SYNTHESIS AND PROPERTIES OF JAROSITE-TYPE COMPOUNDS

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ABSTRACT

All known members of the jarosite family, MFe_3-$(SO_4)_2(OH)_6$, where M is: H_3O^+, Na^+, K^+, Rb^+, Ag^+, NH_4^+, Tl^+, $½Pb^{2+}$ or $½Hg^{2+}$, have been synthesized as single-phase products by precipitation from hot aqueous solution, by precipitation from solution under conditions of elevated temperature and pressure, or by a slow solution-addition technique. A substantial deficiency of "alkali" metal and a general excess of water were observed and were interpreted as indicating hydronium ion substitution in the "alkali" position. A small but consistent deficiency of iron was also noted. All the synthetic jarosites were hexagonal ($R3m$) with similar unit cell dimensions. Methods for distinguishing the various jarosites have been presented; both X-ray diffraction and chemical analyses are required for the precise identification of these compounds.

SOMMAIRE

On a synthétisé tous les membres connus de la famille des jarosites, $MFe_3(SO_4)_2(OH)_6$, où M est: H_3O^+, Na^+, K^+, Rb^+, Ag^+, NH_4^+, Tl^+, $½Pb^{2+}$ ou $½Hg^{2+}$, soit par précipitation à partir d'une solution aqueuse chaude ou d'une solution portée à température et pression élevées, soit par une nouvelle technique fondée sur l'addition lente d'une solution métallifère. Chacun de ces composés se présente en une seule phase, qui montre un déficit notable de métal "alcalin" et un excédent d'eau. On interprète ces résultats par substitution de l'ion hydronium au métal "alcalin". On remarque aussi un léger mais constant déficit en fer. Toutes les jarosites sont hexagonales ($R3m$) avec mailles de dimensions analogues. Des méthodes pour distinguer les diverses jarosites sont présentées dans le texte. L'identification de ces composés requiert la diffraction des rayons X et l'analyse chimique.

INTRODUCTION

The jarosite family of compounds, $MFe_3(SO_4)_2$ $(OH)_6$, where M is: H_3O^+, Na^+, K^+, Rb^+, Ag^+, NH_4^+, Tl^+, $½Pb^{2+}$, or $½Hg^{2+}$, is of interest to

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TABLE 1. CHEMICAL AND MINERAL NAMES OF JAROSITES

Formula	Chemical Name	Mineral Name
$(H_3O)Fe_3(SO_4)_2(OH)_6$	hydronium jarosite	hydronium jarosite (carphosiderite in early literature)
$NaFe_3(SO_4)_2(OH)_6$	sodium jarosite	natrojarosite
$KFe_3(SO_4)_2(OH)_6$	potassium jarosite	jarosite
$RbFe_3(SO_4)_2(OH)_6$	rubidium jarosite	no mineral equivalent
$AgFe_3(SO_4)_2(OH)_6$	silver jarosite	argentojarosite
$(NH_4)Fe_3(SO_4)_2(OH)_6$	ammonium jarosite	ammoniojarosite
$TlFe_3(SO_4)_2(OH)_6$	thallium jarosite	no mineral equivalent
$Pb_{0.5}Fe_3(SO_4)_2(OH)_6$	lead jarosite	plumbojarosite
$Hg_{0.5}Fe_3(SO_4)_2(OH)_6$	mercury jarosite	no mineral equivalent

mineralogists and, especially, to metallurgists engaged in a wide variety of hydrometallurgical activities. Although nine jarosites can be synthesized, only six of these have been found as minerals. The corresponding chemical and mineral names are set out in Table 1 for all nine compounds. In the present study, chemical names are used for synthetic products and mineral names are reserved for naturally occurring jarosites.

Jarosite precipitation is a convenient means of removing unwanted iron, alkali metal ions or sulfate ion from hydrometallurgical processing solutions. One of the advantages of this type of precipitation is the relative ease of filtration of the resulting jarosite; the problems associated with settling and filtering neutralized iron solutions are avoided. Another advantage is that the precipitation can be carried out in strongly acidic media; it is not necessary to neutralize the leaching solution to remove its iron content. This is particularly useful in leaching circuits where an acidified leaching medium is to be recycled. A conventional iron-removal step would require that the solution firstly be neutralized to precipitate iron and subsequently be re-acidified for the leaching operation. This neutralization-acidification cycle is wasteful and can be completely avoided by precipitating the iron as a jarosite directly from the hot acidic leach solutions (Orekhov *et al.* 1971). A variation of this process is now used widely in the zinc

industry to purify acidic zinc sulfate solutions prior to zinc electrolysis (Cotterill & Cigan 1970). When large amounts of zinc are leached from calcined zinc concentrates, considerable quantities of the associated iron also enter the solution. This iron must be removed before zinc electrolysis, and many zinc plants have opted for jarosite precipitation which also assists in maintaining an alkali and sulfate balance in the system. The precipitation of trace metals, such as silver, as jarosite during dump leaching has been postulated as one cause for erratic recoveries of these values (Dutrizac et al. 1975). It has also been shown that the precipitation of silver as silver jarosite can prevent its recovery during conventional cyanidation processing (May et al. 1973). Thus, the formation of jarosites in hydrometallurgical processes can be either beneficial or deleterious, and this points to the need for a careful study of the conditions under which jarosites will or will not form and of the properties of these compounds.

