*The Canadian Mineralogist*
Vol. 33, pp. 1311-1319 (1995)

# CHARACTERIZATION OF ARGENTOJAROSITE FORMED FROM BIOLOGICALLY OXIDIZED $Fe^{3+}$ IONS

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## ABSTRACT

Argentojarosite [$AgFe_3(SO_4)_2(OH)_6$] was synthesized without by-products at ambient temperatures from $Fe^{3+}$ ions formed from $Fe^{2+}$ ions by the iron-oxidizing bacteria *Thiobacillus ferrooxidans*. The product was characterized using X-ray-fluorescence (XRF) analysis, powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), diffuse-reflectance infrared Fourier-transform spectrometry (DRIFTS), inductively coupled plasma – atomic emission spectrometry (ICP–AES) and scanning electron microscopy (SEM). We found, using XRD, DRIFTS, and chemical analysis, that argentojarosite was formed from $Fe^{3+}$ ions oxidized both biologically by *T. ferrooxidans* and chemically by $H_2O_2$. Differences were noted in the morphologies and intensities at two $\upsilon_3$ ($SO_4^{2-}$) bands of DRIFTS between biological and chemical products, but there is no major difference in chemical compositions, chemical species and XRD patterns. It is likely that the extracellular substances (secretions) from bacteria take part in the aggregation of the argentojarosite formed.

*Keywords:* argentojarosite, *Thiobacillus ferrooxidans*, inorganic synthesis, morphology, biological oxidation, biomineralization.

## SOMMAIRE

Nous avons synthétisé l'argentojarosite [$AgFe_3(SO_4)_2(OH)_6$] sans autres produits à température ambiante à partir d'ions $Fe^{2+}$ transformés en $Fe^{3+}$ par oxydation effectuée par la bactérie *Thiobacillus ferrooxidans*. Nous avons utilisé les méthodes suivantes pour caractériser les produits: analyse par fluorescence X, diffraction X (méthode des poudres), spectroscopie des photo-électrons X, spectrométrie infra-rouge en réflectance diffuse avec transformation de Fourier, analyse avec plasma à couplage inductif – spectrométrie des émissions atomiques, et microscopie électronique à balayage. Les résultats obtenus par diffraction X, spectrométrie infra-rouge et analyse chimique montrent que l'argentojarosite s'est formée à partir des ions $Fe^{3+}$ oxydés soit biologiquement par *T. ferrooxidans*, soit chimiquement par traitement au $H_2O_2$. Certaines différences existent dans la morphologie des agrégats formés biologiquement et chimiquement, et dans l'intensité de deux bandes $\upsilon_4$ ($SO_4^{2-}$) dans l'infra-rouge. Malgré celles-ci, il n'existe aucune différence importante dans leur composition chimique, dans les espèces chimiques présentes, ou dans les spectres de diffraction X. Il semble probable que des substances extracellulaires (sécrétions) issues des bactéries participent à la formation d'agrégats d'argentojarosite.

(Traduit par la Rédaction)

*Mots-clés:* argentojarosite, *Thiobacillus ferrooxidans*, synthèse inorganique, morphologie, oxydation biologique, biominéralisation.

## INTRODUCTION

The jarosite group of minerals [$M_nFe_3(SO_4)_2(OH)_6$, where $M$ is a monovalent or divalent cation, and $n$ is 1 or ½] is recognized as an iron-containing mineral that needs to be rejected in hydrometallurgical processes (*e.g.*, Fairchild 1933), and also as secondary minerals formed in biogeochemical cycles of Fe and S (Nordstrom 1982, Taylor *et al.* 1984). Jarosite-group minerals commonly occur in acidic, sulfate-rich environments such as acid mine-drainage, and they develop as a result of pyrite weathering. According to the model of Singer & Stumm (1970) on pyrite weathering, iron-oxidizing bacteria (mainly *Thiobacillus ferrooxidans*) play an important role in the formation of acid mine-drainage. In previous work, we reported compositional changes of the pyrite surface in the bacterial dissolution of pyrite with *T. ferrooxidans*, and suggested that jarosite formation may suppress the weathering of pyrite (Konno *et al.* 1991, Sasaki *et al.* 1993). Potassium-dominant jarosite ($M^+ = K^+$), natrojarosite ($M^+ = Na^+$), and ammoniojarosite ($M^+ = NH_4^+$) are known to be formed environmentally in the presence of *T. ferrooxidans* (Ivarson *et al.* 1979, Lazaroff *et al.* 1982), whereas formation of argentojarosite ($M^+ = Ag^+$) and plumbojarosite ($M^+ = ½Pb^{2+}$) in the presence of iron-oxidizing bacteria has not been reported.

