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SULFATE STUDIES IV: THE JAROSITE—NATROJAROSITE—HYDRONIUM JAROSITE SOLID SOLUTION SERIES

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ABSTRACT

A synthetic and natural solid solution series exists among jarosites by virtue of a K^+-Na^+-H_3O^+ substitution. The presence of hydronium ion can best be detected from a study of thermal and *x*-ray data. There is a pronounced weight loss from 240° to 280° C. which corresponds to the amount that can be assigned as hydronium ion in each of the jarosites. With increasing H_3O^+ content there is a marked variation in *c*, which decreases from 17.192 Å for K jarosite, but increases from 16.620 Å for Na jarosite. There is, however, little change in *a*. With increasing T and P the amount of H_3O^+ in the structure of synthetic materials decreases.

INTRODUCTION

The substitution limits in the alunite group of minerals has been investigated for $K\ Al_3(SO_4)_2\ (OH)_6 - Na\ Al_3(SO_4)_2\ (OH)_6$ by Parker (1962), for $K\ Al_3(SO_4)_2(OH)_6 - K\ Fe_3(SO_4)_2(OH)_6$ by Brophy *et al.* (1962), and partially for $K\ Fe_3(SO_4)_2(OH)_6 - (H_3O)Fe_3(SO_4)_2(OH)_6$ by Kubisz (1960, 1961). In this present work the K^+-Na^+-H_3O^+ substitution in jarosites is reported.

The role of bonded H-O as a water molecule in the structure of these minerals has been questioned for some time. The existence of the mineral carphosiderite, listed in Dana as $(H_2O)Fe_3(SO_4)_2(OH)_5H_2O$, and related species cyprusite, utahite and borgstromite has been questioned by Moss (1957) and Van Tassel (1958), and it is, in fact, a hydronium-bearing natrojarosite. Szyszkin *et al.* (1958) demonstrated the hydronium character of $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, *i.e.* $(H_3O)Fe_3(SO_4)_2(OH)_6$, and further, a connection between this sulfate and jarosite. Kubisz (1961) has shown that hydronium jarosite, as, for example, $(H_3O)_{0.88}Na_{0.07}K_{0.05}Fe_3(SO_4)_2(OH)_6$, does exist in nature.

A general discussion concerning the alunite structure is to be found in Hendricks (1937) and Brophy *et al.* (1962) and need not be repeated here.

OCCURRENCE OF JAROSITES

Jarosite has been reported from a number of different geologic environments, a few of which are as follows: In glauconitic sandstones (Briggs, 1951; Warshaw, 1956; Mitchell, 1962); filling of cavities in Triassic arkoses (Lacroix, 1915); with other sulfates in bedded cherts in California (Foshag, 1931); as part of the heavy mineral assemblages from the St. Peter Sandstone (Tyler, 1936); in Eocene clays from Denmark (Bogvard, 1942) and Arkansas (Mitchell and Jordan, 1962); as an alteration of sulfides in the Tintic area of Utah (Butler *et al.* 1920); in the oxidized lead ores at Leadville, Colorado (Emmons *et al.*, 1927); in the oxidized zones of the mines of northern Chile (Bandy, 1938); as an oxidation product of pyrite deposits in the Urals (Breshenkov, 1946); in association with alunite deposits at Marysvale, Utah (Kerr *et al.*, 1957); as an oxidation product in altered quartz porphyry at Potosi, Bolivia (Milton, 1935); and in association with tourmaline, rutile, kyanite, sericite and barite in an altered quartz porphyry in California (Hutton and Bowen, 1950). Natrojarosite is far less common than the potassium rich variety. The carphosiderite from the type locality in Greenland has been proven by Van Tassel (1958) to be a natrojarosite. Bandy (1938) reports the material from Chuquicamata, and Kubisz (1958) from the Polska Mine in Upper Silesia. Others are listed in Palache *et al.* (1951) and Hintze (1929).