Kubisz (1964) and Brophy & Sheridan (1965) have established that most natural jarosites can be considered to be a solid solution of jarosite $KFe_3(SO_4)_2(OH)_6$, natrojarosite $NaFe_3(SO_4)_2(OH)_6$, and hydronium jarosite $H_3OFe_3(SO_4)_2(OH)_6$. These three common jarosites have been prepared by dissolving ferric sulfate and the alkali sulfate in a suitable volume of water and then heating the solution to near its boiling point (Kubisz 1970, 1964, 1961; Brown 1970; Brophy & Sheridan 1965). These compounds can also be prepared by heating the solutions in autoclaves to temperatures above the normal boiling point (Kostenko et al. 1972; Fairchild 1933). A complete solid-solution series exists among these jarosites, and the cell dimensions have been shown to vary systematically with changes in composition. Most workers report a deficiency of sodium and potassium ions under all synthesis conditions.

In spite of the metallurgical importance of ammonium jarosite, comparatively little has been reported for this compound. Shishkin et al. (1958) synthesized ammonium jarosite from the corresponding sulfate salts and concluded that the ammonium ion was substantially replaced by hydronium ion. Haigh (1967) prepared this jarosite from the simple sulfates by heating them to 140-220°C in pressure vessels. Shokarev et al. (1972) prepared an ammonium-hydronium jarosite and determined its infrared spectrum. Maryanchik & Zapolskii (1972) synthesized an impure ammonium jarosite by heating sulfate solutions to 125-200°C and determined the d-spacings for a very iron-rich, and probably impure, material.

Impure rubidium jarosite was first prepared by Fairchild (1933) who heated impure rubidium sulfate-ferric sulfate solutions to 165-180°C in a pressure vessel. More recently, Dutrizac & Kaiman (1975) synthesized "pure" rubidium jarosite from sulfate solutions at 95°C and subsequently characterized this compound. Silver jarosite was also prepared by Fairchild (1933) who heated silver sulfate–ferric sulfate–sulfuric acid solutions to 110-200°C in a pressure device; he did not identify the product by X-ray methods. May et al. (1973) used similar solutions at the boiling point to prepare a "pure" silver jarosite which they characterized by X-ray and by thermal analyses. Thallium jarosite has been synthesized by Dutrizac & Kaiman (1975) who heated suitable concentrations of thallous sulfate and ferric sulfate to 95°C to precipitate the jarosite which was subsequently analyzed by X-ray, by chemical and by thermal methods.

The synthesis of either a lead or a mercury jarosite is complicated by the fact that the addition of these metal ions to a sulfate solution results in the immediate precipitation of lead sulfate ($PbSO_4$) or mercury oxysulfate ($HgSO_4\cdot 2HgO$), respectively. Mumme & Scott (1966) claimed to have overcome this problem for lead jarosite by heating $PbSO_4$ with $0.125M$ ferric sulfate solution for 2 hr at 140°C, and then dissolving away the unreacted lead sulfate with either ammonium acetate or diethylenetriamine solutions. Their purified product was analyzed both chemically and structurally. Mercury jarosite does not occur in nature and as far as is known no syntheses of this material have been reported that are free of the mercury oxysulfate impurity.

In the present study all nine jarosite-type compounds indicated above have been prepared as single-phase materials using a variety of techniques. These compounds have been characterized by chemical and by X-ray diffraction analyses; for many of the jarosites the X-ray data obtained are more complete and accurate than those currently available in the literature.

