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SULFATE STUDIES II.

SOLID SOLUTION BETWEEN ALUNITE AND JAROSITE

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ABSTRACT

An alunite-jarosite solid solution series has been synthesized at 78° C./1 atm., 105° C./1 atm., and 150° C./6.1 atm., with a 1:3 molar ratio of K^+ to total trivalent (Al-Fe) cation using H_2SO_4 as solvent to prevent hydrolysis of ferric ions. The Fe^{3+}-Al^{3+} substitution produces little effect upon c_0 (17.21 Å for jarosite to 17.29 Å for alunite) but causes a continuous change in a_0 from 7.30 Å (jarosite) to 6.98 Å (alunite).

The Fe:Al ratio is higher in all products than in the original solutions, but the preference for Fe^{3+} in the structure is lowered with increased temperature and reduced acidity. It is suggested therefore that most alunite deposits that are formed during alteration of iron bearing rocks crystallize under reducing conditions which inhibit the production of ferric ion. The postulation of pyrite oxidation as the source for supergene sulfate ion responsible for the formation of the Tolfa, Italy alunite deposits and in part for those at Marysvale, Utah is questioned on the basis of lack of Fe^{3+} in the alunite structure at these localities.

The existence of a natural solid solution series is proposed, but intermediate compounds are rare.

INTRODUCTION

Alunite and jarosite are two relatively common basic sulphates that occur under a wide range of geologic environments. The alunite group, which includes jarosite, has the general composition, $AB_3(SO_4)_2(OH)_6$, in which A may be K^+, Na^+, Pb^{2+}, NH_4^+ or Ag^+ and B either Fe^{3+} or Al^{3+}. For alunite $A=K^+$, $B=Al^{3+}$ and in jarosite $A=K^+$ and $B=Fe^{3+}$. The alunite group, and related plumbogummite and beudanite groups, have been of interest to a number of investigators because of the wide range of ionic substitution possibilities and frequent association with hydrothermal mineral deposits.

Much excellent work has been accomplished on the study of the occurrence, synthesis and mode of origin of these minerals, but the bulk of the investigations has been directed towards alunite. This paper is the result of laboratory investigations prompted by the co-existence of jarosite and alunite in replacement type alunite deposits at Marysvale, Utah.

The alunite group includes eight mineral species assigned to the space group R3m, as follows:

Alunite	$KAl_3(SO_4)_2(OH)_6$
Natroalunite	$NaAl_3(SO_4)_2(OH)_6$
Jarosite	$KFe_3(SO_4)_2(OH)_6$
Natrojarosite	$NaFe_3(SO_4)_2(OH)_6$
Ammoniojarosite	$NH_4Fe_3(SO_4)_2(OH)_6$
Argentojarosite	$AgFe_3(SO_4)_2(OH)_6$
Beaverite	$Pb(Cu, Fe, Al)_3(SO_4)_2(OH)_6$
Plumbojarosite	$PbFe_6(SO_4)_4(OH)_{12}$

Hendricks (1937) determined the crystal structure of alunite, and a diagram of the hexagonal unit cell with $Z=3$ is given in Figure 1. The K^+ is present in 12-coordination between six O and six (OH) ions. The Al (or Fe^{3+}) is in 6-coordination between four (OH) and two O ions. The K position is relatively tolerant to ionic size. Hendricks states (p. 776) " . . . the univalent jarosites probably have the same structure," and gives the unit cell dimensions (here converted to angstrom units) as follows:

	a	c
Alunite, Rosita Hills, Colorado	6.97	17.38
Jarosite, Meadow Valley Mine, Pioche, Nevada	7.21	17.03

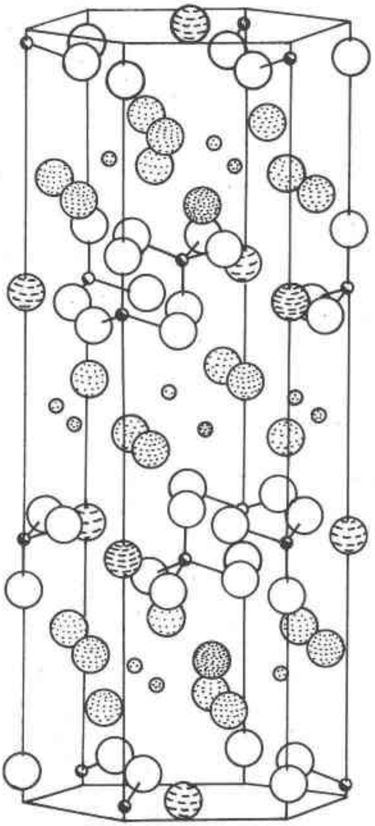

FIG. 1. The structure of alunite-jarosite shown as the hexagonal unit cell, with the cell content $K_3(Al,Fe)_9(SO_4)_6(OH)_{18}$. The large circles represent the following ions:

K^+ dashed, OH^- stippled, $O^=$ unshaded.