Argentojarosite has been mainly related to hydrometallurgical circuits (May *et al.* 1973, Dutrizac & Jambor 1984) and occasionally occurs as a mineral,

a valuable ore of silver (Dutrizac & Jambor 1984). Silver ions are extremely toxic to a wide range of bacteria (Sugio *et al.* 1981), whereas there is a report that *T. ferrooxidans* and *T. thiooxidans* accumulate silver during leaching of sulfide ores (Pooley 1982). In view of these conflicting reports, it seems significant to attempt the formation of argentojarosite in the presence of bacteria. This could also lead to the better understanding of the biogeochemical cycle of silver.

In the present work, argentojarosite was synthesized with the assistance of *T. ferrooxidans* at ambient temperatures, and characterized in comparison with that formed chemically. The mechanism of formation of jarosite-group minerals also is discussed.

## Materials and Methods

### *Microorganism and culture*

A strain of *Thiobacillus ferrooxidans* (HUTY8906) was isolated from acid drainage in the Toyoha mines (Hokkaido, Japan) (Sasaki *et al.* 1993), and cultivated conventionally in 150 $cm^3$ of 9K medium adjusted to a pH of 2.0 with $H_2SO_4$ (Silverman & Lundgren 1959), using silico-plugged 500-$cm^3$ Erlenmeyer flasks. The 9K medium consists of the following components: 15 mmol $dm^{-3}$ $(NH_4)_2SO_4$, 2.0 mmol $dm^{-3}$ $MgSO_4 \cdot 7H_2O$, 1.3 mmol $dm^{-3}$ KCl, 5.7 mmol $dm^{-3}$ $K_2HPO_4$, 0.061 mmol $dm^{-3}$ $Ca(NO_3)_2$, and 160 mmol $dm^{-3}$ $FeSO_4 \cdot 7H_2O$ as an energy source. All components of the culture media other than $Fe^{2+}$ salts were sterilized by autoclaving at 120°C for 20 min, and glass assemblies were sterilized in a hot-air oven at 180°C for two hours. All cultures were grown in a rotary shaking incubator (Takasaki Kagaku Co. Ltd., TB–16) at 30°C at 175 rpm. Cells were harvested by centrifugation at 18,000 × g for 20 min and resuspended in acidic solutions adjusted to a pH of 2.0 with $H_2SO_4$. Cell numbers were counted directly by microscopic observation.

### *Formation of argentojarosite*

*Biological formation*: The bacterial formation of argentojarosite was carried out in silico-plugged and light-shielded 500 $cm^3$ Erlenmeyer flasks with 150 $cm^3$ of 160 mmol $dm^{-3}$ $FeSO_4 \cdot 7H_2O$ solutions, adjusted to a pH of 2.2 using $H_2SO_4$ and $Li_2CO_3$, because lithium ions are not incorporated in jarosite-type compounds (Dutrizac & Kaiman 1976). Then, $2 \times 10^8$ cells/flask of *T. ferrooxidans* were inoculated. The flasks were incubated on a rotary shaker for several days at 30°C. Under such conditions, bacteria cannot grow fully owing to a lack of N and P sources. When $Ag^+$ ions were added to the solution before $Fe^{2+}$ ions had been entirely oxidized, metal Ag was formed with argentojarosite, because the standard redox potential of $Ag^+/Ag$ ($E^0$ = 799 mV) is higher than that of $Fe^{3+}/Fe^{2+}$ ($E^0$ = 771 mV). When more than the stoichiometric amount of $Ag^+$ ions was added, $Ag_2SO_4$ was formed as a by-product owing to its low solubility. Therefore, after $Fe^{2+}$ ions were completely oxidized, the stoichiometric amount of $AgNO_3$ (1.3515 g) was added to the solution ($[Ag^+]$ = 53 mmol $dm^{-3}$) in the presence of bacteria (Biological preparation 1) or after filtering three times with a 0.20-μm Millipore filter to remove bacteria (Biological preparation 2). After $Ag^+$ ions were added, aging for precipitation was continued for 168 hours in the incubator under the same conditions. The precipitate was collected by filtration with a 0.20-μm Millipore filter, and kept in a desiccator at room temperature after air-drying.