EXPERIMENTAL

Synthesis

Reagent-grade chemicals were used for all the jarosite syntheses. Many of the jarosites could be prepared simply by heating the appropriate "alkali" sulfate with ferric sulfate to temperatures near the solution boiling point. Accordingly, sodium jarosite was prepared by dissolving 64g of Na_2SO_4 in one litre of a filtered solution containing 10g of Fe^{3+} as ferric sulfate and $0.01M$ H_2SO_4 to prevent iron hydrolysis and

precipitation. The solution was heated in air to 95°C and was stirred at this temperature for 1½ to 3 hr. The precipitate was allowed to settle and the hot residual solution was then decanted. The precipitate was scraped from the beaker, filtered, washed with water and then dried with acetone. The precipitate was heated at 110°C for several hours to remove any loosely-bound water and was stored in a desiccator. Although potassium jarosite could be prepared by the same method, it was found that the use of potassium nitrate in place of potassium sulfate produced a product richer in alkali. Thus the potassium jarosite was prepared by heating to 95°C a solution containing 30 g/l KNO_3, 8 g/l of Fe^{3+} as ferric sulfate and $0.01M$ H_2SO_4. The precipitate which formed was treated in the same manner as the sodium jarosite. Both rubidium and thallium jarosites were also prepared by this method by Dutrizac & Kaiman (1975). Ammonium jarosite was synthesized using this general method, but by employing solutions containing 132 g/l ammonium sulfate, 15 g/l Fe^{3+} as ferric sulfate and $0.01M$ H_2SO_4.

Although both hydronium jarosite and silver jarosite can be prepared by the above procedure, it was found advantageous to synthesize these compounds by a different method. The hydronium jarosite was prepared by heating a filtered solution containing 15 g/l Fe^{3+} as ferric sulfate (with no H_2SO_4) to 140°C in an autoclave. A thin reddish ring of precipitate formed around the glass liner at the solution line; this ring, thought to be ferric hydroxide, was physically separated at the end of the experiment. The jarosite product was then scraped from the glass liner, filtered, washed with water and acetone and then dried at 110°C for several hours. Silver jarosite was prepared by the same procedure except that the solution contained 20 g/l Ag_2SO_4, 20 g/l of Fe^{3+} as ferric sulfate and 25 g/l H_2SO_4. The presence of the acid was necessary to retard the formation of hydronium jarosite during synthesis. The silver-bearing solution was heated to 140°C for 2 hr, cooled, and the precipitate washed and dried as was done for the other jarosites.

All attempts to prepare lead jarosite or mercury jarosite by mixing solutions of suitable salts and heating to high temperatures for various times resulted in products contaminated with lead sulfate or mercury oxysulfate. Attempts to remove these impurities by leaching were never wholly successful. To overcome these problems, a slow-addition technique was developed whereby a solution of a lead or mercury salt was slowly pumped into a hot ferric sulfate solution. If the rate of addition of the lead or mercury was sufficiently slow, then only the jarosite compound was formed. To prepare the lead jarosite, one litre of a filtered solution containing 6 g/l of Fe^{3+} as ferric sulfate and $0.01M$ H_2SO_4 was heated to 95°C. A second solution containing 1.1 g of $Pb(NO_3)_2$ in 120 ml of water was pumped steadily at 6 ml/hr into the hot, stirred ferric sulfate solution. The precipitate was filtered, washed with water and acetone and dried at 110°C. Mercury jarosite was also synthesized by this technique. Six grams of $Hg(NO_3)_2 \cdot H_2O$ were dissolved in 120 ml of water; it was necessary to add a few drops of HNO_3 to produce a clear solution. The mercury-bearing solution was then pumped at 6 ml/hr into 1 litre of hot stirred ferric sulfate solution to produce the jarosite precipitate which was filtered, washed and dried.

Sodium, potassium, rubidium, thallium and lead were determined by atomic absorption spectroscopy. Silver was determined by Volhard titration, by atomic absorption and by fire assaying methods; mercury was analyzed by titration with thiocyanate solution. Ammonium ion concentrations were calculated from the total nitrogen content determined by the Kjeldahl method. Iron was analyzed by both atomic absorption spectroscopy and dichromate titration. Sulfate was determined by barium sulfate precipitation and by calculation from the total sulfur as determined by combustion methods; the two methods agreed within experimental error. Water was estimated by difference.

X-ray diffraction

Powder diffraction patterns of all nine jarosite-type compounds synthesized were obtained using both a Guinier-de Wolff focusing camera and a Philips 114.6 mm diameter Debye-Scherrer powder camera using cobalt radiation. First, patterns were obtained on the Guinier-de Wolff camera to resolve any closely-spaced lines and then patterns were prepared on the Philips camera. Interplanar spacings were read from Philips charts (Parrish & Irwin 1953). The relative intensities of the various diffraction lines were estimated visually and, as such, are only approximate.

It was assumed that all compounds possessed the same hexagonal structure *(R3m)* as jarosite, $KFe_3(SO_4)_2(OH)_6$. By comparing the patterns with those published in the Diffraction Index (1972) for this structure, some lines could be indexed unequivocally and approximate cell dimensions were obtained. These cell dimensions were processed through several iterations of a least-squares computer program, PARAM (Stewart *et al.* 1972), to refine the cell dimen-

sions. The final cell dimensions thus obtained were used to calculate the interplanar spacings for all reflections permitted by the extinction condition $(-h+k+l=3n)$ and indices were assigned to all the observed diffraction lines. It was possible to index all observed reflections. Densities were computed and compared to those obtained using a pycnometer.

