10	17.09	16.94	16.97	16.099

^a Represents relative atomic percentages of K and Na.

^b In Å computed from (2240).

^c In Å computed from (0006).

- Sample from Yellow Jacket deposit, Marysvale, Utah, at northeast corner of lower excavation in quarry, J. G. Fairchild, analyst.
- Sample of purest alite from Mineral Products mine, Marysvale, Utah, believed to be representative of the material analyzed by W. T. Schaller.
- Sample from V and W deposit, Marysvale, Utah, taken across 4.3 feet on face of west drift in tunnel on south slope, R. K. Bailey, analyst.
- Sample from Y and Z deposit, Marysvale, Utah, taken across 4.8 feet at same location as No. 1, J. C. Fairchild, analyst.
- Sample from S and N deposit, Marysvale, Utah, taken across 9.4 feet crystal vein in T-shaped cut above big tunnel cut, R. K. Bailey, analyst.
- Sample from Sunshine district, Colorado, J. B. McHugh, analyst.
- Sample from Sunshine deposit, Marysvale, Utah, taken through 4.2 feet across crystal vein east of main tunnel, R. K. Bailey, analyst.
- Sample from Sunshine deposit, Marysvale, Utah, taken from hanging wall side of vein at south end of glory hole, R. K. Bailey, analyst.
- Sample from White Horse deposit, Marysvale, Utah, taken at south side of rise from tunnel at northwest end of glory hole, R. K. Bailey, analyst.
- Sample from Summitville deposit, Marysvale, Utah, taken from hanging wall side of vein at south end of glory hole, R. K. Bailey, analyst.
- Sample from Summitville district, Colorado, Lucile N. Tarrant, analyst. (Steven and Ratté, 1960, p. 43).
- Sample from Summitville district, Colorado, Lucile N. Tarrant, analyst. (Steven and Ratté, 1960, p. 43).
- Sample from Cerro La Tiza, Conerito, Puerto Rico, H. F. Phillips, and Elizabeth A. Nygard, P. L. D. Elmore, and Catrine E. White, analysts. (Hildebrand and Smith, 1959).
- Sample from Cerro La Tiza, Conerito, Puerto Rico, H. F. Phillips, Elizabeth A. Nygard, P. L. D. Elmore, and Catrine E. White, analysts. (Hildebrand and Smith, 1959).
- Sample from Cerro La Tiza, Conerito, Puerto Rico, H. F. Phillips, Elizabeth A. Nygard, P. L. D. Elmore, and Catrine E. White, analysts. (Hildebrand and Smith, 1959).
- Sample from Big Star deposit, Marysvale, Utah, taken through 9.2 feet on south side of main quarry, R. E. Stevens, analyst.
- Natroalunite, B. M. 92951, collected by Breithaupt from Sierra Almagrera, Spain; chemically analyzed and cell dimensions determined by Moss (1958).