Hydronium jarosite has been found by Kubisz (1961) in Poland at the Staszic Mine sulfide mine wherein it occurs as crusts deposited on a dolomitic zone in the mine, formed after a gallery had been opened. At the Thorez coal mine jarosite with a low alkali content was found in a gallery wherein the temperature was 32° C. The jarosite occurs in the coal bed shale along with melanterite and goethite. The low alkali content in the mine waters, due to the more rapid decay of the sulfides rather than the rock forming minerals gives rise to the hydronium jarosite.

Jarosite has also been found to deposit at hydrothermal springs in Yellowstone National Park (Allen and Day, 1935). In certain springs jarosite is found to occur interstratified with sinter several millimeters in thickness. The jarosite found as hot spring deposits contains an anomalous amount of water. Their analyses agree well with the formula $K_2O \cdot 3Fe_2O_3 \cdot 4SO_4 \cdot 10H_2O$, whereas regular jarosite contains only six molecules of water. The analysts concluded that only 0.2% was nonstructural, since this represents the weight loss on heating to 105° C.

In reviewing much of the literature on alunites and jarosites—especially those with reliable chemical analyses—it is often noted that a deficiency of alkali is usually accompanied by an excess of water.

EXPERIMENTAL WORK

The original investigation under consideration by the writers was a synthesis of jarosites from solutions whose compositions would be varied from 100% K^+/alkali to 100% Na^+/alkali, and a comparison of the products with natural materials. This plan was followed (see below), and the products analyzed chemically at which point the "problem" of excess water arose. Unit cell dimensions were determined in every case.

Synthesis of jarosites. Fairchild (1933), using a 1:3 molar ratio of K_2SO_4

to $Fe_2(SO_4)_3$ in 20 cc of 0.75 N H_2 SO_4 plus an additional 20% of $Fe_2(SO_4)_3$, produced synthetic jarosite by heating his preparation in a sealed tube for 24 hours at 110° C., then elevating the temperature to between 165–180° C. for an additional 24 hours. The product had the color and habit of jarosite. At steam bath temperatures, a product resembling jarosite but high in water formed, and he assumed these products to be basic iron sulphates rather than a compound with the jarosite structure.

The synthesis procedure in this investigation is the same as described by Brophy *et al.* (1962). A molar ratio of 1:3 for Na+K:Fe was maintained, 0.05 moles of alkali sulfate and 0.15 moles of $Fe_2(SO_4)_3$ were dissolved in 100 ml. of 0.2 m H_2SO_4, and the solutions in flasks placed in an oil bath at 114±2° C. for 72 hours. The product was removed from the flasks, washed and air dried.

Chemical analysis. The chemical analyses were made in four steps. Water content was determined by weight loss on heating, iron volumetrically by titration with ceric ion, sulphate by precipitation as $BaSO_4$, and Na and K photometrically with a Beckman flame photometer. All samples were heated to 500° C. prior to determination of Fe,K,Na and SO_4. The analyses were recalculated to include the water remaining after heating to 150° C.

From the work of Fairchild (1933), Brophy *et al.* (1962) and Parker (1962), an "anomalous" amount of water could be expected in synthetic jarosites. Hence, analysis for the total water content was made with this in mind, and the following procedure used. Each sample was initially heated to 120° C. for four hours to remove any absorbed water. Three synthetic samples were chosen to determine a typical weight loss curve over the range of 120–500° C. Samples were heated over a 25–35° C. increment, and held at each desired temperature for 24 hours. The samples were removed to a desiccator to cool and then weighed. A plot of total weight loss (Fig. 1) shows that in the range of 80–150° C. there is a substantial loss which is attributed to removal of absorbed water. A plateau occurs until another loss is noted to take place around 240–280° C. The third, and major, weight loss begins at approximtely 365° C. and is completed by 470° C. The water loss between 365 and 470° C. very closely approximates the theoretical amount of water held as hydroxyl in the crystal lattice, and above this temperature the structure of jarosite is destroyed. The water loss from 120° to 300° C. has caused a change in the cell dimensions and a change in diffraction maxima intensities. Not all the loss in the range 120–300° C. can be attributed to being structurally held. The minute particle size of the synthetic material probably allows the retention of some surface absorbed water to high temperatures.