The small stippled circles represent (Al, Fe) and the small shaded circles represent S^{6+}. Data derived and modified from Hendricks (1937).

TABLE I. CHEMICAL ANALYSES OF ALUNITES AND JAROSITES

	1	2	3	4	5	6	7	8	9	10	11	12
Na_2O				0.33	4.62		1.68			0.80		
K_2O	11.37	9.8	10.02	10.46	6.08	10.35	6.00	6.7	9.4	5.90	9.5	9.4
Al_2O_3	36.92	32.1	39.65	37.18	34.64	31.63	18.90	1.7				
Fe_2O_3				Tr.	2.16	8.01	28.73	52.5	47.9	49.25	48.1	47.9
SO_3	38.66	39.2	35.50	38.34	37.02	36.98	29.47	28.8	31.9	31.76	32.1	31.9
H_2O	13.05	18.8	14.83	12.99	15.38	12.10	10.57	9.2	10.8	11.35	10.3	10.8
Rem.				0.80	0.92	1.23	4.65					
Total	100.00	99.9	100.00	100.10	100.82	100.30	100.00	98.9	100.0	100.33	100.0	100.0

1. Theoretical alunite.
2. Synthetic alunite—Parker (1954).
3. Alunite. Tolfa, Italy (Dana, 7th Ed., Vol. II, p. 558).
4. Alunite. Mineral Products Mine, Marysvale, Utah. Parker (1954). Rem. is SiO_2 0.22, P_2O_5 0.58.
5. Alunite. Molokai, Hawaii. Laudermilk (1935). Rem. is CaO 0.28, SiO_2 0.04, TiO_2 0.60.
6. Alunite. Copper Cap Uranium Prospect, Marysvale, Utah. $(K\,(Al_{.87}Fe_{.13})_3(SO_4)_2(OH_6)$ G. P. Brophy.
7. Alunite-Jarosite. Kopec, near Prague. Jirkovsky (1937). Rem. is CaO 0.84, MgO 1.55, insol. 2.26. $(K_{.7}Na_{.3})(Fe_{.5}Al_{.5})_3(SO_4)_2(OH)_6$.
8. Jarosite-Jaroso Blanco, Spain—Hintze (1930) p. 4200.
9. Jarosite. Mammoth Mine, Tintic District, Utah. Rem. is SiO_2 (Dana, 7th Ed., Vol. II, p. 561).
10. Jarosite. Jaroso Blanco, Spain, Hintze (1930), p. 4200.
11. Synthetic jarosite. Fairchild (1933).
12. Theoretical jarosite.

EXPERIMENTAL WORK

General Statement

Optical investigation of material collected at the Yellowjacket and Copper Cap prospects near Marysvale, Utah (Kerr, Brophy, Dahl, Green and Woolard, 1957) suggests that jarosite replaces alunite in some cases by a substitution of Fe^{3+} for Al^{3+}. An analysis by Jirkovsky (1937) (Table I, anal. 7) gives an almost 1:1 ratio of Al:Fe, yet most available analyses of alunite show little, if any, Fe^{3+} even when the mineral occurs in an iron rich environment. This is quite evident in the analysis given by Laudermilk (1935) (Table I, anal. 5) of alunite from Molokai, Hawaii, containing 2.16 per cent Fe_2O_3.

Experimental work was outlined (1) to determine whether or not a solid solution could exist in synthetic material, and (2) if so, why it is not more evident in natural materials.

Plan of Investigation

The first step in attempting to synthesize a continuous series was the preparation of alunite, jarosite and intermediate compounds under one set of conditions with the only variable being the Al:Fe ratio in the reactants. All materials possible were studied by *x*-ray diffraction techniques and analyzed for the amounts of Fe^{3+}, Al, and H_2O (Tables II, III). One experimental series was completely analyzed (Table VI), as well as one mineral of intermediate composition (Table I, anal. 6).

Other series were synthesized wherein temperature pressure and pH were varied (Tables IV, V). The range of syntheses possible was limited by lack of high temperature-pressure equipment.