RESULTS AND DISCUSSION

Chemical characterization

The chemical analyses obtained for sodium, potassium, and ammonium jarosites are given in Table 2 together with the theoretical analyses

TABLE 2. COMPOSITIONS OF SODIUM, POTASSIUM AND AMMONIUM JAROSITES

Element	Sodium jarosite		Potassium jarosite		Ammonium jarosite	
	Synthetic wt.%	Theoretical wt.%	Synthetic wt.%	Theoretical wt.%	Synthetic wt.%	Theoretical wt.%
Na	4.00*	4.74	-	-	-	-
K	-	-	7.17**	7.81	-	-
NH$_4$	-	-	-	-	3.44***	3.76
Fe	33.14	34.57	29.5	33.45	30.92	34.92
SO$_4$	40.78	39.64		38.36	41.29	40.05
H$_3$O+OH†	22.08	21.05	22.63	20.38	24.35	21.27
Approx. formula	Na$_{0.82}$ (H$_3$O)$_{0.18}$ Fe$_{2.80}$ (SO$_4$)$_2$ (OH)$_6$	NaFe$_3$ (SO$_4$)$_2$ (OH)$_6$	K$_{0.86}$ (H$_3$O)$_{0.14}$ Fe$_{2.49}$ (SO$_4$)$_2$ (OH)$_6$	KFe$_3$ (SO$_4$)$_2$ (OH)$_6$	(NH$_4$)$_{0.89}$ (H$_3$O)$_{0.11}$ Fe$_{2.57}$ (SO$_4$)$_2$ (OH)$_6$	NH$_4$Fe$_3$ (SO$_4$)$_2$ (OH)$_6$

*84% of theoretical value **92% of theoretical value
***91% of theoretical value †H$_3$O+OH by difference

for these compounds. The analyses of rubidium and thallium jarosites have been presented previously (Dutrizac & Kaiman 1975) and were similar to the other jarosites prepared from near-boiling solutions with regard to the slight iron deficiency, the substantial deficit of "alkali" metal and the general excess of water. It appears that the "alkali" deficiency and excess water are caused by the substitution of hydronium ion (H$_3$O$^+$) for the "alkali" metal (Kubisz 1970). Jarosites prepared by the general procedure above are characterized by apparent hydronium ion substitutions varying from 10 to 20 mole percent. Such analyses are typical of those reported for both synthetic phases and natural jarosites.

TABLE 3. COMPOSITIONS OF HYDRONIUM JAROSITE AND SILVER JAROSITE

Element	Hydronium jarosite		Silver jarosite	
	Synthetic wt.%	Theoretical wt.%	Synthetic wt.%	Theoretical wt.%
H$_3$O	-	3.96	-	-
Ag	-	-	18.16*	18.94
Fe	34.6	34.82	28.6	29.41
SO$_4$	40.4	39.96	35.4	33.73
H$_3$O+OH†	25.0	25.22††	17.84	17.92
Approx. formula	(H$_3$O)$_{1.00}$ Fe$_{2.94}$(SO$_4$)$_2$ (OH)$_6$	H$_3$O Fe (SO$_4$)$_2$(OH)$_6$	Ag$_{0.91}$(H$_3$O)$_{0.09}$ Fe$_{2.78}$(SO$_4$)$_2$ (OH)$_6$	AgFe$_3$ (SO$_4$)$_2$(OH)$_6$

*96% of theoretical value shown above †H$_3$O+OH by difference ††includes 3.96% H$_3$O

Table 3 presents the actual and theoretical chemical analyses for hydronium jarosite and silver jarosite. As above, there is an apparent hydronium ion substitution for the "alkali" metal and a slight, but consistent, iron deficiency. When silver jarosite was prepared at temperatures below 140°C the extent of hydronium substitution was found to increase greatly and, hence, the need for its synthesis at elevated temperatures. The silver jarosite prepared by May *et al.* (1973) contained about 17.1 wt. % Ag as opposed to about 18 wt. % Ag when the compound was synthesized at the higher temperatures. Silver jarosite prepared in the present study at 75°C contained only 16 wt. % Ag.