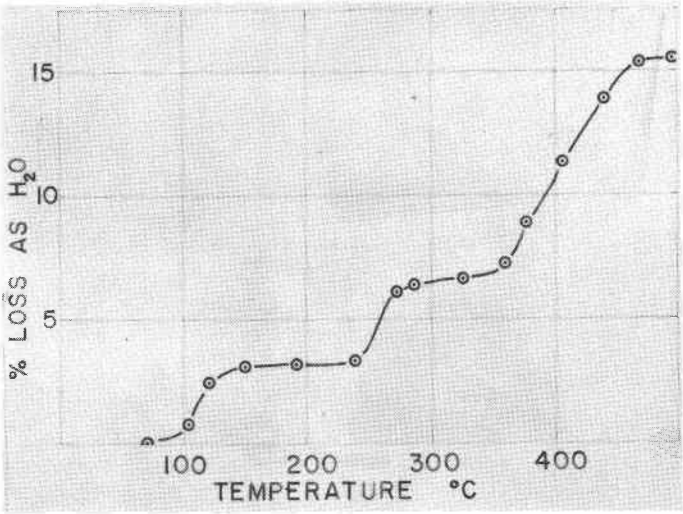

FIG. 1. Weight loss as a function of rising temperature in synthetic jarosite. Each temperature point has been maintained for 24 hours.

All analyses were recalculated to unit cell contents, assuming all the sulphate positions to be filled (six in all) and assigning OH to 18 structural positions. The recalculated synthetic jarosites have been tabulated (Table 1) and plotted (Fig. 2). The excess water can be almost entirely

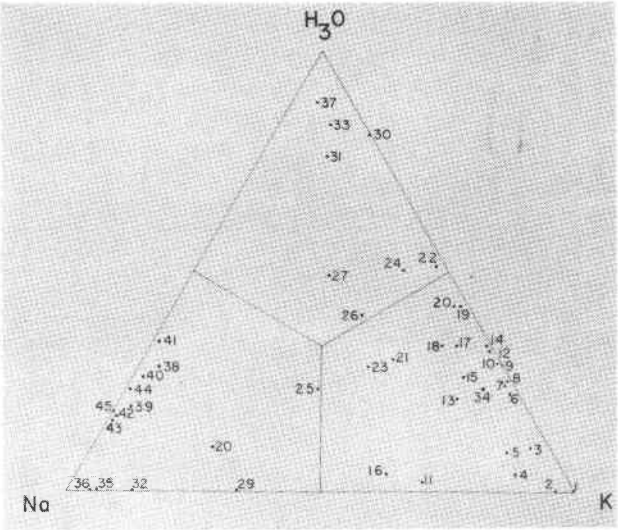

FIG. 2. Plot of the chemical analyses used in this study (Table I).