TABLE 4. X-RAY DIFFRACTION DATA FOR NATURAL AND SYNTHETIC ALUNITE AND NATROALUNITE

hkil	Specimen 2 Alunite ¹			Specimen S-5 ² Synthetic Alunite			Specimen S-7 ² Synthetic Natroalunite			Specimen 18 ¹ Natroalunite						
	Observed		I	Observed		I	Observed		I	Observed		I				
	Calcu- lated	$\sin^2 \theta$		d	$\sin^2 \theta$		d	Calcu- lated		$\sin^2 \theta$	d		Calcu- lated	$\sin^2 \theta$	d	
0003	0.178	0.179	5.77	28	0.185	0.182	5.71	9	0.194	0.183	5.57	4	0.191	0.184	5.58	12
1011	0.182	0.182	5.72	15	0.182	0.182	5.72	15	0.183	0.183	5.69	4	0.184	0.184	5.69	12
0112	0.242	0.242	4.96	53	0.243	0.244	4.94	56	0.246	0.247	4.91	93	0.247	0.247	4.90	76
1014	0.479	0.479			0.489	0.489			0.501	0.502	3.44	3	0.502	0.502		
1120	0.487	0.487	3.49	21	0.483	0.483	3.50	32	0.484	0.485	3.50	30	0.487	0.487	3.49	24
0115	0.658	0.658			0.674	0.674			0.692	0.694	2.93	15	0.692	0.694	2.93	17
1123	0.666	0.666	2.99	100	0.668	0.667	2.98	100	0.675	0.676	2.97	100	0.678	0.678	2.96	100
0221	0.670	0.670			0.665	0.665			0.668	0.667	2.98	60	0.671	0.671	2.97	70
0006	0.713	0.713	2.89	106	0.738	0.738	2.84	5	0.765	0.765	2.79	10	0.763	0.763	2.79	17
0224	0.967	0.967	2.477	6	0.972	0.973	2.469	25	0.985	0.988	2.451	3	0.989	0.989	2.451	48
1017	1.133	1.128	2.293	81	1.166	1.167	2.257	23	1.202	1.204	2.220	38	1.201	1.204	2.221	48
2025	1.145	1.145			1.157	1.157			1.178	1.181	2.241	3	1.179	1.179		
1232	1.217	1.213	2.211	6	1.209	1.209	2.214	6	1.214	1.214			1.222	1.222	2.202	12
0118	1.430	1.429	2.038	2	1.473	1.473			1.521	1.521			1.519	1.519		
2134	1.454	1.452	2.022	2	1.455	1.455			1.469	1.469			1.476	1.476		
3030	1.462	1.462			1.449	1.449			1.453	1.453			1.462	1.462		
0009	1.604	1.600	1.926	70	1.661	1.659	1.890	4	1.720	1.723	1.856	70	1.716	1.720	1.857	10
0227	1.620	1.620			1.649	1.634	1.905	29	1.687	1.688	1.875	4	1.688	1.689	1.874	2
3033	1.641	1.637	1.903	29	1.634	1.634	1.905	29	1.644	1.645	1.899	35	1.652	1.654	1.894	29
2028	1.917	1.921	1.762	2	1.956	1.932	1.746	16	2.005	2.006			2.006	2.006		
2240	1.950	1.947	1.746	16	1.932	1.934	1.752	19	1.937	1.938	1.749	22	1.949	1.950	1.744	21
1129	2.081	2.093	1.684	2	2.144	2.144			2.205	2.205			2.204	2.204	1.643	5
2243	2.128	2.128			2.116	2.116			2.128	2.128			2.140	2.140		
1311	2.132	2.136	1.667	2	2.114	2.114			2.119	2.119			2.132	2.132		
3036	2.175	2.185	1.648	2	2.187	2.178	1.650	3	2.217	2.217			2.224	2.224		
3142	2.192	2.203	1.572	2	2.175	2.185	1.648	2	2.187	2.183	1.648	6	2.196	2.196		
1238	2.405	2.403	1.572	2	2.439	2.437	1.560	3	2.488	2.493	1.543	6	2.493	2.493		
1344	2.429	2.429			2.421	2.438			2.438	2.440	1.559	3	2.450	2.450		
3145	2.608	2.607	1.509	4	2.606	2.607	1.509	3	2.629	2.629			2.641	2.641	1.501	5
02210	2.630	2.625	1.503	36	2.694	2.694	1.484	9	2.770	2.770	1.462	15	2.769	2.769	1.463	12
2246	2.663	2.659	1.494	9	2.670	2.673	1.490	6	2.702	2.704	1.481	6	2.712	2.712		

¹ Specimen number is the same as in Table 3.² Specimen number is the same as in Tables 1 and 2. Specimen is not heat-treated.

tions with 2θ less than 36° and $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54050 \text{ \AA}$) for reflections with 2θ greater than 36° .

The previous work of Pabst (1947) gives indices for diffraction lines in the alunite diffraction pattern so that it is possible to correlate alunite lines with those of the synthetic mineral. Using the (0006) and (2240) reflections so assigned to the synthetic alunite patterns, the unit cell dimensions, a and c have been computed ($a = 4d_{2240}$; $c = 6d_{0006}$), and the validity of the indexing for synthetic alunite has been established by comparing the calculated $\sin^2\theta$ value with the observed $\sin^2\theta$ value (see Table 4) for each line of the diffraction patterns as determined by the equation (Henry, Lipson, and Wooster, 1951, p. 178):

$$\sin^2_{hkl}\theta = \frac{\lambda^2}{3a^2} (h^2 + hk + l^2) + \frac{\lambda^2}{4c^2} l^2.$$

Natural alunite and natroalunite also have been indexed in this manner in order to confirm the assignment of indices to diffraction lines that are present in the diffractometer patterns but which are not given in the powder diffraction data of Pabst (1947).