Table 4 lists the theoretical and analytical compositions of lead jarosite and mercury jarosite which were synthesized by the slow-addition technique. The jarosites of these divalent ions require only one-half mole of "alkali" ion and

TABLE 4. COMPOSITIONS OF LEAD JAROSITE AND MERCURY JAROSITE

Element	Lead jarosite		Mercury jarosite	
	Synthetic wt.%	Theoretical wt.%	Synthetic wt.%	Theoretical wt.%
Pb	8.35*	18.32	-	-
Hg	-	-	14.62**	17.85
Fe	30.6	29.63	35.65	34.19
SO$_4$	38.0	33.98	28.37	29.81
H$_3$O+OH†	23.05	18.07	21.36	18.15
Approx. formula	Pb$_{0.20}$(H$_3$O)$_{0.60}$ Fe$_{2.77}$(SO$_4$)$_2$ (OH)$_6$	Pb$_{0.5}$Fe$_3$ (SO$_4$)$_2$(OH)$_6$	Hg$_{0.39}$(H$_3$O)$_{0.22}$ Fe$_{2.76}$(SO$_4$)$_2$ (OH)$_6$	Hg$_{0.5}$ Fe$_3$ (SO$_4$)$_2$(OH)$_6$

*45% of theoretical value **82% of theoretical value
†H$_3$O+OH by difference

the theoretical formula would be, for example: Pb$_{0.5}$Fe$_3$(SO$_4$)$_2$(OH)$_6$. In spite of the lower requirement for the metal ion, there is a substantial deficit of "alkali" as compared to the theoretical.

This deficiency can be explained by the substitution of hydronium ion for the "alkali" metal. The slow-addition technique forms the jarosite slowly enough to avoid second-phase contamination, but such slow rates favor the substitution of hydronium ion for the heavy metals. If the metals were added more rapidly or if the solution concentration were doubled, then impurity phases were detected. The lead jarosite formed by stirring lead sulfate with ferric sulfate solution was much richer in lead, but since, at least in our experiments, this material was always contaminated with lead sulfate (Pb=68%), it is impossible to state the true lead content of the jarosite. Because of the great differences in the molecular weights of lead and hydronium ions, a substantial degree of hydronium ion substitution is required to compensate for a small reduction in the lead content of the jarosite. For example, decreasing the lead concentration from

15.1 wt. % to 13.4 wt. %, *i.e.*, from $(H_3O)_{0.20}$ $Pb_{0.40}Fe_3(SO_4)_2(OH)_6$ to $(H_3O)_{0.30}Pb_{0.35}Fe_3(SO_4)_2$ $(OH)_6$, requires a one-third increase in the hydronium concentration. Although natural plumbojarosites have been reported to contain nearly theoretical amounts of lead (Mumme & Scott 1966), some of the lead may be associated with impurities. Plumbojarosites with considerably less than the theoretical amounts of lead are also quite common in nature (Kubisz & Zabinski 1958).

All the jarosites synthesized were deficient in both "alkali" metal and in iron when compared to the theoretical formula. As will be shown, X-ray diffraction analyses using sensitive Guinier-de Wolff techniques indicated that each jarosite was single-phase; that is, the low metal analyses are not caused by contamination of the product with other phases. Kubisz (1970) has established that both natural and synthetic potassium jarosites and sodium jarosites always contain a deficiency of alkali metal and an excess of water. He concluded that hydronium ion substitution for alkali ions is a constitutional property of these jarosites and is responsible for the low metal analyses. The present analyses confirm this observation and suggest that all jarosites will contain some hydronium ion substitution or the "alkali" metal. The extent of hydronium substitution is probably dependant on the formation conditions. In this regard it is interesting to note that the jarosites synthesized by Kubisz (1970) contained more than 25% hydronium ion substitution for the alkali metal. A slight deficiency of iron relative to sulfate appears to be common for jarosites and was also observed in this study. The approximate formulas shown are based on the assumption that there are two sulfate groups per formula and that sufficient water (estimated by difference in this work) is present to satisfy both the hydronium and hydroxide requirements. It should be noted that the H_2O values are only approximate since they incorporate all the analytical errors associated with the other elements. Within experimental error there was always sufficient H_2O to satisfy the requirements for 6 OH groups plus the hydronium ion needed to make up for the "alkali" deficiency. In certain instances extra water was present in excess of the above requirements; the nature of this "additional" water has been discussed by Kubisz (1970).

X-ray data

The interplanar *d*-values and visually-estimated intensities of the X-ray diffraction patterns for sodium, potassium, ammonium, hydro-

nium, silver, lead and mercury jarosites are presented in Tables 5 and 6. The corresponding values for rubidium jarosite and thallium jarosite have been published recently (Dutrizac & Kaiman 1975) and will not be repeated here.