TABLE 1. COMPOSITIONS OF SYNTHETIC AND NATURAL JAROSITES

No.	Composition	Locality	Reference
1	$(K_{1.00})_3Fe_9(SO_4)_6(OH)_{18}$	Syn.	Brophy *et al.* (1962)
2	$(K_{.96}Na_{.04})_3Fe_9(SO_4)_6(OH)_{18}$	Soda Springs, Nev. USNM 86932	
3	$(K_{.86}Na_{.04}(H_3O)_{.10})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 1	
4	$(K_{.86}Na_{.10}(H_3O)_{.04})_3Fe_9(SO_4)_6(OH)_{18}$	Otravarra, Finland (original Bergstromite)	Moss (1957)
5	$(K_{.82}Na_{.09}(H_3O)_{.09})_3Fe_9(SO_4)_6(OH)_{18}$	St. Felix de Pallieres, France (original Carphosiderite)	Palache *et al.* (1951)
6	$(K_{.76}Na_{.22}(H_3O)_{.03})_3Fe_9(SO_4)_6(OH)_{18}$	St. Leger Macon, Fr.	Moss (1957)
7	$(K_{.74}Na_{.02}(H_3O)_{.24})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 2	
8	$(K_{.74}Na_{.01}(H_3O)_{.25})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 3	
9	$(K_{.71}(H_3O)_{.29})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 4	
10	$(K_{.70}Na_{.01}(H_3O)_{.29})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 5	
11	$(K_{.69}Na_{.29}(H_3O)_{.02})_3Fe_9(SO_4)_6(OH)_{18}$	Kopec, Czech.	Palache *et al.* (1951)
12	$(K_{.67}Na_{.01}(H_3O)_{.32})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 6	
13	$(K_{.66}Na_{.13}(H_3O)_{.21})_3Fe_9(SO_4)_6(OH)_{18}$	Skopow, Poland	Kubisz and Michalek (1959)
14	$(K_{.66}Na_{.01}(H_3O)_{.33})_3Fe_9(SO_4)_6(OH)_{18}$	Syn.	
15	$(K_{.65}Na_{.09}(H_3O)_{.26})_3Fe_9(SO_4)_6(OH)_{18}$	Borek Nowy, Poland	Kubisz and Michalek (1959)
16	$(K_{.61}Na_{.35}(H_3O)_{.04})_3Fe_9(SO_4)_6(OH)_{18}$	Sinyak, USSR	Srebrodolsky (1959)
17	$(K_{.60}Na_{.07}(H_3O)_{.34})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 7	
18	$(K_{.57}Na_{.10}(H_3O)_{.33})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 8	
19	$(K_{.56}Na_{.02}(H_3O)_{.42})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 9	
20	$(K_{.55}Na_{.03}(H_3O)_{.42})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 10	
21	$(K_{.49}Na_{.16}(H_3O)_{.35})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 11	
22	$(K_{.47}Na_{.02}(H_3O)_{.51})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 12	
23	$(K_{.45}Na_{.27})H_3O(_{.28})_3Fe_9(SO_4)_6(OH)_{18}$	Delatin, USSR	Gabinet (1957)
24	$(K_{.41}Na_{.09}(H_3O)_{.50})_3Fe_9(SO_4)_6(OH)_{18}$	Rudawaka, Poland	Kubisz and Michalek (1959)
25	$(K_{.38}Na_{.39}(H_3O)_{.23})_3Fe_9(SO_4)_6(OH)_{18}$	Upper Freemont, Pa.	Warshaw (1956)
26	$(K_{.38}Na_{.22}(H_3O)_{.40})_3Fe_9(SO_4)_6(OH)_{18}$	Kolacztce, Poland	Kubisz and Michalek (1959)
27	$(K_{.27}Na_{.24}(H_3O)_{.49})_3Fe_9(SO_4)_6(OH)_{18}$	Bezmiechowa, Poland	Kubisz (1958)
28	$(K_{.24}Na_{.66}(H_3O)_{.10})_3Fe_9(SO_4)_6(OH)_{18}$	Mina San Toy Santa Eulalia	
29	$(K_{.33}Na_{.66})_3Fe_9(SO_4)_6(OH)_{18}$	Sunset Claim Kingman, Arizona	
30	$(K_{.19}(H_3O)_{.81})_3Fe_9(SO_4)_6(OH)_{18}$	Syn.	Kubisz (1961)
31	$(K_{.13}Na_{.11}(H_3O)_{.76})_3Fe_9(SO_4)_6(OH)_{18}$	Malka Mine, Caucasus	Serdiucezenko (1951)
32	$(K_{.13}Na_{.87})_3Fe_9(SO_4)_6(OH)_{18}$	"Cyprussite" USBM 67210	

(*Continued on next page*)

TABLE 1.—(*continued*)