The lattice constants a and c , for natural alunite specimens are given in Table 3 and those for synthetic specimens are given in Table 2. The same data are plotted in Fig. 2 as curves showing the relation between the unit cell dimensions and the relative atomic percentage of sodium and potassium in the specimens.

INTERPRETATION AND CONCLUSIONS

Synthetic and natural alunites of this study form an isomorphous series between their sodium and potassium end members as shown by contraction of the unit cell with substitution of Na^+ (0.95 \AA , Pauling, 1960, p. 514) for the larger K^+ (1.33 \AA) in the crystal structure. Slight differences in chemical composition and unit cell dimensions between synthetic and natural alunite are ascribed to the substitution of H_3O^+ (hydronium ion) for Na^+ and K^+ in the synthetic alunite structure.

The chemical composition of the synthetic alunite specimens differs from the theoretical composition of alunite in the slight deficiency of total alkalis and alumina and in the excess of water. The excess water is too great to be ascribed to slight analytical errors or minor compositional irregularities. A small part of this excess probably represents absorbed water and any impurities (possibly a little H_2SO_4) which are totaled with combined water when the water content of the samples is obtained by subtracting the total alkalis, alumina and sulfur trioxide from 100 per cent. Most of the excess water, however, is attributed to the replacement of K^+ and Na^+ by H_3O^+ in the synthetic alunite. Recalculations of the analyses into $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, $\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$, and $(\text{H}_3\text{O})\text{Al}_3-$

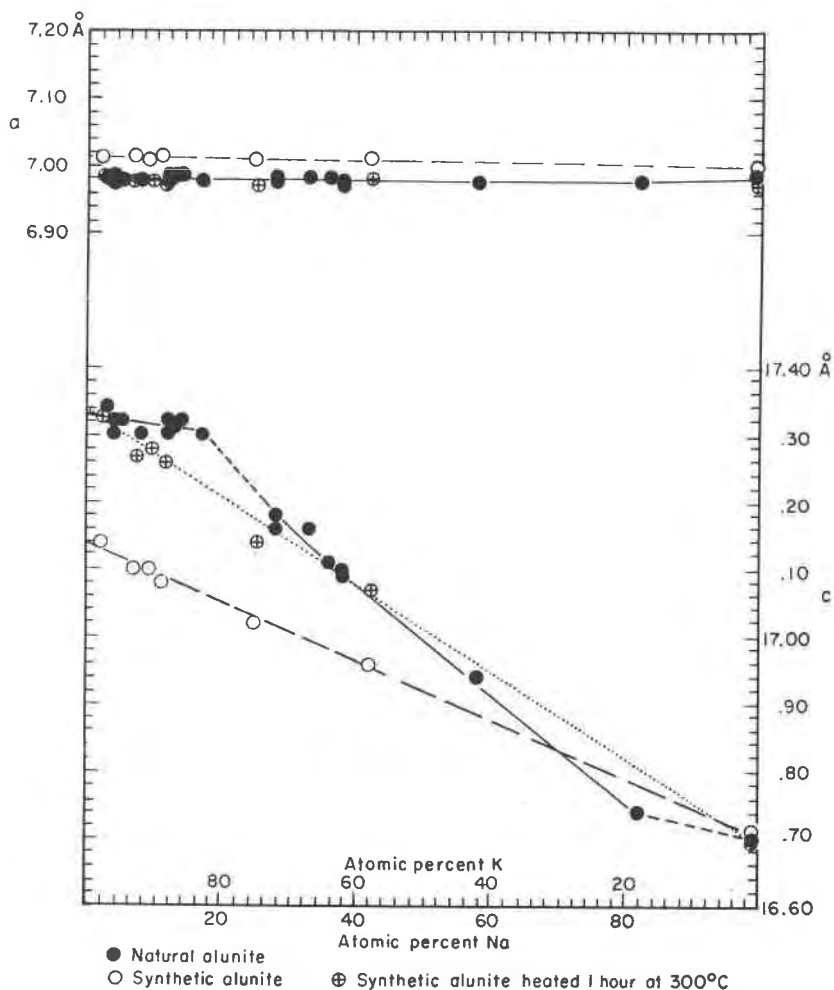


FIG. 2. Variation of the unit cell dimensions, a and c , with changes in the relative atomic percentages of potassium and sodium in synthetic and natural alunites.

