ARTIFICIAL JAROSITES—THE SEPARATION OF POTASSIUM FROM CESIUM[1]

J. G. Fairchild, *U. S. Geological Survey.*

Abstract

Mitscherlich[2] prepared alunite and jarosite, $K_2O \cdot 3Fe_2O_3 \cdot 4SO_3 \cdot 6H_2O$, at 230°C. by heating the sulphates in a closed tube but the writer has obtained good crystals of jarosite at temperatures as low as 110°C. and nearly equal in size to those of the natural mineral. Higher temperatures may be used, in order to increase the yield by promoting more rapid hydrolysis of the iron salt, but a temperature as low as 90°C. produces a basic sulphate of iron and potassium containing twice as much water and less alkali metal. At temperatures above 110°C. cesium, if present, does not enter the jarosite molecule.

Introduction

About five different jarosites occur in nature. These are the potassium or ordinary jarosite, natrojarosite, ammoniojarosite, argentojarosite, and plumbojarosite. Of these, the potassium compound became of interest to the writer because of the lack of information in the literature regarding its preparation under laboratory conditions, the experiments of Mitscherlich apparently being the only ones on record.

Several attempts by the writer to prepare jarosite, $K_2O \cdot 3Fe_2O_3 \cdot 4SO_3 \cdot 6H_2O$, at a steam bath temperature have yielded basic sulphates of varying compositions but possessing simple molecular ratios. Two or three different compounds obtained at this temperature, but made from different porportions of the reagents, potassium and ferric sulphates, were analyzed. They were not altogether insoluble in water, thereby differing from jarosite. Optically, they were biaxial and varied in sign. The lowest index was slightly less than 1.70, the highest about 1.80. The crystals were minute and of a lighter brown color than jarosite, which is uniaxial (−) with $\epsilon = 1.71$, $\omega = 1.80$, for both the artificial and the natural mineral. Dana gives $\omega = 1.820$, and Larsen $1.82 \pm .01$.

Conditions Favoring the Formation of Jarosite

From its formula, jarosite should require 1 mole K_2SO_4:3 moles $Fe_2(SO_4)_3$, or 0.17 gram to 1.2 gram. To provide for about 20 per cent excess of ferric sulphate 0.19 and 1.6 grams, respectively, were

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[1] Published by permission of the Director of the U. S. Geological Survey.

[2] Hintze, Handbuch der Mineralogie, vol. **1**, pt. 3:2, p. 4182.

dissolved in 20 cc. of 0.75 *N* H_2SO_4 and the solution was heated in a sealed pyrex tube for 24 hours at 110° C. The test was continued 24 hours longer at 165°–180°. The purpose of the acid is to favor larger crystals by retarding the hydrolysis of the ferric sulphate. After washing the crystals in water they were examined optically and found to have the color and habit of jarosite—small rhombohedrons. The indices were found as given above. The analysis is shown in Table 1.

TABLE 1. ANALYSIS OF ARTIFICIAL POTASSIUM JAROSITE

	Percent	Ratios
Fe_2O_3	48.1	301 or 3.0
SO_3	32.1	401 or 4.0
K_2O	9.5	101 or 1.0
H_2O (diff.)	10.3	572 or 5.7
	100.0	

OTHER JAROSITES

A solution of ferric sulphate containing lithium sulphate was similarly treated, but no crystals developed. After potassium sulphate was added to this solution the jarosite produced was tested for lithium; none was found. No definite jarosite crystals were formed containing copper, gold, or cesium. The absence of cesium was determined by use of the spectroscope. Gold, which was present as aurous chloride, seemed to be reduced to the finely divided metal.

Rubidium jarosite was prepared under conditions similar to those already given using an acidity 1.5 *N* in H_2SO_4. The reagent used contained only 85 percent of the pure rubidium salt, 15 percent being potassium. The analysis of the product is shown in Table 2.

TABLE 2. ANALYSIS OF RUBIDIUM JAROSITE

	Percent	Ratios	
Fe_2O_3	45.8	286 or 2.9	
SO_3	31.3	390 or 3.9	
Rb_2O	9.5	51	0.8
K_2O	2.8	30	
H_2O	11.2	622 6.2	
	100.6		

A second jarosite prepared from a rubidium salt nearly free from potassium gave a smaller yield of crystals which contained sodium, evidently introduced from the glass tube. The usual quantity of these crystals was about 1 gram. It thus appears somewhat doubtful whether a rubidium jarosite could be prepared free from sodium or potassium. Such a test could not be conducted in glass. The mother liquors from the three tests with rubidium were combined and analyzed in order to show the extent to which the small quantity of potassium entered the jarosite molecule. The percentage of platinum in the mixed chloroplatinates gave the rubidium.