Synthesis of alunite and jarosite

A systematic approach to the synthesis of jarosite was first reported by Fairchild (1933). A one to three molar ratio of potassium sulphate to ferric sulphate plus 20 per cent excess of the latter (0.2 g K_2SO_4 and 1.6 g $Fe_2(SO_4)_3$ were dissolved in 20 ml of 0.75 N sulfuric acid and heated in a sealed tube. Fairchild found that the nature of the product was strongly dependent upon the temperature of preparation. A reaction started at 110° C. and completed at 180° C. for 24 hours gave small rhombohedral crystals of jarosite (Table I, anal. 11), but reactions carried out at steam bath temperatures resulted in products called basic ferric sulfates by Fairchild.

Parker (1954) prepared synthetic alunite by dissolving one gram K_2SO_4 with four grams of $Al(SO_4)_3 \cdot 18H_2O$ in 150 ml distilled water. The reaction was carried out by refluxing the solution 2 to 4 days at its boiling point. The product was identified as alunite by x-ray diffraction, although it did contain an anomalous amount of water (Table I, anal. 2).

Barrington (1957) was able to prepare alunite, jarosite and intermediate compounds using the procedure of Parker but substituting 0.2N H_2SO_4 as the solvent and increasing the concentration of the reactants.

Morey and Ingerson (1937) produced alunite by placing a mixture of microcline and albite in a sulphuric acid solution of potassium and aluminum sulfates. Seven days at the boiling point of the solution was sufficient for nearly complete conversion of the feldspar to alunite, and lower temperatures gave partial conversion.

In this study four series of compounds were prepared, differing from each other in the temperature of preparation. Series I and II were synthesized at 105° C. and 1 atmosphere pressure. Series III was prepared at 150° C. and 6.1 atmospheres, while Series IV was prepared at 78° C. and 1 atmosphere. Each method of synthesis required a somewhat different experimental procedure, although the general approach was the same in all cases.

Series I, II

The conditions of preparation of Series I (Table II) and Series II (Table III) were derived mainly from a consideration of Parker's (1954) and Barrington's (1957) methods. Since an open system was more convenient than sealed tubes, the reactions were carried out by refluxing the solutions at 105° C. and 1 atmosphere for three days. The above condi-

TABLE II. ANALYTICAL DATA FOR SERIES I SYNTHESIZED AT 105° C.—1 ATMOSPHERE PRESSURE

Sample #	Initial Al/Al+Fe	Wgt. K_2SO_4	Wgt. $Al_2(SO_4)_3 \cdot 18H_2O$	Wgt. $Fe_2(SO_4)_3$	Product Wgt.	Initial pH	Yield	Final Al/Al+Fe	H_2O loss 120° C. to 300° C.	H_2O retained	c	a
I-10	00%	4.4g	0.0g	39.0g	6.5g	0.5	26%	00.0%	5.28%	9.48%	17.21 Å	7.300 Å
I-13	74	4.4	35.5	10.7	6.6	1.1	27	117.9	3.5	11.16	17.26	7.244
I-12	81	4.4	40.0	8.0	4.8	1.2	20	30.0	3.32	11.45	17.26	7.212
I-9	85	4.4	42.7	6.4	4.6	1.3	20	38.4	3.04	11.58	17.27	7.192
I-8	89	4.4	45.6	4.6	4.4	1.3	19	52.3	3.34	11.68	17.27	7.108
I-6	93	4.4	48.4	2.9	3.5	1.3	16	69.2	4.69	11.84	17.29	7.052
I-11	95	4.4	49.7	2.1	2.8	1.4	13	75.0	5.21	12.12	17.29	7.032
I-5	100	4.4	53.3	0.0	3.8	1.6	18	100.0	6.93	12.49	17.29	6.980

Table III. Analytical Data for Series II Synthesized at 105° C.—2 Atmosphere Pressure