*Chemical formation*: The chemical formation of argentojarosite was carried out using $H_2O_2$ as an oxidant. First, 6.672 g of $FeSO_4 \cdot 7H_2O$ was dissolved into 50 $cm^3$ of $H_2SO_4$ (pH 2.00) in a 500 $cm^3$ Erlenmeyer flask. Then, 100 $cm^3$ of 0.42 % $H_2O_2$ was added to the flask at 0.7 $cm^3$ $min^{-1}$ using a peristaltic pump to oxidize $Fe^{2+}$ ions slowly (Chemical preparation 1), giving a final pH of 2.10. Addition of $Ag^+$ ions and aging for precipitation were carried out similarly to

TABLE 1. MOLE RATIO, SPECIFIC SURFACE-AREA, AND FWHM OF 113 XRD PEAK FOR BIOLOGICALLY AND CHEMICALLY PRODUCED ARGENTOJAROSITE

| Sample | Composition/ wt% | | | Color*1 | Specific surface area / $m^2$ $g^{-1}$ | FWHM*2 of 113 XRD peak / 2θ |
|---|---|---|---|---|---|---|
| | Ag | Fe | S | | | |
| | (mole ratio | Ag: | Fe:S) | | | |
| Standard | 17.3 | 29.8 | 11.9 | 5.0Y 8.5/11 | $2.7_1$ | 0.106 |
| | (1: | 3.31: | 2.33) | | | |
| Biological 1 | 14.6 | 29.1 | 11.2 | 5.0Y 8.5/11 | $1.7_4$ | 0.111 |
| | (1: | 3.71: | 2.50) | | | |
| Chemical 1 | 15.5 | 31.4 | 11.7 | 5.0Y 8.5/11 | $1.2_5$ | 0.097 |
| (slow oxidation of Fe(II) ions) | (1: | 3.93: | 2.55) | | | |
| Chemical 2 | 14.5 | 29.6 | 11.1 | 5.0Y 8.5/11 | $1.4_6$ | 0.106 |
| (rapid oxidation of Fe(II) ions) | (1: | 3.95: | 2.58) | | | |

*1 Expressed by JIS number.

*2 Excluded intensities of $K\alpha_2$ lines.

the biological formation. As a reference, an experiment with rapid addition of $H_2O_2$ was also carried out (Chemical preparation 2). The precipitate was collected and kept in the same manner as above.

*Standard substance*: the standard substance was synthesized by autoclaving methods (Dutrizac & Kaiman 1976) and supplied by Dr. J.E. Dutrizac of CANMET, Canada. The elemental composition is listed in Table 1.

### *Characterization of products*

The amounts of Fe and S species were established, first by inductively coupled plasma – atomic emission spectrometry, ICP–AES (Shimazu ICPS–1000IV), after decomposition in hydrochloric acid. Here, however, AgCl precipitated, so that bulk analysis was abandoned. Then, elemental analysis was carried out by X-ray-fluorescence spectrometry, XRF (JEOL JSX–603). The 0.100-g samples were diluted in 1.100 g of cellulose powder to determine Fe, S and Ag by calibration with the standard substance.

X-ray-diffraction (XRD) patterns of the samples were collected with a diffractometer (JEOL JDX–3500) equipped with a monochromator. The operating conditions were: Cu*K*α radiation, 30 kV, 200 mA; step-scanning method; time constant, 0.5 second. Peak correction was done by reference to the 200 peak of NaCl.