No.	Composition	Locality	Reference
33	$(K_{.10}Na_{.07}(H_3O)_{.83})_3Fe_9(SO_4)_6(OH)_{18}$	Staszic Mine, Poland	Kubisz (1961)
34	$(K_{.07}Na_{.70}(H_3O)_{.23})_3Fe_9(SO_4)_6(OH)_{18}$	Polska Mine, Upper Silesia	Kubisz (1958)
35	$(K_{.06}Na_{.94})_3Fe_9(SO_4)_6(OH)_{18}$	Kundip, W. Australia	
36	$(K_{.05}Na_{.95})_3Fe_9(SO_4)_6(OH)_{18}$	"Utahite" A.C. 786	
37	$(K_{.05}Na_{.07}(H_3O)_{.88})_3Fe_9(SO_4)_6(OH)_{18}$	Thorez Mine, Poland	Kubisz (1961)
38	$(K_{.04}Na_{.68}(H_3O)_{.28})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 13	
39	$(K_{.03}Na_{.78}(H_3O)_{.19})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 14	
40	$(K_{.02}Na_{.72}(H_3O)_{.27})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 15	
41	$(K_{.01}Na_{.65}(H_3O)_{.34})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 16	
42	$(K_{.01}Na_{.82}(H_3O)_{.17})_3Fe_9(SO_4)_6(OH)_{18}$	Chuquicamata, Chile	Palache *et al.* (1951)
43	$(K_{.01}Na_{.83}(H_3O)_{.16})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 17	
44	$(K_{.01}Na_{.76}(H_3O)_{.21})_3Fe_9(SO_4)_6(OH)_{18}$	Greenland USNM R 6262	Van Tassel (1950)
45	$(Na_{.83}(H_3O)_{.17})_3Fe_9(SO_4)_6(OH)_{18}$	Syn. 18	

accounted for in each case by assignment as H_3O^+ to the univalent cation position in the structure.

X-ray analysis. All synthetic and natural jarosites, natrojarosites and intermediate compounds were analyzed using both film and diffractometer techniques on powdered samples. The unit cell of each sample was determined from the (22.0) and (00.6) reflections, using a geiger tube equipped Norelco diffractometer and filtered Fe radiation. Calibration of the diffractometer was frequently checked using a silicon standard provided by the manufacturer. A plot of the effect of the Na^+-K^+-H_3O^+ substitution upon the unit cell parameters (Fig. 3) shows that the *a* dimension is essentially invariant, but *c* undergoes a non-linear variation. The variation in the *c* parameter is to be expected if the effective radius of H_3O^+ is considered smaller than that for K^+. Richards and Smith (1951), give 0.99 Å for the radius of H_3O^+ in acid monohydrates.

Pure hydronium jarosite has the greatest *a*—7.355 Å. This decreases to 7.312 Å for sodium jarosite and even further to 7.288 Å for potassium jarosite. The plane described by the *a* variation shows a uniform variation within the limit of experimental error.

The change in *c* due to A position substitution is ten times as great as in *a*. Potassium jarosite has the largest *c* at 17.192 Å. This is reduced to 16.980 Å for hydronium jarosite and has its smallest value of 16.620 Å for natrojarosite. The surface outlined by *c* values is not a regular tilting plane, but rather shows an irregular variation with substitution.

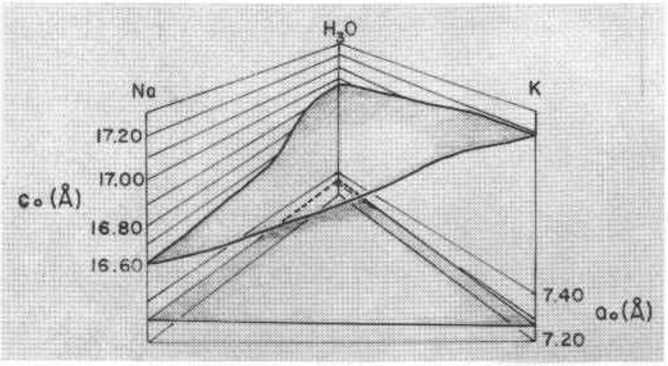

FIG. 3. Plot of the effect of composition on the cell parameters of natural and synthetic jarosites, natrojarosites and hydronium jarosites.