Sample #	Initial Al/Al +Fe	Wgt. K_2SO_4	Wgt. $Al_2(SO_4)_3 \cdot 18H_2O$	Wgt. $Fe_2(SO_4)_3$	Product Wgt.	Yield	Final Al/Al +Fe	H_2O loss 120° C. to 300° C.	H_2O retained	c	a
II-1	0.0%	4.4g	0.0g	44.0g	8.73g	35%	00.0%	4.34%	10.07%	17.17 Å	7.288 Å
II-2	76.	4.4	40.5	10.5	3.77	15.4	14.2	5.37	10.14	17.19	7.248
II-3	80.	4.4	42.5	8.9	3.27	13.5	18.3	5.07	10.81	17.20	7.232
II-10	86.	4.4	45.7	6.2	4.67	20.1	41.5	3.27	11.31	17.21	7.184
II-9	88.	4.4	46.8	5.3	4.91	21.5	51.5	3.85	11.25	17.23	
II-4	93.	4.4	49.5	3.1	1.98	8.7	52.3	4.42	11.28	17.24	7.128
II-8	91.	4.4	48.4	4.0	4.18	18.5	58.7	3.90	11.00	17.23	7.108
II-7	92.	4.4	49.0	3.6	3.96	17.7	63.8	3.70	11.23	17.26	7.064
II-5	97.	4.4	51.5	1.3	2.30	10.8	84.9	5.27	11.31	17.26	7.004
II-6	100.	4.4	53.0	0.0	3.33	16.0	100.0	—	—	17.26	6.976

tions were obtained by immersing 200 ml. round bottomed flasks, to the level of the contained reactants in a constant temperature oil bath held at 117° C. Condensers were attached to the flasks to maintain the level of the solutions. Fairchild (1933) reported failure in preparing jarosite under these conditions.

The reactants were prepared by using a 1:3 molar ratio of potassium ion to total trivalent cation, with aluminum and ferric iron being mixed in any desired molar ratio. To obtain fairly concentrated solutions 0.5 mole of potassium ion and 1.5 moles of trivalent cation were used, the required sulphate being calculated from the molar ratios. The solvent was 100 ml of 0.2 N sulfuric acid. Sulfuric acid was chosen because it is a common acid in nature, contains no interfering ions, and gives a still larger sulfate concentration tending to push the reaction further toward completion.

Upon dissolution of the sulfates, the mixture was placed in a bath preheated to 80° C. to prevent cooling with resulting crystallization of the alums. The bath temperature was then raised to 117° C. over 3 hours time. After 72 hours the products were separated and boiled in H_2SO_4 to dissolve any alum or starting material present, then boiled in distilled water and finally collected with thorough washing in a Buechner filter. After drying at 120° C. for 4 hours, the product was weighed to determine the yield.

Series III

Series III, was prepared in order to observe the effects of increased temperature and pressure on the preparation of synthetic alunite, jarosite and a few intermediate compounds. The 1:3 molar ratio of potassium to trivalent cation was maintained, but the amount of reactant varied in each case. The data are given in Table IV.

TABLE IV. ANALYTICAL DATA FOR SERIES III SYNTHESIZED AT 150° C.—6.1 ATMOSPHERES PRESSURE

Sample #	Initial Al/Al+Fe	Wgt. K_2SO_4	Wgt. $Al_2(SO_4)_3 \cdot 18H_2O$	Wgt. $Fe_2(SO_4)_3$	Solvent	Time	Product Wgt.	Yield	Al/Al+Fe	% H_2O loss at 120° C.	% H_2O retained at 120° C.	*c*	*a*
III-2	00.0%	4.4g	—	44.0g	0.2N H_2SO_4	15 hr.	11.0g	44%		2.92	10.83	17.20Å	7.296Å
III-3	00.0	3.5	—	31.4	.1N H_2SO_4	15	13.1	63		2.77	10.82	17.20	7.296
III-4	0.00	3.5	—	31.4	.04N H_2SO_4	15	15.0	75	00.0%	2.41	10.87	17.20	7.296
III-5	00.0	1.8	—	15.3	.1N H_2SO_4	18	9.0	90		1.64	10.99	17.22	7.296
III-9	70.0	1.8	14.0g	4.6	.1N H_2SO_4	18	3.7	39	28.00	3.46	11.56		
III-10	90.0	1.8	18.0	1.5	.1N H_2SO_4	18	2.8	32	79.00	5.85	11.03		
III-1	100.0	4.4	53.0	—	.2N H_2SO_4	15	3.9	19		7.02	12.04	17.29	6.980
III-6	100.0	1.8	20.0	—	.1N H_2SO_4	18	3.1	37	100.0	6.87	12.52	17.29	6.980
III-7	100.0	1.8	20.0	—	H_2O	18	3.8	46		6.76	10.32		

The synthesis conditions of 150° C. and 6.1 atm. were achieved by placing a 125 ml flask containing the reactants and solvent into a sealed steel bomb and heating the bomb in the oil bath. The neck of the flask was partially closed to prevent the entrance of impurities.