$(\text{SO}_4)_2(\text{OH})_6$ indicate that about 15 per cent of the latter compound is present in each synthetic sample.

Isomorphous substitution of H_3O^+ for K^+ and NH_4^+ in analogous synthetic compounds in the jarosite group of minerals (iron-bearing analogues of the alunite series) has been demonstrated by Shishkin (1951). These jarosites were produced in sulfate solutions of low pH at temperatures ranging from 100–170° C., conditions which are similar to those of the alunite synthesized by the writer. A similar synthetic compound was

shown by Hendricks (1937) to have the jarosite crystal structure, though he interpreted the isomorphous substitution as H_2O molecules substituting for K^+ with the balance of charge preserved by the simultaneous replacement of OH^- by H_2O .

The values of a of the synthetic alunite samples are only slightly larger than those of natural alunite and natroalunite. The value of c of synthetic potassium alunite is 0.20 \AA smaller than the corresponding natural alunite, but the value for synthetic sodium alunite and natural natroalunite is nearly the same (see Table 3 and Fig. 2). The smaller c of the synthetic alunite can be explained by the partial substitution of H_3O^+ for K^+ if the effective radius of H_3O^+ is considered smaller than that of K^+ and close to that of Na^+ . Richards and Smith (1951) report a radius of 0.99 \AA for H_3O^+ in acid monohydrates ($\text{HNO}_3 \cdot \text{H}_2\text{O}$ or H_3ONO_3).

Brophy (personal comm.) heated synthetic alunite similar to that of this study from 120° to 300° C. and found that the excess water was driven off and the unit cell dimensions approached the values of natural alunite. Accordingly, the seven synthetic specimens of this study were heated to 300° C. for 1 hour, and after cooling, their cell dimensions were measured. All the cell dimensions of the heat-treated specimens were in the range of values for natural alunite of corresponding potassium-sodium content. The least change in unit cell size on loss of water was shown by the sodium end member, as would be expected if the expelled H_3O^+ has nearly the same ionic radius as Na^+ .

The plot of a and c of the synthetic alunites against their relative atomic percentages of potassium and sodium indicates the nature of the isomorphous series. The a dimension is nearly constant both in the untreated specimens (about 7.01 \AA) and in the heat-treated specimens (about 6.98 \AA), the value for the heat-treated specimens being about the same as that for natural alunites. The c dimension, however, shows a marked linear shrinkage of the unit cell with increasing content of sodium for both untreated and heat treated series. (See Fig. 2.) Such relationships satisfy Vegard's law, which requires that unit cell dimensions vary linearly with change in composition, expressed in atomic per cent.

Nineteen specimens indicate the nature of isomorphous substitution in naturally occurring alunites. Substitution of Na^+ for K^+ occurs over the entire alunite-natroalunite system although the resulting contraction of the unit cell is not exactly a linear function. The plotted positions of specimens in Fig. 2 outlines a shallow reverse S-shaped curve that deviates slightly from the straight line defined by Vegard's law. The potassium-rich part of the system shows positive deviation from Vegard's law and the sodium-rich part shows negative deviation.

The synthetic specimens that were heated to 100° C. define a straight

line which is also the line defined by Vegard's law for the natural alunites.

Two samples from the Al Kee Mee deposit, Marysvale, Utah, with bulk compositions $K_{56}Na_{44}$ and $K_{44}Na_{56}$ (not shown in Table 3 or Fig. 2), on the basis of x-ray diffraction prove to be mixtures of alunite and natroalunite end members. No distinction of the two minerals has been possible by optical means because the minerals are so finely mixed that they appear homogeneous under the microscope. Possibly these mixtures represent unmixed phases from originally unstable homogeneous alunite, but at present there are insufficient data to prove the existence of such a region of instability in the alunite-natroalunite system.

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