It has been noted earlier (Brophy *et al.*, 1962) that the substitution of Fe^{3+} for Al^{3+} in alunite causes a linear decrease in *c* and a linear increase in *a*, and Parker (1962) shows that the K-Na substitution in alunite produces little change in *a* and a marked decrease in *c* with increasing Na content. The cell dimension data from Parker (1962) and Brophy *et al.*, (1962) has been combined with present data in Fig. 3.

The large variation in *c* compared with that in *a* can be described in

TABLE 2. ANALYSES OF SYNTHETIC AND NATURAL JAROSITES FROM SOURCES OTHER THAN THIS WORK

	1	2	3	4	5	6	7	8	9
K_2O	1.84	0.52	0.35	2.02	0.68	2.28	0.6	1.2	0.1
Na_2O	—	0.43	6.03	4.20	6.32	4.28	5.8	5.4	5.5
Fe_2O_3	49.31	48.90	50.98	50.94	49.86	48.23	51.0	49.1	49.1
SO_3	33.21	32.71	30.96	30.43	32.30	33.71	31.7	31.8	31.4
H_2O	15.64	15.09	11.15	11.73	10.93	10.76	11.2	11.3	13.9
Rem.	—	2.35						1.5	
	100.00	100.00	99.47	99.32	100.09	99.26	100.3	100.3	100.0

1. Synthetic hydronium jarosite (No. 30, Table 1)
2. Hydronium jarosite, Thorez Mine (No. 37, Table 1)
3. Soda Springs, Nevada USNM 86932 (No. 2, Table 1)
4. Mina San Toy, Santa Eulalia, Mexico (No. 28, Table 1)
5. Kundip, W. Australia (No. 35, Table 1)
6. Sunset Claim, Kingman, Arizona (No. 29, Table 1)
7. "Utahite," Tintic, Utah. Amherst College 786 (No. 36, Table 1)
8. "Cyprussite" USBM 67210 (No. 32, Table 1)
9. "Carphosiderite" USNM R 6266 (No. 44, Table I)

TABLE 3. ANALYSES OF SYNTHETIC JAROSITES

	1	2	3	4	5	6	7	8	9
K_2O	8.16	7.14	7.11	6.85	6.77	6.37	5.79	5.48	5.44
Na_2O	.25	.06	.06	0.00	0.07	.05	.44	.64	.13
Fe_2O_3	48.29	48.43	48.86	48.86	49.33	49.08	49.15	48.22	49.44
SO_3	32.28	32.38	32.67	32.66	32.95	31.81	32.86	32.80	33.05
H_2O	11.07	11.35	11.46	11.55	11.64	11.67	11.71	11.73	12.05
Total	100.05	99.36	100.16	99.92	100.76	98.98	99.95	98.87	100.11

	10	11	12	13	14	15	16	17	18
K_2O	5.38	4.79	4.67	4.40	4.82	4.65	4.21	.10	—
Na_2O	.21	1.02	.13	.40	.33	.19	.08	5.36	5.37
Fe_2O_3	49.54	49.37	50.16	50.01	49.75	49.94	50.06	49.73	49.30
SO_3	33.15	33.00	33.53	33.43	33.34	33.39	33.33	33.24	33.29
H_2O	11.97	11.77	12.17	11.80	11.59	11.79	11.85	11.51	11.55
Total	100.25	99.95	100.66	100.04	99.83	99.96	99.53	99.94	99.51

Analysts: G. P. Brophy and M. F. Sheridan

terms of the lattice structure. The hydroxyl adjustment to A-position replacement will be mainly in the *c* direction because the hydroxyl groups appear directly above the A-position cation in the structure. The sulfate oxygens also coordinated to the univalent cation must also adjust to the tighter coordination of H_3O^+ and Na^+ by a contraction mainly in a vertical direction. As the oxygen comes closer to the univalent cation of smaller radius the sulfate tetrahedra keep a relatively constant separation. Brophy *et al.* (1962) have shown that the hydroxyl groups are the controlling factor in *a* expansion when aluminum is substituted for iron in the B-position. Here too, the hydroxyls appear to be the control as they adjust the bonding in the *c* dimension in A-position substitution.