Series IV

Series IV was prepared at 78° C. and 1 atm. pressure. The solutions were sealed in glass tubes and heated 7 days in boiling ethyl alcohol contained in a 3–1 reaction flask fitted with a reflux condenser. Only 35 ml. of solvent was used and the quantity of reagent reduced accordingly. The same 1:3 molar ratio of potassium to trivalent cation was maintained. Product was obtained in all cases but only three of the five reactions gave sufficient product to be collected. The data pertaining to this synthesis are given in Table V.

Chemical Analysis

The analysis of the yields was carried out in two separate procedures, one to determine the water content and one to determine the amount of iron and aluminum present. The iron was determined by titration with ceric ion after reduction by zinc amalgam. Aluminum was separated from iron by extraction of ferric chloride into ether followed by precipitation and weighing of the aluminum as the 8-hydroxyquinolate. The work of Parker (1954) had indicated a probable deficiency of trivalent ion and an excess of water, and this was found to be the case. Excess water was removed by heating the samples Series I and II to 300° C., and the remaining water was found to be nearly that of the theoretical content. The same results were obtained for Series III after heating to 120° C.

Complete analyses of the products of Series II are given in Table VI.

X-ray diffraction analysis

All synthetic and natural alunites, jarosites and intermediate compounds were analyzed by x-ray diffraction using both film and diffractom-

TABLE V. ANALYTICAL DATA FOR SERIES IV SYNTHESIZED AT 78° C.—1 ATMOSPHERE PRESSURE FOR 168 HOURS

Sample #	Initial Al/Al +Fe	Wgt. K_2SO_4	Wgt. $Al_2(SO_4)_3 \cdot 18H_2O$	Wgt. $Fe_2(SO_4)_3$	Solvent	Product Wgt.	Yield	c[1]	a[1]
IV-1	100%	1.8g	20.0g	—	0.2N H_2SO_4	—	—	—	—
IV-2	100	1.3	15.0	—	0.2N H_2SO_4	—	—	—	—
IV-3	100	1.8	20.0	—	0.1N H_2SO_4	0.21g	2.5%	17.09 Å	7.012 Å
IV-4	00.0	1.8	—	16.7g	0.2N H_2SO_4	0.44	4.4	—	—
IV-5	00.0	1.3	—	12.5	0.1N H_2SO_4	0.47	6.3	17.13	7.316

[1] The product yield was too small to permit determination of water loss, so the diffraction data is representative of yields containing excess H_2O.

TABLE VI. CHEMICAL ANALYSES—SERIES II SYNTHETIC ALUNITE—JAROSITE

	II-3	II-3	II-10	II-9	II-8	II-7	II-5	II-6
K_2O	9.61	9.61	9.82	9.97	10.36	10.38	10.71	11.28
Al_2O_3	4.41	5.70	13.91	17.49	20.08	22.03	30.37	36.91
Fe_2O_3	42.20	40.45	29.88	25.15	21.95	19.45	8.41	—
SO_3	32.88	33.05	34.53	35.10	35.63	36.02	37.40	38.13
H_2O	10.17	10.82	11.33	11.24	11.04	11.27	11.27	13.31
Rem.	1.01	0.47	0.67	0.92	1.69	1.07	1.57	0.70
	100.28	100.10	100.14	99.87	100.75	100.22	99.63	100.33

2. $K(Al_{.14}Fe_{.86})_3(SO_4)_2(OH)_6$
3. $K(Al_{.18}Fe_{.82})_3(SO_4)_2(OH)_6$
10. $K(Al_{.42}Fe_{.58})_3(SO_4)_2(OH)_6$
9. $K(Al_{.52}Fe_{.48})_3(SO_4)_2(OH)_6$
8. $K(Al_{.59}Fe_{.41})_3(SO_4)_2(OH)_6$
7. $K(Al_{.64}Fe_{.36})_3(SO_4)_2(OH)_6$
5. $K(Al_{.85}Fe_{.15})_3(SO_4)_2(OH)_6$
6. $KAl_3(SO_4)_3(SO_4)_2(OH_6$

Analyst—G. P. Brophy.

eter techniques on powdered samples. Unfiltered Fe radiation was used in the diffractometer study and filtered Fe radiation with the film technique.

The unit cell dimensions of the materials were calculated from the (0006) and $(22\bar{4}0)$ reflections. Calibration of the diffractometer was checked before and after each run using a silicon standard.

