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FORMATION OF RUBIDIUM JAROSITE DURING THE MICROBIOLOGICAL OXIDATION OF FERROUS IRON AT ROOM TEMPERATURE*

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ABSTRACT

During the microbial (*Thiobacillus ferrooxidans*) oxidation of ferrous ions at room temperature, in a solution containing Rb as the sole alkali cation, rubidium jarosite formed. After 17 weeks of incubation, 99% of the Rb in solution had reacted to form rubidium jarosite. Although Rb reacts somewhat more slowly than K to form jarosite, it reacts appreciably faster than NH_4 and much faster than Na. The cell dimensions (*a* 7.316(2), *c* 17.568(2) Å) and the X-ray-diffraction (powder) pattern of the rubidium jarosite are very close to those of ammoniojarosite; this may well reflect similar ionic radii (1.44 Å for NH_4 and 1.47 Å for Rb).

Keywords: microbial oxidation, ferrous iron, rubidium jarosite (formation, cell dimensions), *Thiobacillus ferrooxidans*.

SOMMAIRE

L'oxydation d'ions ferreux par le microbe *Thiobacillus ferrooxidans* à température ambiante dans une solution qui contient uniquement le rubidium comme cation alcalin mène à la formation de jarosite rubidique. Après une incubation de 17 semaines, 99% du Rb originellement en solution se trouve sous forme de jarosite. Quoique la réaction du Rb soit plus lente que celle du K, elle est plus rapide que celle du NH_4 et beaucoup plus rapide que celle du Na. Par les dimensions de la maille (*a* 7.316(2), *c* 17.568(2) Å) et le cliché de poudre, la jarosite rubidique ressemble beaucoup à l'ammoniojarosite, conséquence probable de la ressemblance des rayons ioniques (1.44 Å pour le NH_4, 1.47 Å pour le Rb).

(Traduit par la Rédaction)

Mots-clés: oxydation microbiale, *Thiobacillus ferrooxidans*, ions ferreux, jarosite rubidique (formation, dimensions de la maille).

INTRODUCTION

Naturally occurring jarosites have the general formula $A\mathrm{Fe}_3(\mathrm{SO}_4)_2(\mathrm{OH})_6$, in which *A* may be K, Na, NH_4, H_3O, ½ Pb or Ag. Although rubidium, thallium and mercury jarosite have not been found in nature, metallurgical scientists (Dutrizac & Kaiman 1975, 1976) have synthesized single-phase products of these jarosites by precipitation from hot aqueous solutions. They have found the method to be a convenient means of removing unwanted iron, alkali metal ions or sulfate ions from hydrometallurgical processing solutions.

Over the last two decades soil scientists (Clark *et al.* 1961, Fleming & Alexander 1961, van Breemen 1976, Ross & Ivarson 1981) have found jarosite-type compounds to be the main components of conspicuous yellow mottles of acid sulfate soils. These worldwide soils (~ 20 million ha) are highly acidic, pH 3–4, and have developed generally on marine sediments containing pyrite. Ivarson *et al.* (1979) showed that, under laboratory conditions, the acidophilic iron-oxidizing bacterium *Thiobacillus ferrooxidans* plays an important role in the formation of the naturally occurring single-phase potassium, sodium and ammonium jarosite and their solid-solution series. Additional studies (Ivarson *et al.* 1980) showed that the microbe was involved in the production of naturally occurring hydronium jarosite.

The main reactions involved can be written as:

$$2\mathrm{FeS}_2(\text{pyrite}) + 7\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{FeSO}_4 + 2\mathrm{H}_2\mathrm{SO}_4 \quad (1)$$

$$4\mathrm{FeSO}_4 + 2\mathrm{H}_2\mathrm{SO}_4 + \mathrm{O}_2 \rightarrow 2\mathrm{Fe}_2(\mathrm{SO}_4)_3 + 2\mathrm{H}_2\mathrm{O} \quad (2)$$

$$3\mathrm{Fe}_2(\mathrm{SO}_4)_3 + 11\mathrm{H}_2\mathrm{O} + 2A^+ \rightarrow 2A\mathrm{Fe}_3(\mathrm{SO}_4)_2(\mathrm{OH})_6 + 5\mathrm{H}_2\mathrm{SO}_4 \quad (3)$$

Equations (1) and (3) are chemical reactions. However, because (i) the rate of the chemical oxidation of ferrous ions is very slow at pH values below 4 (Ivarson & Sojak 1978) and (ii) that by *T. ferrooxidans* is very rapid (Silverman & Lundgren 1959), the reaction in equation (2) is mainly bacteriological.