To examine the secondary compounds that cannot be detected by other analytical technique, X-ray photoelectron spectroscopy (XPS) analysis was carried out. The samples were pressed onto copper foil on a holder and introduced into the spectrometer (V.G. Scientific ESCALAB MkII). After evacuating to better than $10^{-5}$ Pa within 15 min, the sample was transferred into an analyzer chamber of better than $5 \times 10^{-8}$ Pa and cooled below 150 K, then irradiated with Mg*K*α X rays (15 kV, 10 mA). The binding energies, $E_B$, were calibrated with $E_B$[Au $4f_{7/2}$] = 84.0 eV. Details of the data analysis were described by Konno *et al.* (1991).

Morphologies were observed with a scanning electron microscope (SEM: JEOL JSM–6300F) at 2–3 kV. This field-emission-type SEM enabled observation with very thinly evaporated platinum on the sample to avoid differential charging.

The specific surface-area of the product was determined by the $N_2$ gas adsorption B.E.T. method by a Quantasorb instrument (Yuasa Ionics QS–13 with a cell QS–300 for low-value measurements).

Infrared spectra were recorded with a JASCO VALOR III Fourier-transform infrared spectrometer (FTIR) using diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFTS), with 0.3 (w/w) % of sample precipitate in KBr, under the following conditions: accumulation, 64 times; resolution, 4 $cm^{-1}$; detector, TGS; range of wavenumbers, 400–4000 $cm^{-1}$.

## Results and Discussion

As shown in Figure 1, argentojarosite was formed without crystalline by-products such as Ag or $Ag_2SO_4$ under all conditions. The XRD data for argentojarosite formed from biologically oxidized $Fe^{3+}$ ions (Biological preparation 1) are listed in Table 2, and are in good agreement with JCPDS 25–1327. The results for the other three products are very similar to those for Biological product 1. The cell parameters of biologically produced argentojarosite were calculated to be *a* 7.353 ± 0.004, *c* 16.607 ± 0.074 Å, coincident with the JCPDS data, *a* 7.35, *c* 16.58 Å. Since argentojarosite was also formed from chemically oxidized $Fe^{3+}$ ions, *T. ferrooxidans* itself or its extracellular substances are not indispensable to crystallize argentojarosite.

The chemical composition of products is summarized in Table 1. The ratios of Fe to S is around 1.5 in

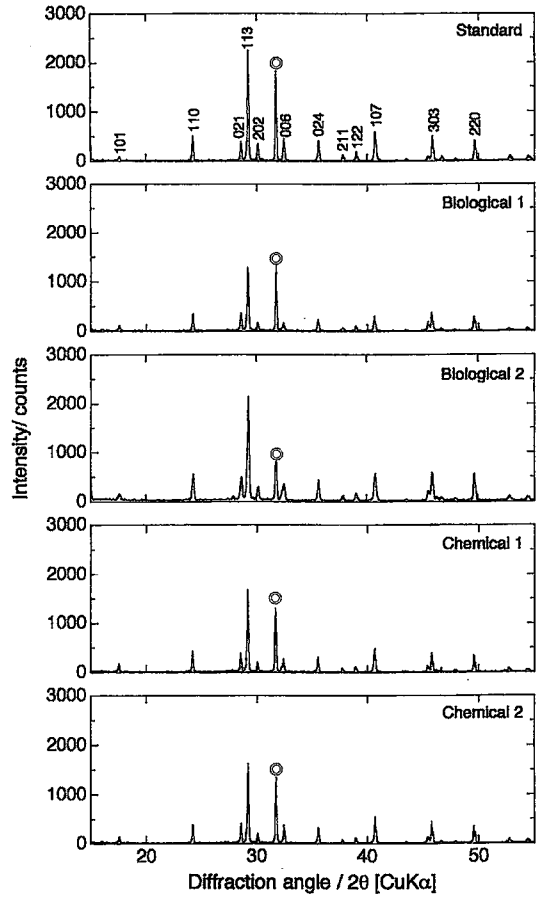



FIG. 1. XRD patterns of biological and chemical products with the standard pattern. ◎: the 200 peak of NaCl.