Results

A complete solid solution series has been produced synthetically. The major change is noted in the *a* dimension which increased from 6.976 Å for synthetic alunite to 7.288 Å for synthetic jarosite. The change is nearly linear, and a plot (Fig. 2) shows a continuous change in the *a* dimension. The *c* dimension ranges from 17.26 Å for synthetic alunite to 17.17 Å for synthetic jarosite. Comparison of the data for Series I and II (Tables II and III) shows the variation in *a* to be 0.320 Å and 0.312 Å and in *c* to be 0.08 Å and 0.09 Å respectively.

The unit cell dimensions for alunites and jarosites have been taken from the literature and plotted on Fig. 2. The unit cell dimensions of an intermediate compound from Kopec (Table I, anal. 7) have been determined and plotted.

An alunite sample from the Copper Cap Uranium prospect (Kerr *et al.*, 1957) has iron present and gives the formula, $K(Al_{.87}Fe_{.13})_3(SO_4)_2(OH)_6$.

The plot of the unit cell dimensions (Fig. 2) of the synthetic series shows that the Fe^{3+} substitution produces a greater change in *a* than *c*.

In the synthesis of intermediates between alunite and jarosite at 105° C. the preferential incorporation of iron over aluminum is quite noticeable

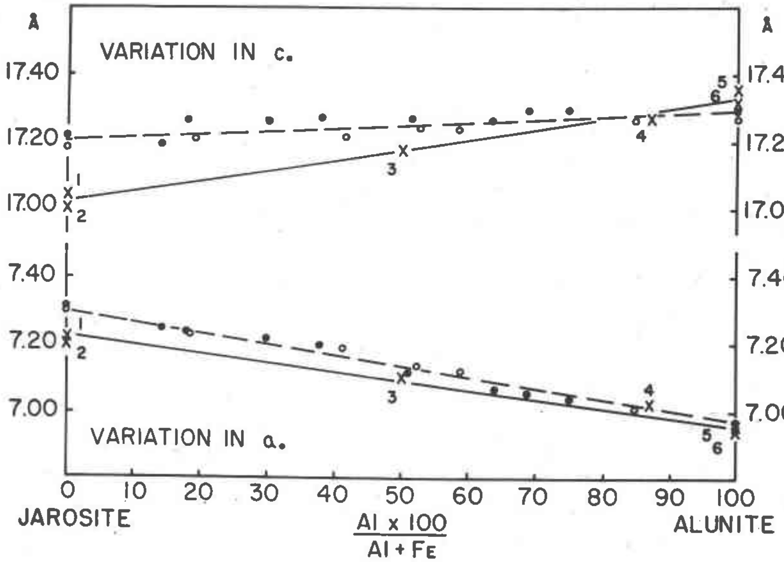

FIG. 2. Variation in *a* and *c* for the products of Series I (open circles) and Series II (solid circles) experiments are shown by dashed lines. Proposed variations in lattice dimensions for an alunite-jarosite solid solution are shown by the solid lines. The numbers on the natural series (x) plots refer to the following:

1. Jarosite, Pioche, Nevada
2. Jarosite, Tolfa, Italy
3. Alunite-jarosite, Kopec, Czechoslovakia
4. Alunite, Copper Cap Prospect, Marysvale, Utah
5. Alunite, Rosita Hills, Colorado
6. Alunite, Mineral Products Mine, Marysvale, Utah

(Fig. 3). However, at conditions of higher temperature and pressure and lower acidity this preference for iron is greatly reduced (Products III-9, III-10, Table IV).

The intermediates prepared at 105° C. and 1 atm. in 0.2N sulfuric acid showed a large preferential removal of iron from the reaction solution. For example, product II-2 (Table III) was prepared from a solution containing an initial Al/Al+Fe of 76 per cent, and in the resultant product Al/Al+Fe was only 27 per cent. The final composition of the products is plotted as a function of the composition of the initial solution (Fig. 3).