The X-ray patterns for hydronium jarosite and potassium jarosite are well-established; the data obtained in the present study on these compounds agree closely with the previous values as concerns both *d*-spacings and the derived *a* and *c* parameters. The hydronium jarosite line at $d = 2.984$ shown in the reference file was not detected, but an additional weak line at $d = 1.412$ was revealed. For potassium jarosite, good agreement was obtained except that the reference lines at $d = 2.368$ and $d = 1.656$ were not detected, and that the line at $d = 1.717$ of the reference pattern has been resolved into two lines at $d = 1.723$ and $d = 1.711$. The data obtained in this study for sodium jarosite and ammonium jarosite are more complete and more accurate than those currently available in the Diffraction Index (1972). All lines shown in the reference file for sodium jarosite were reproduced in the present study which also detected an additional seven lines for this compound. The available data for ammonium jarosite have been greatly extended, especially for $d < 1.73$. The cell parameters for sodium jarosite agree closely with those derived for Na-H_3O jarosite of this composition by Kubisz (1970). May *et al.* (1973) produced reliable X-ray data for silver jarosite; the present results agree very well with those of May *et al.* and, in addition, several new diffraction lines have been identified for $d < 1.68$. The X-ray data for lead jarosite obtained by Mumme & Scott (1966) have been greatly extended, especially at higher diffraction angles; there is very good agreement (cell parameters differing by 0.01Å) between the two studies in spite of the reported differences in the lead contents of the two jarosites. No reliable X-ray data for mercury jarosite appear to have been published prior to the present study.

Density data

Densities of all nine jarosite compounds prepared in this work have been calculated from their refined cell dimensions (Table 7) assuming three formula units per unit cell (except for lead and mercury jarosite where $Z = 6$). Pycnometric densities were also measured using water as the immersing fluid and ultrasonic vibration to remove trapped air bubbles. The pycnometric apparatus was calibrated with natural quartz whose density was found to be 2.63±0.02 g/cm³ (theoretical value = 2.65 g/cm³).

In general, the densities of the jarosites are not dramatically affected by changing the "alkali" metal. This is in part indicative of the hydro-nium ion substitution problem but is mainly caused by the identical network-forming ions that largely determine the volume of the unit

TABLE 5. X-RAY DIFFRACTION DATA FOR JAROSITES

Synthetic $NaFe_3(SO_4)_2(OH)_6$
$a=7.329\pm0.002$, $c=16.703\pm0.004$Å

d_{meas}	I_{est}	hkl	d_{calc}
5.94	3	101	5.933
5.57	4	003	5.568
5.06	9	012	5.053
3.66	3	110	3.664
3.49	2	104	3.483
3.12	9	021	3.118
3.06	10	113	3.061
2.960	2	{ 202 / 015	{ 2.966 / 2.956
2.783	3	006	2.784
2.527	3	024	2.527
2.308	1	122	2.306
2.236	5	107	2.234
1.979	5	033	1.978
1.909	3	027	1.907
1.857	1	009	1.856
1.834	5	220	1.832
1.743	2	{ 208 / 223	{ 1.744 / 1.740
1.724	2	312	1.722
1.693	½	217	1.692
1.657	½	119	1.656
1.623	2	134	1.622
1.578	2B	{ 401 / 128	{ 1.580 / 1.575
1.560	2	{ 042 / 315	{ 1.559 / 1.557
1.532	3	226	1.530
1.484	1	404	1.483
1.479	4B	{ 0.2.10 / 0.1.11	{ 1.478 / 1.477

Synthetic $KFe_3(SO_4)_2(OH)_6$
$a=7.315\pm0.001$, $c=17.119\pm0.004$Å

d_{meas}	I_{est}	hkl	d_{calc}	$d(ref)$*
5.95	3	101	5.941	5.93
5.71	2	003	5.706	5.72
5.10	7	012	5.092	5.09
3.66	3	110	3.658	3.65
3.54	½	104	3.546	3.55
3.12	6	021	3.115	3.11
3.08	10	113	3.079	3.08
3.02	½	015	3.012	3.02
2.977	½	202	2.971	2.965
2.859	3	006	2.853	2.861
2.549	3	024	2.546	2.542
--	--	211	--	2.368
2.307	½	122	2.306	2.302
2.283	5	107	2.282	2.287
1.982	6	033	1.980	1.977
1.938	1	027	1.936	1.937
1.903	1	009	1.902	1.909
1.830	6	220	1.829	1.825
1.774	½	208	1.773	1.776
1.743	½	223	1.742	1.738
1.723	1	312	1.721 }	1.717
1.711	<½	217	1.711 }	
1.689	<½	119	1.688	1.690
--	--	1.0.10	--	1.656
1.625	1	134	1.625	1.621
1.597	1	128	1.596	1.595
1.579	½	401	1.577	1.572
1.563	1	315	1.563	1.560
1.559	1	042	1.557	1.552
1.541	3	226	1.540	1.536
1.507	4	0.2.10	1.506	1.507
1.487	1	404	1.485	1.480