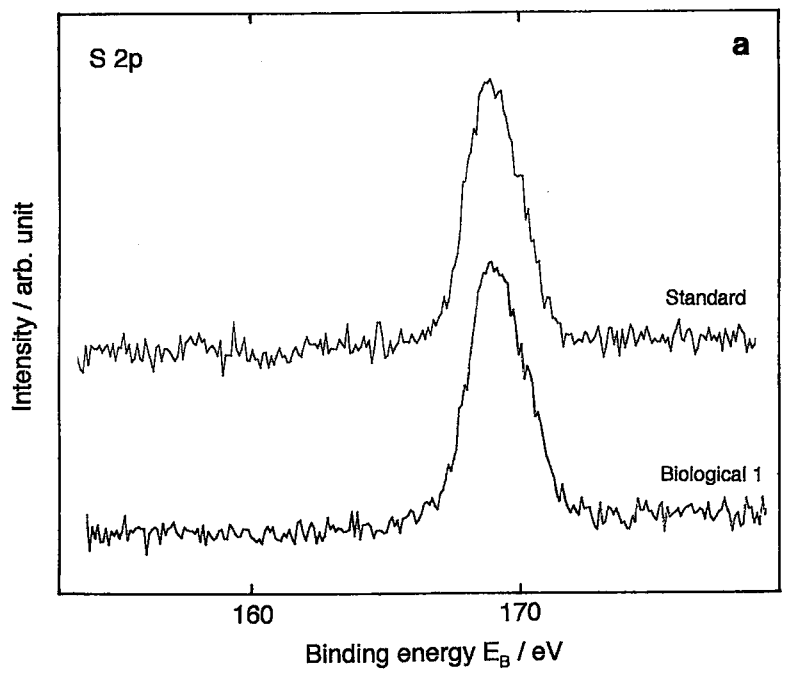
TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR ARGENTOJAROSITE FROM BIOLOGICALLY OXIDIZED $Fe^{3+}$ IONS (BIOLOGICAL PRODUCT 1)

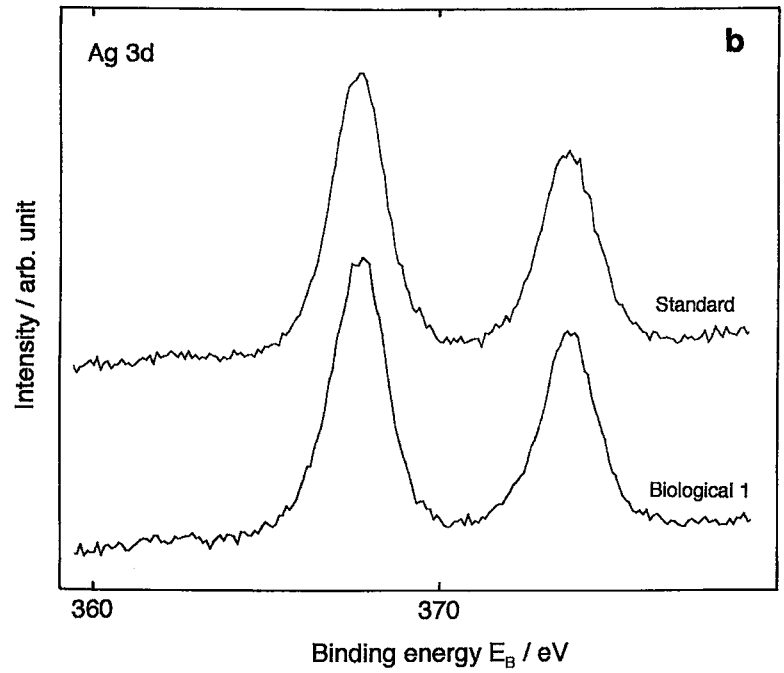
| | Observed | | JPCDS 25-1327 | |
|---|---|---|---|---|
| *hkl* | $d_{obs}$/Å | $I/I_0$ | $d_{cal}$/Å | $I/I_0$ |
| 012 | 5.065 | 9 | 5.08 | 6 |
| 110 | 3.678 | 30 | 3.68 | 30 |
| 021 | 3.130 | 22 | 3.130 | 20 |
| 113 | 3.062 | 100 | 3.060 | 100 |
| 202 | 2.974 | 12 | 2.972 | 15 |
| 006 | 2.763 | 12 | 2.763 | 20 |
| 024 | 2.524 | 17 | 2.524 | 30 |
| 122 | 2.311 | 9 | 2.309 | 8 |
| 107 | 2.219 | 26 | 2.218 | 30 |
| 303 | 1.980 | 25 | 1.979 | 25 |
| 220 | 1.837 | 20 | 1.837 | 20 |
| 226 | 1.530 | 10 | 1.529 | 8 |
| 404 | 1.483 | 10 | 1.485 | 5 |