Because of the tight bonding of hydroxyls to the trivalent cation the B position is very intolerant of size difference in the *a* direction, and the incorporation of the larger ferric ion expands the entire hydroxyl sheet. Aluminum and ferric ions have nearly the same attraction for hydroxyl

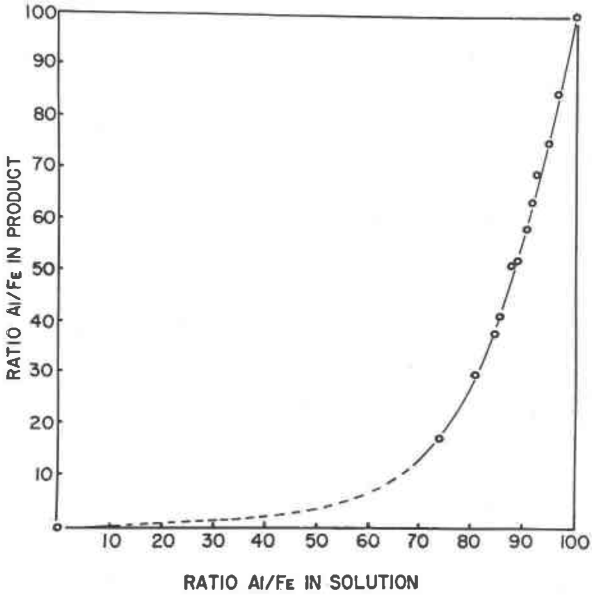

FIG. 3. Comparison of the initial solution and final reaction product ratios of Al/Fe. The data are from Series I and II experiments, obtained at 105° C., 1 atmosphere pressure.

ion in the crystalline state, this being demonstrated, for example, by the almost identical parameters of the ions in their respective hydrous oxides (Bernal and Megaw, 1935). Actually the fact that alunite requires a higher temperature for dehydration than jarosite (Kulp and Adler, 1950) may indicate that the aluminum forms a slightly stronger bond to hydroxyl.

Hypothesis concerning the mechanism of reaction

Because of their small size and high charge aluminum and ferric ions are undoubtedly hydrated in aqueous solution being coordinated with six water molecules. Both of these complex ions tend to hydrolyze extensively, with hydrated ferric ion hydrolyzing to a considerably greater degree than the hydrated aluminum ion, as is shown by the contrast in the initial pH values of the Series I solutions (Table II) or by comparison of the ferric hydrolysis constant (630×10^{-5}) with the aluminum hydrolysis constant (1.3×10^{-5}) for the reaction

$$X(H_2O)_6{}^{+++}\rightarrow X(H_2O)^5\ OH^{++}+H^+$$

Acid solution retards this hydrolysis but at any one value of pH the hydrated ferric ion will contain more hydroxyl and less water in its coordination sphere than does the hydrated aluminum ion, and only at considerably higher pH will the aluminum hydrate convert sufficient water into hydroxyl so that it resembles the ferric complex of the lower pH.

A necessary condition for the formation of the alunite crystal structure is the presence of hydroxyl ions; the hydroxyls found in the lattice must be the same hydroxyls associated with the aqueous trivalent ion. This leads to the basic postulate that the reaction does not form a compound directly related to the ratio of trivalent cations in solution, but favors the ion which has on the average the greatest number of hydroxyls coordinated with it. Naturally the concentration of trivalent ion does play a role, but the actual position of the equilibrium depends upon the ratio of the average number of hydroxyls coordinated to the ferric ion to the average number of hydroxyls coordinated to the aluminum ion.

The preferential incorporation of iron into samples prepared at 105° C. in 0.2 N H_2SO_4 is demonstrated in synthetic Series I and II. At pH ranging from 0.5 to 1.6 the ferric ion has far more associated hydroxyl ions than does the aluminum and so it is definitely preferred over aluminum in the formation of the alunite-jarosite lattice. Reduction of acidity and increase in temperature in Series III (Table IV) greatly reduces the preferential incorporation of iron since the ratio of ferric coordinated hydroxyl to aluminum coordinated hydroxyls is also greatly reduced.

DISCUSSION

Alunite is known from numerous localities that have undergone hydrothermal alteration, and is often associated with metallic mineralization. Jarosite is also fairly common but is usually associated with a supergene environment. This investigation has produced the information listed below that is of interest with respect to these sulfates.

With regard to the synthetic alunite-jarosite compounds the following may be noted:

1. A solid solution series between synthetic alunite and synthetic jarosite does exist.
2. The Fe^{3+}-Al^{3+} substitution produces a greater effect upon the *a* dimension of the unit cell, than upon the *c* dimension.
3. Under the experimental conditions outlined Fe^{3+} is preferentially taken up over Al^{3+}.
4. Increase in temperature and reduction of acidity reduces the preference of Fe^{3+} over Al^{3+}.
5. Increase in temperature and pressure reduces the amount of excess water in the structure.