Synthetic $NH_4Fe_3(SO_4)_2(OH)_6$
$a=7.325\pm0.001$, $c=17.374\pm0.004$Å

d_{meas}	I_{est}	hkl	d_{calc}
5.97	2	101	5.959
5.80	4	003	5.791
5.13	8	012	5.123
3.66	3	110	3.662
3.59	1	104	3.584
3.11	10	{ 021 / 113	{ 3.120 / 3.095
3.05	1	015	3.048
2.985	<½B	202	2.979
2.900	3	006	2.896
2.562	3	024	2.562
2.313	5	107	2.311
1.988	5	033	1.986
1.957	2	027	1.955
1.932	2	009	1.930
1.833	5	220	1.831
1.794	½B	208	1.792
1.746	2	223	1.746
1.726	2	312	1.724
1.630	2	134	1.631
1.611	2	128	1.610
1.581	1	401	1.579
1.562	<½	042	1.560
1.548	3	226	1.548
1.525	4B	0.2.10	1.524
1.492	1	404	1.490
1.436	2	{ 137 / 232	{ 1.435 / 1.435
1.415	½	2.0.11	1.414
1.384	½B	140	1.384
1.348	2	{ 1.1.12 / 143	{ 1.346 / 1.346

B = broad line　　　　*PDF 22-827 for hexagonal cell with $a=7.29$, $c=17.16$Å.

TABLE 6. X-RAY DIFFRACTION DATA FOR JAROSITES

Synthetic $(H_3O)Fe_3(SO_4)_2(OH)_6$
$a=7.347\pm0.002$, $c=16.994\pm0.005$Å

d_{meas}	I_{est}	hkl	d_{calc}	$d(ref)$*
5.96	2	101	5.959	5.97
5.67	3	003	5.665	5.67
5.10	10	012	5.093	5.10
3.67	2	110	3.674	3.68
3.54	1	104	3.533	3.54
3.13	9	021	3.127	3.13
3.08	10	113	3.082	3.09
3.00	1	015	2.998	3.00
--	--	202	--	2.984
2.840	3	006	2.832	2.835
2.548	3	024	2.546	2.549
2.317	½	122	2.314	2.318
2.270	4	107	2.268	2.271
1.987	4	033	1.986	1.990
1.932	2	027	1.930	1.933
1.890	1	009	1.888	1.891
1.838	4	220	1.837	1.839
1.769	½	208	1.767	1.767
1.750	1	223	1.747	1.749
1.728	1	312	1.728	1.730
1.631	1	134	1.630	1.631
1.594	1	128	1.592	1.594
1.583	½	401	1.584	1.585
1.566	1	{ 315 / 042	{ 1.566 / 1.564	{ -- / 1.566
1.542	2	226	1.541	1.542
1.501	2	0.1.11	1.501	1.500
1.490	½	404	1.490	1.491
1.441	1	{ 045 / 232	{ 1.441 / 1.439 }	1.442
1.427	½	137	1.427	1.429
1.412	½	039	1.410	--

Synthetic $AgFe_3(SO_4)_2(OH)_6$
$a=7.348\pm0.001$, $c=16.551\pm0.005$Å

d_{meas}	I_{est}	hkl	d_{calc}
5.95	6	101	5.940
5.06	1	012	5.045
3.67	4	110	3.674
3.12	2	021	3.125
3.06	10	113	3.058
2.973	1	202	2.970
2.761	2	006	2.758
2.524	3	024	2.522
2.381	1	211	2.380
2.310	2	122	2.310
2.219	4	107	2.216
2.079	½	214	2.079
1.981	4	033	1.980
1.947	½	125	1.946
1.896	½	027	1.898
1.838	4	{ 009 / 220	{ 1.839 / 1.837
1.737	1	208	1.734
1.686	2	217	1.686
1.646	1	119	1.644
1.624	<½	134	1.623
1.604	½	1.0.10	1.602
1.585	<½	401	1.584
1.560	2B	{ 042 / 315	{ 1.562 / 1.557
1.530	3	226	1.529
1.486	1	404	1.485
1.470	3	0.2.10	1.468
1.456	½	321	1.454
1.438	<½	232	1.438
1.415	1	137	1.414
1.391	2	{ 039 / 140	{ 1.390 / 1.389
1.348	3	413	1.347

Synthetic $Pb_{0.5}Fe_3(SO_4)_2(OH)_6$
$a=7.335\pm0.001$, $c=33.850\pm0.008$Å

d_{meas}	I_{est}	hkl	d_{calc}
5.95	4	012	5.947
5.64	2	006	5.642
5.09	5	104	5.080
3.67	3	110	3.668
3.52	½	018	3.522
3.12	5	202	3.122
3.08	10	116	3.075
2.980	2B	024	2.974
2.823	3	0.0.12	2.821
2.542	3	208	2.540
2.377	½	122	2.377
2.311	1	214	2.310
2.263	4	{ 125 / 0.1.14	{ 2.263 / 2.260
1.984	4	036	1.982
1.960	½	2.1.10	1.958
1.927	1	2.0.14	1.924
1.883	1	0.0.18	1.881
1.834	4	220	1.834
1.762	1	{ 0.2.16 / 131	{ 1.761 / 1.759
1.746	½	226	1.744
1.725	1	134	1.725
1.706	1	{ 315 / 1.2.14	{ 1.705 / 1.704
1.675	½	1.1.18	1.673
1.626	1	318	1.626
1.588	1	{ 2.1.16 / 401	{ 1.587 / 1.586
1.583	1	042	1.581
1.563	2	{ 1.3.10 / 404	{ 1.563 / 1.561
1.539	3	2.2.12	1.537
1.496	3	1.0.22	1.495
1.488	1	048	1.487