all samples, whereas the proportion of Ag is slightly below the stoichiometric proportion of the argentojarosite. The colors of the biological and chemical products were similar to the standard substance. Table 1 also lists the specific surface-area.

The XP spectra in Figure 2 confirm that the chemical species in Biological product 1 are in good agreement with those in the standard. The peak at $E_B$[S $2p_{3/2}$] = 168.9 eV is assigned to sulfate, that at $E_B$[Ag $3d_{5/2}$] = 367.7 eV to $Ag^+$, taking into account the Auger parameter, $\alpha$ = 723.0 eV, calculated from $E_B$[Ag $3d_{5/2}$] and the Ag MNN spectra. The $E_B$[Fe 2p] could not be determined owing to interference of the Ag 3s spectrum, but the results suggest that biological products do not contain appreciable amounts of by-products. Further, there were no large differences between biological and chemical products.

The SEM photographs, however, show that each preparation of argentojarosite is mostly automorphic *i.e.*, different from the standard substance (Fig. 3a), and there are differences in the morphologies of the biological and chemical products, as shown in Figures 3b, c, d, and e. The biological products consist of "aggregates" of many approximately squared-faced crystals with sharp edges and submicrometric microintergrowths (Figs. 3b, c), whereas chemical products consist of several micrometric large particles, which form separate pyramidal rhombohedra with smooth surfaces (Figs. 3d, e). A similar state of aggregation also was observed for the K-dominant jarosite formed in the presence of *T. ferrooxidans*. Aggregation is a common characteristic in biologically formed jarosite-group minerals. According to Sugio *et al.* (1981), $10^{-5}$ mol $dm^{-3}$ $Ag^+$ ions inhibited cell growth of *T. ferrooxidans* ($\sim 1 \times 10^9$ cells/100 $cm^3$ 9K medium) for the initial 80 hours. Furthermore, $5 \times 10^{-3}$ mol $dm^{-3}$ $Ag^+$ ions completely suppressed the iron-oxidizing





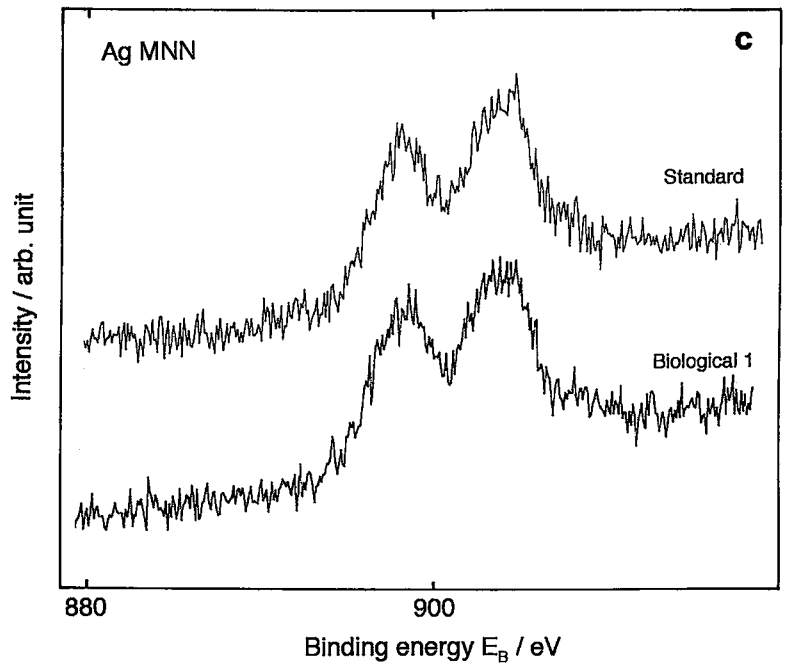




FIG. 2. X-ray photoelectron spectra for Biological product 1 and Standard substance. (a) S 2p, (b) Ag 3d, and (c) Ag MNN (Auger).