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*C.B.R.I. Contribution No. 1224.

As part of an overall program to investigate the microbiological formation of jarosites at room temperature, and considering ion sizes and other properties, Rb and Cs were chosen to determine whether they would be incorporated in jarosites following microbial oxidation of ferrous ions. Thus this study was set up to determine (1) whether rubidium jarosite would crystallize, at room temperature, in a solution containing $FeSO_4$, the iron-oxidizing bacterium and rubidium salts and, if so, (2) its rate of formation in comparison with other microbiologically formed jarosites. Also, a solution of $FeSO_4$ containing cesium salts was inoculated with the bacterium to determine if cesium jarosite could be produced under similar conditions.

METHODS AND MATERIALS

Culture systems

The culture systems were the same as those described previously (Ivarson *et al.* 1979). For convenience, a brief description of the set-up follows. Three 2-litre reagent bottles each containing 1.5 litres of filter-sterilized basal medium were each inoculated with a 5 ml active culture of *T. ferrooxidans*. The basal medium contained $MgSO_4 \cdot 7H_2O$ (0.5%), $Ca(NO_3)_2 \cdot 4H_2O$ (0.3%), $FeSO_4 \cdot 7H_2O$ (0.5%) and H_3PO_4 to adjust the pH to 2.7 and supply the bacterium's phosphorus needs. To promote the formation of rubidium jarosite, we added 0.38% Rb_2SO_4 and 0.02% RbCl to one of the systems. To study the possible formation of cesium jarosite, the contents of the second bottle were supplemented with 0.52% Cs_2SO_4 and 0.02% CsCl. In order to make a more accurate comparison with the results reported in Ivarson *et al.* (1979), we added 0.25% K_2SO_4 and 0.01% KCl to the medium in the third bottle. The Rb and Cs were both added on an equivalent K basis. All three solution systems were aerated with filter-sterilized air at about one bubble *per* two seconds and incubated for one year at 28°C. Controls (systems without the bacterium) were not set up, because previous studies had shown that in such systems oxidation of ferrous iron and the formation of basic ferric sulfates did not occur, even after four months of incubation (Ivarson *et al.* 1979).

Analyses for jarosite formation

At various times during the incubation period, pH values of the solutions were determined and samples of the suspensions from the basic ferric sulfate systems were removed, as described previously (Ivarson *et al.* 1979). The suspensions were centrifuged and washed, and the supernatant solution and part of the precipitates, after dissolution in HCl, were analyzed for K, Rb and Cs by atomic absorption. At the end of the experiment, the precipitate from the rubidium-bearing system was heated at 150°C for 4 hours, which resulted in a weight loss of 2.3% due to loss of adsorbed water. The precipitate was then dissolved in 3 N HCl for analysis of Rb and Fe by atomic absorption and of SO_4 by $BaSO_4$ precipitation (Ross & Ivarson 1981). Because some H_3PO_4 had been added to the systems, the dissolved precipitate was analyzed for PO_4 by the ammonium molybdate method (Analytical Methods Manual 1974).

The precipitates were X-rayed using (1) a Philips diffractometer with Fe-filtered Co radiation and (2) a Guinier–de Wolff camera. Quartz was used as an internal standard in both procedures. All diffraction data obtained were refined by processing through a least-squares computer program. In presenting the X-ray-diffraction patterns to demonstrate the rates at which the precipitate crystallized, we show only the essential patterns, up to and including the one in which maximum peak-heights were obtained.

RESULTS AND DISCUSSION

On the second day of incubation the three yellowish-green solutions turned red, indicating oxidation of ferrous iron. On the third day (Table 1) there were slight decreases in the pH values of the three systems. Then for the next 18 days the pH values decreased fairly rapidly and thereafter very slowly until they leveled off at 119 days. There were noticeable differences in the rates at which the pH values decreased, the relative rates being K > Rb > Cs.