Synthetic $Hg_{0.5}Fe_3(SO_4)_2(OH)_6$
$a=7.354\pm0.002$, $c=33.141\pm0.010$Å

d_{meas}	I_{est}	hkl	d_{calc}
5.95	6	012	5.945
5.53	1/2	006	5.524
5.06	4	104	5.049
3.67	5	110	3.677
3.13	5	202	3.127
3.06	10	116	3.061
2.973	2	024	2.972
2.763	3	0.0.12	2.762
2.528	4	208	2.525
2.384	1	122	2.382
2.312	2	214	2.312
2.222	5B	0.1.14	2.219
1.983	6	036	1.982
1.949	1/2	2.1.10	1.948
1.901	1/2	2.0.14	1.900
1.840	6	{ 039 / 220	{ 1.839 / 1.838
1.736	2B	0.2.16	1.736
1.688	2	1.2.14	1.688
1.647	1	{ 1.1.18 / 229	{ 1.646 / 1.645
1.561	3	1.3.10	1.559
1.532	5	{ 0.3.15 / 2.2.12	{ 1.531 / 1.530
1.487	2	048	1.486
1.472	3B	2.0.20	1.470

B = broad line　　　　*PDF 21-932 for hexagonal cell with $a=7.3559$, $c=17.0097$Å.

TABLE 7. CELL PARAMETERS AND DENSITIES FOR THE JAROSITES
INVESTIGATED

Synthetic Jarosite	Hexagonal Cell (Å)		Density (g/cm^3)	
	a	c	Calculated	Observed
H_3O^+	7.35	16.99	3.01	2.93
Na^+	7.33	16.70	3.11	2.94
K^+	7.32	17.12	3.15	2.82
Rb^+ (*)	7.32	17.36	3.38	3.12
Ag^+	7.35	16.55	3.67	3.26
NH_4^+	7.33	17.37	2.96	2.66
Tl^+ (*)	7.33	17.42	4.10	3.54
$1/2\ Pb^{2+}$	7.34	33.85	3.57	3.11
$1/2\ Hg^{2+}$	7.35	33.14	3.61	3.40

(*) Dutrizac & Kaiman (1975)

cell and contribute significantly to its mass. Ammonium jarosite is the least dense of all the compounds studied and thallium jarosite is the most dense. The densities of lead jarosite and mercury jarosite are not exceptionally great because these compounds contain only ½ Pb or ½ Hg, respectively, per formula weight. The pycnometric densities are considerably lower than the computed values. This effect is commonly noted in jarosites where appreciable H_3O^+ substitution for heavy cations appears to be a constitutional property of these compounds and where there is a considerable deficiency of iron (Palache *et al.* 1951; Hrynkiewicz *et al.* 1965).

Methods of identifying jarosites

The various jarosites have very similar X-ray diffraction patterns. For the "pure" jarosites there are sufficient differences in line spacings and, particularly, in line intensities to permit a fairly reliable identification. The high *d*-value lines (*d*>3) are most useful although the whole pattern should be examined. If the jarosite is not "pure" but is, in fact, a multi-component solid-solution series, X-ray diffraction becomes unreliable as a unique means of identification. The best method of characterizing any jarosite, whether "pure" or a solid-solution series, involves both X-ray diffraction and chemical analysis. X-ray diffraction analysis should be used first to show that the material has the jarosite structure and that it is not contaminated with impurity phases. The use of precision Guinier-de Wolff X-ray diffraction analysis to detect possible small quantities of impurities is strongly recommended. Once the compound has been identified as a jarosite, chemical analysis for Na, K, Rb, NH₄, Pb, etc. must be performed to determine which jarosite is being studied. Unless the jarosite is single-phase, chemical analysis is of limited value since many basic iron sulfates have compositions close to jarosites.

Also, the compositions of the heavy-metal jarosites are strongly influenced by the true heavy-metal composition of the jarosite, and the presence of even one or two percent of a metal sulfate impurity can drastically affect the heavy metal-to-hydronium ratio. Accordingly, the analyses for the heavier ions must be carried out with care and on single-phase material.

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