Due to the tolerance in A-position substitution most jarosites occurring in nature will probably contain a combination of potassium sodium and hydronium in the A-position. Hydronium jarosites are rare and exist only in areas where iron-bearing sulfate solutions have a deficiency of alkali due to rapid oxidation of pyrite as other iron mineral accompanied by rapid neutralization of the solution such as by carbonate rocks to precipitate the jarosite before the alkali in the country rock can be dissolved.

Thermal investigation. Kulp and Adler (1950) and Kubisz (1961) have investigated the thermal decomposition of jarosite and its relation to the structure of the mineral. Kulp and Adler found that an endothermic reaction occurs at 460° C. according to the following reaction:

$$K_2Fe_6(SO_4)(OH)_{12} = K_2SO_4 \cdot Fe_2(SO_4)_3 + 2(Fe_2O_3) + 6H_2O$$

and noted that this breakdown temperature is approximately 100° C. lower than for alunite, indicating that the energy of Al-OH bond is greater than that of the Fe-OH bond.

Kubisz (1961) found from DTA studies of the hydronium jarosites that a second endothermic reaction occurs at 340° C. and attributed this reaction to the loss of hydronium ion. While this temperature is higher than that obtained in this study (Fig. 1), it should be noted that (1) only one of the materials prepared in our study has more than 50% of the univalent cation position occupied by hydronium ion (Table 1, No. 22); (2) the actual samples used for the DTA work in our study (Nos. 9, 12, 14, Table 1) contained far less hydronium ion, while those used by Kubisz contained 79%, 81% and 88% hydronium ion respectively (Nos. 33, 30 and 37, Table 1). It would appear that the decrease in the presence of alkali ions in the structure raises the temperature at which the hydronium ion is expelled, or that the heating rate used in the DTA study by Kubisz

TABLE 4. *X*-RAY DATA ON SYNTHETIC JAROSITES

Material	*a* (Å) ±0.004 Å	*c* (Å) ±0.002 Å	*c/a*
Syn. 1	7.293	17.192	2.357
Syn. 2	7.293	17.182	2.356
Syn. 3	7.295	17.175	2.354
Syn. 4	7.294	17.175	2.354
Syn. 5	7.295	17.172	2.354
Syn. 6	7.296	17.177	2.354
Syn. 7	7.300	17.160	2.351
Syn. 8	7.300	17.156	2.350
Syn. 9	7.305	17.153	2.348
Syn. 10	7.305	17.152	2.348
Syn. 11	7.311	17.121	2.342
Syn. 12	7.313	17.120	2.341
Syn. 13	7.321	16.640	2.273
Syn. 14	7.321	16.630	2.272
Syn. 15	7.322	16.640	2.273
Syn. 16	7.321	16.651	2.274
Syn. 17	7.321	16.631	2.272
Syn. 18	7.322	16.626	2.271

Filtered Fe radiation
Diffractometer traverse $\frac{1}{8}$° 2θ/minute
See Tables 1 and 3 for composition

(10° C./minute) was too rapid to permit recording of the endothermic reaction correctly.