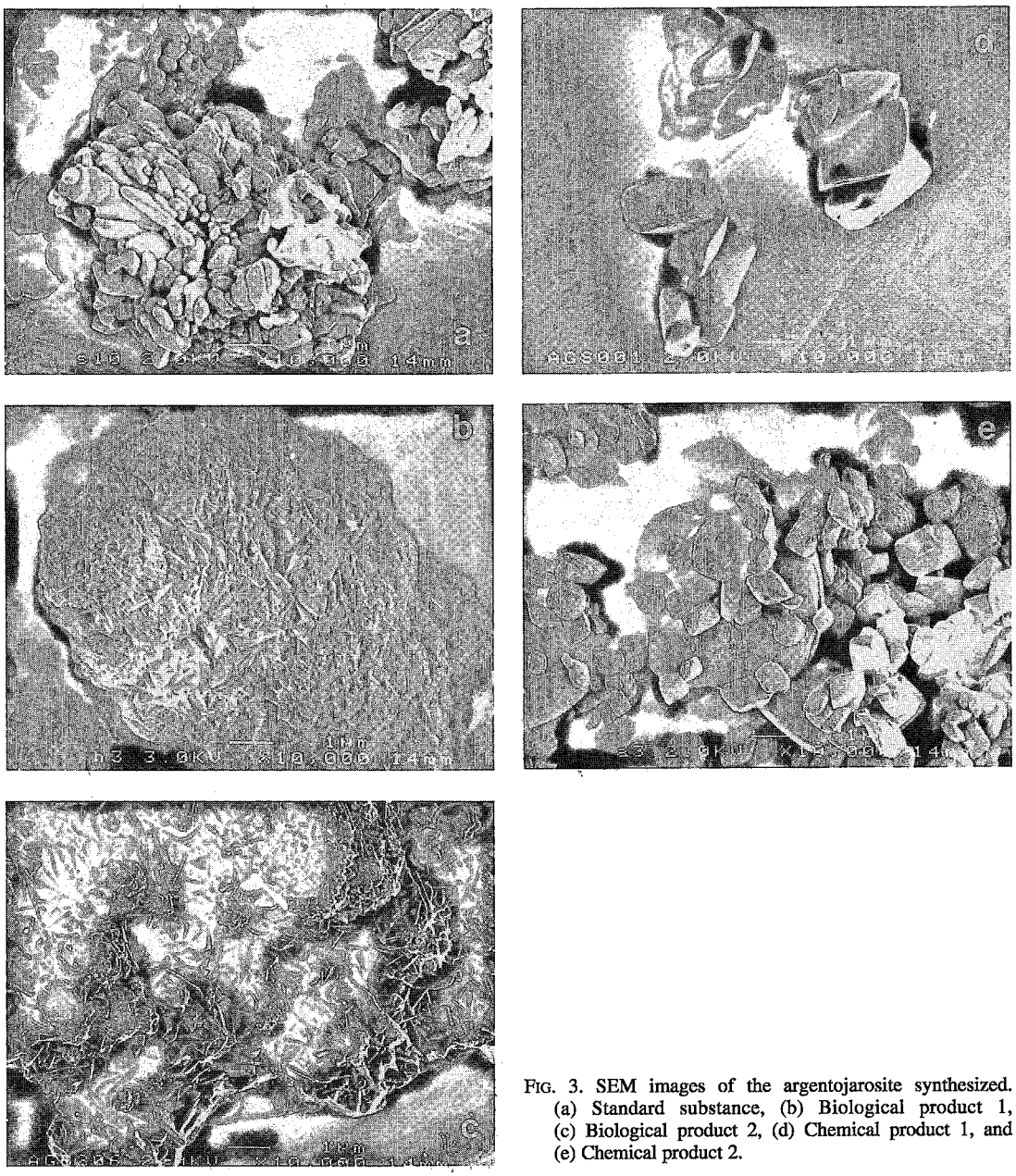



FIG. 3. SEM images of the argentojarosite synthesized. (a) Standard substance, (b) Biological product 1, (c) Biological product 2, (d) Chemical product 1, and (e) Chemical product 2.