The chemical and X-ray data show that the rate and amount of acid produced and the rate

TABLE 1. CHANGES IN pH IN THE K, Rb AND Cs SYSTEMS*

	Days of incubation						
System	3	4	5	7	21	119	175
K	2.60	2.38	2.08	1.65	1.49	1.48	1.49
Rb	2.60	2.48	2.45	2.35	1.54	1.49	1.49
Cs	2.63	2.54	2.57	2.56	2.34	2.20	2.20

*Initial pH 2.70

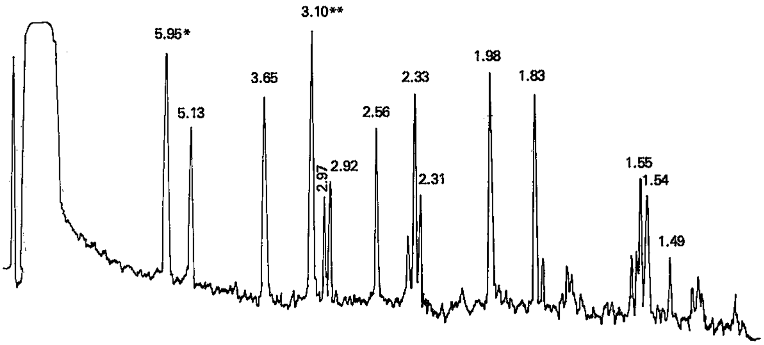

FIG. 1. Photodensitometer trace of X-ray film pattern (Guinier–de Wolff camera) of rubidium jarosite. Spacings in Angstrom units.

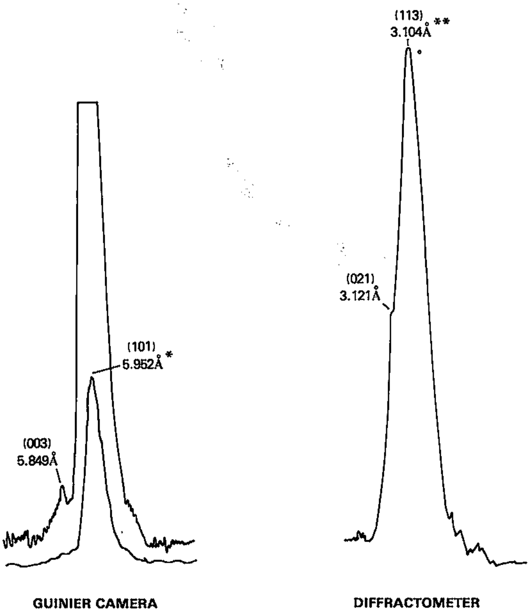

FIG. 2. X-ray-diffraction data for rubidium jarosite. Photodensitometer trace (Guinier camera); scanning speed = 1 mm/min. For diffractometer, scanning speed = 0.5°/min.

at which the bright yellow precipitate (potassium jarosite) crystallized in the potassium system parallel those of an identical system in the previous experiment (Ivarson *et al.* 1979). A bright yellow precipitate formed also in the rubidium system. This precipitate had a slightly different X-ray-diffraction pattern from that of the potassium jarosite. The material in the rubidium system shows six strong peaks (Figs. 1, 2), at 5.95, 3.65, 3.10, 2.33, 1.98 and 1.83 Å and seven medium peaks at 5.13, 2.97, 2.92, 2.56, 2.31, 1.55 and 1.54 Å. These values, along with 14 weaker reflections, agree very closely with values reported for ammoniojarosite (Ivarson *et al.* 1976). This may be expected from the similar ionic radii of their alkali ions (1.44 Å for NH_4 and 1.47 Å for Rb). Interestingly, the doublets at the 021 and 113 reflections, which can be used to help characterize potassium, sodium, ammonium and hydronium jarosite (Ivarson *et al.* 1979, 1980), appear in rubidium jarosite (Fig. 1) as a single strong peak at 3.10 Å. The pattern produced (Fig. 2) using a scanning speed of 0.5°/min shows that two peaks are actually present: a weak one at 3.12 Å and a strong one at 3.10 Å. This agrees closely with the findings of Dutrizac & Kaiman (1975), who reported the doublet occurring at 3.11 and 3.09 Å and obtained *a* 7.320, *c* 17.362 Å. The cell dimensions calculated from our data are *a* 7.316, *c* 1.568 Å (both ± 0.002 Å). The latter values are very close to those reported for ammoniojarosite (Ivarson *et al.* 1976).