DISCUSSION

Investigations of minerals of the alunite group so far undertaken by one of us (GPB) has disclosed that jarosite and various related minerals often show a deficiency of alkali ions with respect to stoichiometric sulfate, whereas the same is not so often true for minerals in the alunite portion of solid solution series alunite-jarosite. The variation has often been attributed to an admixture of various sulfate minerals with the jarosite which is difficult to dispute unless some of the original material is actually available. In the materials used in the study, the natural materials have been studied optically and by *x*-ray diffraction prior to either making a chemical analysis or accepting a previously published analysis. Only where it was clearly stated that the problem of contamination was realized and accounted for were the analyses accepted as published. Analyses of both natural and synthetic materials were recalculated on the basis of 84 cation charges per unit cell ($Z=3$). The chemical formulæ that result from this computation generally show an alkali deficiency and water excess. The highly acid conditions under which the jarosites are normally found to crystallize would be permissive of the incorporation of hydronium ion in the alkali position. However, both temperature and pressure appear to play a role here. In an earlier study (Brophy *et al.*, 1961) it was found that synthetic materials prepared under pressure in the alunite-jarosite solid solution series show a closer agreement to the theoretical alkali:sulfate:water ratio than did those materials prepared under normal atmospheric conditions.

It would seem appropriate to restate the findings of Moss (1957) and Van Tassel (1958) to wit that the water-bearing alkali-deficient iron sulfate known as carphosiderite is in fact a hydronium-bearing jarosite, and that the minerals cyprusite, utahite and bergstromite (Table 1), are in fact either jarosite or natrojarosite. Kubisz (1961) did in fact find several examples of jarosites in which the alkali content was exceedingly small with a concomitant high water content and demonstrated conclusively that hydronium jarosite does exist as a valid species.

From the plot of the compositions of materials having a proven jarosite structure (Fig. 3). it seems appropriate to state that amongst the jarosites there is a continuous solid solution series that exists as a result of K-Na-H_3O substitution under low temperature, low pressure conditions. A second series of synthetic materials has been prepared at 150° C. and analyzed thermally and chemically. The thermal behavior is more like that found for jarosites in which there is near alkali-sulfate stoichiometry.

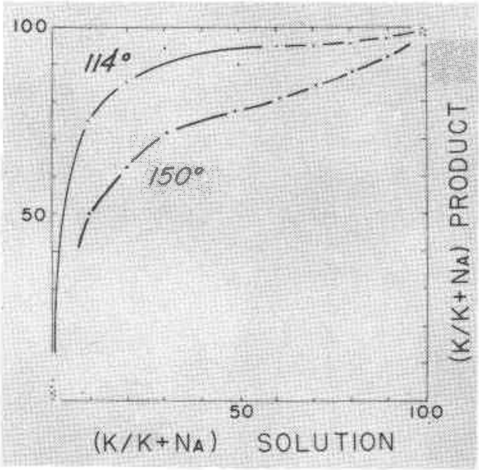

FIG. 4. Relationship of alkali content in starting solution and the resultant jarosite product as a function of temperature. Increasing temperature (and pressure) also reduces the hydronium ion content of the product.

Equally interesting, is the decrease in preference for potassium over sodium in the higher temperature series. A plot of the ratio of potassium to total alkali content in the starting solutions and the final product for both temperature runs clearly demonstrates this change (Fig. 4). Therefore, the incorporation of hydronium ion into the jarosite structure is indeed an indication of a low temperature-low pressure environment of formation. Nevertheless, the preference for K^+ over Na^+ in the jarosite structure suggests that natrojarosites will form only under conditions that eliminate K^+ from the sulfate solutions, and thus explains the relative rarity of natrojarosite and abundance of jarosite in nature. Current investigations of jarosites collected in Nevada and Mexico from what are apparently hydrothermal rather than supergene environments also show a near normal alkali:sulfate ratio without excess water.

It would appear that the identification of the K-Na-H_3O ratio cannot be confirmed by the use of cell parameters alone, but the thermal data in conjunction with the parametal ratio may be used.

The jarosites can be considered as members of a solid solution series in which the principal end members are jarosite, natrojarosite, and hydronium-jarosite, and the limits of each member may be defined by the fields in Fig. 2.

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