Concerning alunites and jarosites the following may be noted:

1. Alunite and jarosite may form a solid solution series in nature.
2. Minerals intermediate between alunite and jarosite are rare.
3. In nature alunite without Fe^{3+} commonly is associated with iron oxides and iron bearing minerals.
4. Many alunite bodies occur in rocks which initially had iron in greater amount than is observed in the alunitized product.
5. Many investigators ascribe alunite formation to sulfate bearing solutions, but the source of the sulfate is open to question.

The lack of jarosite at Goldfield, Nevada is noteworthy even though there is abundant iron present in the mineralized rock as pyrite. Ransome (1909) presents the hypothesis of simultaneous solfatarism and oxidation and states (p. 193) " . . . hot ascending waters carried abundant hydrogen sulphide as shown by the extensive change to pyrite of the iron originally present in the dacite and other rocks as a constituent of magnetite and silicates." It would appear that the original iron available to the altering solutions remained in the lower oxidation state. Merwin and Posnjak (1937) state that in general oxidation of iron lags behind oxidation of sulfur under weathering conditions at the Copper Queen and the oxidation of pyrite produces a mixture of ferrous and ferric sulfates. They also point out that wall rock and the acid react to bring into solution other bases thus lowering the acidity of the solutions.

Turner (1898) describes an alunite locality at Tres Cerritos, California, wherein the alunite had formed from solfataric action on augite andesite tuffs, and a chemical analysis of the material yields only 0.23 per cent Fe_2O_3. The soda alunite described by Laudermilk (1935) from Hawaii contains only 2.16 per cent Fe_2O_3 even though the original rock was basalt.

The mechanism of pyrite oxidation to form alunite has been proposed for several localities. De Launay (1907) in his discussion of the alunite bodies occurring in trachytes at Tolfa, Italy, suggests that the alunite has formed from the oxidation of pyrite-rich zones in the trachytes and that the alunite is of supergene origin.

The role of pyrite in alunite formation at Marysvale, Utah has been discussed by Callaghan (1937) and Willard and Proctor (1946). Two contrasting conclusions were reached.

Callaghan (1937) contends the probable origin of the replacement alunite deposits near Marysvale, Utah involves the oxidation of pyrite. He states (p. 116) "It seems at the present stage of the investigation that ascending sulphate-bearing solutions have been the primary source of the replacement deposits, but that the migration and concentration of alunite may have taken place under the influence of descending sulphate-bearing solutions derived from the oxidation of pyrite." One of the largest replacement type alunite deposits at Marysvale, the White Horse, has been described by Willard and Proctor (1946). Alunite replaces a latite flow which contains 1.27 per cent Fe_2O_3 and 3.93 per cent FeO. An analysis of highly alunitized latite (p. 626, Table II) gives only 0.97 per cent Fe_2O_3. They present the following conclusions (p. 631):

"The alteration to alunite was produced by a sulphate-bearing solution that reacted with the original constituents of the latite, taking into solution, in addition to potash and alumina, all the sodium together with a part of the iron and silica. . . . Most of the dissolved silica and iron were carried beyond the present areas of alunitization before they were deposited. . . . The lack of pyrite in all rocks of the deposit, without evidence of it ever having existed in quantity, makes it doubtful that the mineralizing solution developed from the oxidation of that mineral."

In the same area lie the Yellow Jacket, Mary's Lamb and Al-Kee-Mee prospects wherein replacement type alunite deposits have been formed in pyroxene andesites (see Kerr *et al.*, 1957, pp. 180–181). Overlying these alunite bodies are large masses of ferruginated and silicified rock containing numerous silicified breccias. At the Yellow Jacket prospect the iron-silica cap is underlain by a replacement hematite deposit which is, in turn, underlain by alunite. In all of these places abundant iron was available during the formation of the alunite deposits to yield an iron-bearing alunite. It would seem logical to conclude that the hydrothermal solutions that formed the alunite deposits were only weakly acid in nature.

If alunite is formed in acid sulfate solutions in the temperature range of the experiments of this paper the solutions probably would be sufficiently reducing to prevent the oxidation of Fe^{3+}, since under these conditions the resultant product should contain Fe^{3+}. Therefore the supergene origin of the Tolfa and part of the Marysvale deposits is doubtful. Oxidation of pyrite to yield sulfate ion should also yield sufficient Fe^{3+} which would become a part of the alunite structure.

Higher temperatures attending formation of alunite may reduce the preferential incorporation of iron in the structure. Excess water in alunite might be indicative of crystallization at low temperatures.

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