The results of a chemical analysis of rubidium jarosite are shown in Table 2. A small amount of PO_4 is also present and is considered part of the jarosite structure. The actual amounts of Fe and SO_4 (with PO_4) are close to the theoretical amounts for rubidium jarosite. The

TABLE 2. CHEMICAL COMPOSITION OF RUBIDIUM JAROSITE

Element	Actual (%)	Theoretical (%)
Rb	13.4	15.62
Fe	29.8	30.61
SO_4	32.7	35.11
PO_4	1.4	-
H_3O + OH	22.8	18.66
Approximate Formula	$Rb_{0.86}(H_3O)_{0.14}Fe_{2.92}(SO_4)_{1.86}(PO_4)_{0.04}(OH)_6$	

amount of Rb found, however, is significantly less than the theoretical amount, which is also shown in the rubidium jarosite formula that was calculated from these data. It was assumed that the Rb deficiency was filled by H_3O. Evidence for this substitution was also obtained from a thermogravimetric curve (not included here) that shows a well-defined weight-loss of 12.0% between 200 and 400°C. This loss is 2.1% more than the theoretical weight-loss due to dehydroxylation (*cf.*, Dutrizac & Kaiman 1975). At least part of this excess weight loss may be attributed to loss of H_3O that substituted for Rb. Results of this analysis agree with those of potassium jarosites and sodium jarosites by Kubisz (1970) and of rubidium jarosite by Dutrizac & Kaiman (1975), who established that these compounds always contain a deficiency of alkali metal and an excess of water.

The quantity of precipitate found in the cesium system was, at all sampling times, much smaller than that found in the other two systems. Also, its color was conspicuously different; instead of a bright yellow color, it was brownish red. After 45 days of incubation, the Philips diffractometer pattern showed a very weak peak near 5.10 Å and a very weak doublet near the 021 and 113 reflections. When further incubation increased the intensities of these peaks slightly and chemical analyses showed that the precipitate contained no Cs, it was assumed that instead of cesium jarosite, hydronium jarosite had formed. This assumption was based (1) on the observation that hydronium jarosite could easily be produced when a $Fe_2(SO_4)_3$ solution (pH 2.0) containing Cs salts was autoclaved and (2) on earlier findings (Ivarson *et al.* 1980) showing that it formed slowly in the presence of a $FeSO_4$ solution, the iron-oxidizing bacterium and either Mg, Al or Li cations. However, Guinier–de Wolff camera recordings showed that the pattern of the precipitate at the end of the experiment resembles closely that of potassium jarosite (PDF 22–827). The *d* values for the doublet occur at 3.11 Å (021) and 3.08 Å (113), and the position of the (003) reflection at 5.72 Å. Chemical analysis of the precipitate also showed the presence of 0.07% K, which amounts to 1% potassium jarosite. The K was probably contained as an impurity in required chemical reagents that had been added to the system. In this connection, it is pointed out that there is a strong preference for K in the formation of jarosites in these systems (Ivarson *et al.* 1979).