TABLE 3. SEPARATION OF K_2SO_4 FROM Rb_2SO_4

Alkalies taken (g.)		Alkalies left in mother liquor (g.)	
K_2SO_4	0.154	K_2SO_4	None ?
Rb_2SO_4	1.130	Rb_2SO_4	0.488

The order of preference among the alkalies appears to be potassium, rubidium, and sodium. Natrojarosite could no doubt be prepared in similar manner, also an ammonium jarosite.

The optical properties of the analyzed rubidium jarosite are: Uniaxial (−); $\epsilon=1.720$, $\omega=1.805$; cleavage $\{0001\}$ dist.; color brown. These properties are about the same as for ordinary jarosite.

Argentojarosite and plumbojarosite were also prepared. Although the products were too small, for a complete analysis, Ag_2O was determined as 19.1 percent, compared with 20.3 percent for the theoretical amount. A qualitative test for lead confirmed plumbojarosite. Argentojarosite was prepared from a saturated solution of silver sulphate, 1.5 N to 3 N in H_2SO_4 in order to prevent the formation of an hydroxyjarosite. Plumbojarosite was prepared from a solution containing 0.3 g. lead chloride in 1.5 N HCl, this acid being required to retard the precipitation of lead sulphate. These two tests were continued for three days, the lead compound being particularly slow to crystallize.

The optical properties, as determined by Miss J. J. Glass, of the U. S. Geological Survey, are: Argentojarosite, uniaxial (−), $\epsilon=1.785$, $\omega=1.880$; plumbojarosite, uniaxial (−), $\epsilon=1.783$, $\omega=1.870$; pleochroism: $\epsilon=$yellow, $\omega=$brown for both minerals. These indices were found to agree with determinations on the natural minerals, although Dana gives $\omega=1.905$ for argentojarosite.

THE SEPARATION OF POTASSIUM FROM CESIUM

When the hydrolysis of potassium and ferric sulphates proceeds at steam bath temperature, a fine-grained basic sulphate is deposited. Although its composition may vary slightly according to the quantity of sulphuric acid liberated, yet the following analysis may be given as representative of a typical product, which is also water insoluble like jarosite.

TABLE 4. ANALYSIS OF SUBSTANCE PREPARED AT STEAM BATH TEMPERATURE

	Percent	Ratios	
Fe_2O_3	44.60	279 or	4.0
SO_3	33.50	419	6.0
K_2O	7.24	77	1.1
H_2O	15.07	837	12.0
	100.41		

As much as 5 grams of potassium sulphate may be removed from a solution containing 2 mg. of cesium sulphate without complete absorption of the cesium by the precipitate as shown by the following procedure: Prepare a solution containing 40 grams of anhydrous ferric sulphate in 600 cc. of 0.2 *N* H_2SO_4 to which has been added the previously dissolved potassium sulphate. The whole is placed in a round bottom flask and immersed in a steam bath. A small funnel may be inserted in the neck of the flask in order to retard evaporation. Briefly stated, the process involves three 24-hour periods of hydrolysis with two intervening neutralizations of the greater part of the liberated acid with a little sodium hydroxide dissolved in water, until about 1 gram of iron sulphate remains in solution. After each period of hydrolysis the remaining sulphate solution is put in a clean flask and the heating is continued at one half the previous volume. The final volume after hydrolysis is 150 cc. Concentration is further continued to 50 cc. when any cesium is twice precipitated with the residual potassium as chloroplatinate to free it from sodium and iron. Cesium was confirmed spectroscopically.

TABLE 5. SEPARATION OF POTASSIUM AND RECOVERY OF CESIUM

Alkalies taken (g.)		Alkalies recovered in the solution (g.)	
K_2SO_4	Cs_2SO_4	K_2SO_4	Cs_2SO_4
2.	.020	None ?	.020
2.	.002	.013	.0006
5.	.002	.068	Trace

For concentrating very small percentages of cesium this method is not very satisfactory, as small percentages seem to be carried down with the insoluble iron compound, together with the potassium. Thus only a separation from sodium could be obtained. Sodium, for the most part, remains with the cesium in the presence of potassium. The ferric sulphate should preferably be limited to about 7 times the weight of the potassium sulphate, as a slight loss of cesium occurs with even this proportion. This loss is not easily explained.

BEHAVIOR OF RUBIDIUM

At steam bath temperature rubidium is not removed from solution as it is at higher temperatures in the jarosite molecule, as described above, although small quantities—10 mg. or less of rubidium sulphate in 2.0 g. of potassium sulphate,—are apparently removed from the solution in a similar manner to cesium.

SUMMARY

Four artificial jarosites, the potassium, the rubidium, the lead and the silver, have been prepared, by heating solutions of the respective sulphates to temperatures from 110° to 200° C. By a similar procedure at steam bath temperature it is possible to separate relatively large proportions of potassium from moderate proportions of cesium and rubidium.