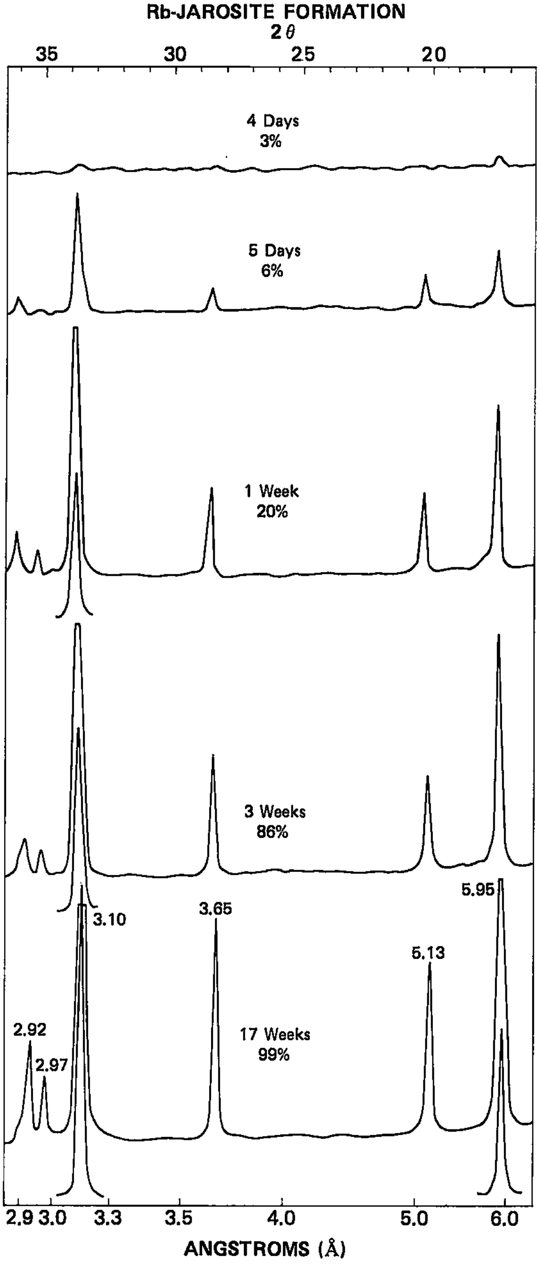

FIG. 3. X-ray-diffraction patterns of Rb jarosite formed in an incubated solution containing $FeSO_4$, Rb and an iron-oxidizing bacterium. Percentages refer to fractions of total Rb present in the solids.

The rubidium jarosite crystallized somewhat more slowly than the potassium form (Fig. 3). It required 17 weeks before its X-ray-diffraction

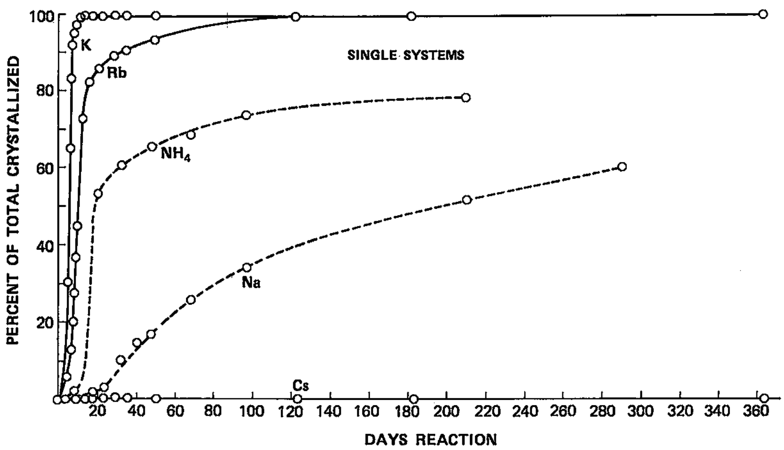

FIG. 4. Cumulative formation of K, Rb, NH_4 and Na jarosite in incubated systems, each containing a single cation. Data calculated from the amount of cations remaining in solution.

peaks reached maximum heights, whereas the potassium jarosite (not shown here) needed only 3 weeks.

The calculated amounts of potassium and rubidium jarosite that crystallized during the one-year incubation period are shown in Figure 4. For comparison, the amounts of ammonium and sodium jarosite that crystallized over a shorter period (Ivarson *et al.* 1979) have been included. The results agree with the X-ray data: Rb reacts slightly more slowly than K to form a jarosite-type compound, but Cs does not. This observation plus the previous one (Ivarson *et al.* 1980), that Li also does not react to form a jarosite-type compound, are in accord with the findings of Tananaev *et al.* (1967a). These authors showed that basic Ga sulfates, having the formula $M\mathrm{Ga_3(SO_4)_2(OH)_6}$, where M is H_3O, Na, K, NH_4 or Rb, could be synthesized. However, in the presence of Cs or Li (Tananaev *et al.* 1967b) a basic Ga sulfate could not be synthesized. Figure 4 also shows that, although Rb reacts somewhat more slowly than K to form a jarosite compound, it reacts appreciably faster than NH_4 and much faster than Na.

The increase in rates of jarosite formation (Fig. 4) parallels the decrease in pH values of the systems (Table 1). This can be explained by equation (3), which shows that the greater the amount of basic ferric sulfates crystallized, the greater the amount of acid produced.

As far as the authors know, this is the first reported evidence showing (1) that Rb-jarosite crystallizes during the microbial oxidation of ferrous iron at room temperature and (2) that cesium jarosite does not form in these conditions. The ionic radius of cesium (1.69 Å) is probably too large for it to fit in the jarosite structure.

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