activity of *T. ferrooxidans* ($\sim 1 \times 10^9$ cells/100 $cm^3$ 9K medium) within 20 min. Therefore, under the present experimental condition ($[Ag^+]$ = 53 mmol $dm^{-3}$), the growth and iron-oxidizing activity of *T. ferrooxidans* had to be very short-lived. Morphologies of biologically mediated argentojarosite were found to be similar with (Fig. 3b) or without (Fig. 3c) bacterial cells during aging. This finding indicates that cell bodies do not take part in aggregation, but extracellular substances (secretions from cells) may contribute to aggregation. The particles formed by rapid addition of $H_2O_2$ are not uniform; larger (approximately 5 μm in diameter) and smaller (less than 1 μm) particles (Fig. 3e), are present, probably because of an inhomogeneous reaction. Lazaroff *et al.* (1985) reported that the morphology of sediments formed from $Fe^{3+}$ ions

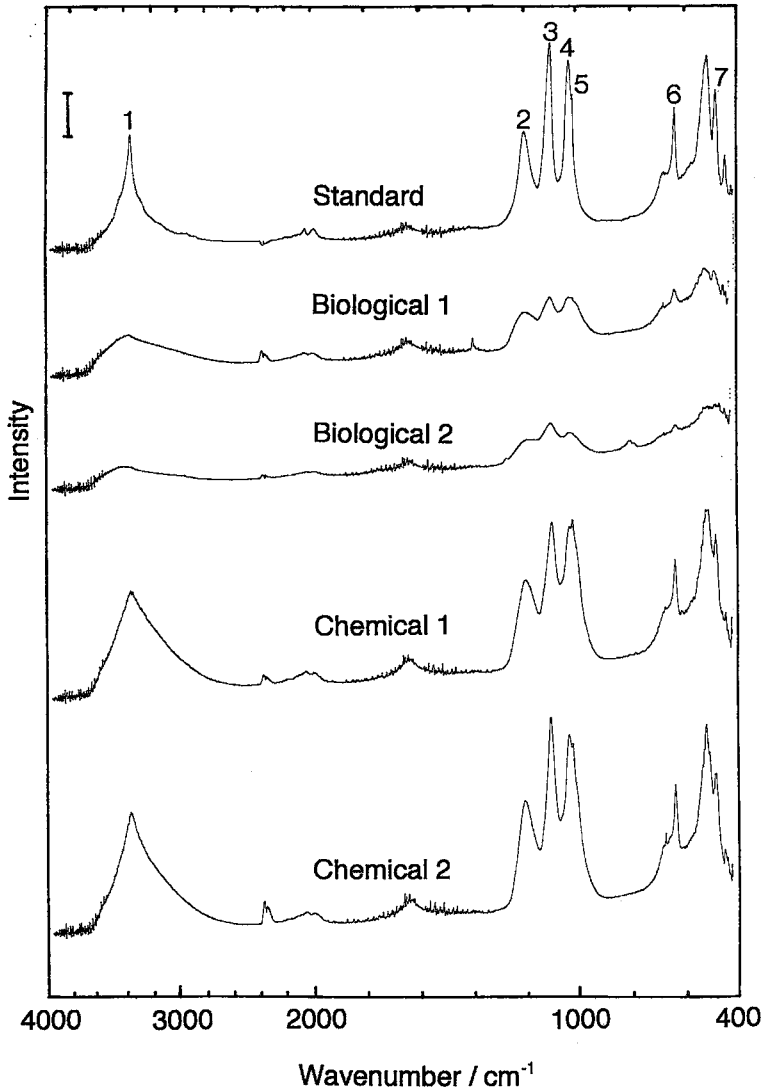



FIG. 4. FTIR spectra of products. Vertical bar indicates one Kubelka–Munk unit. 1: OH stretch, 2 and 3: $\upsilon_3$ ($SO_4^{2-}$), 4: $\upsilon_1$ ($SO_4^{2-}$), 5: $\sigma$(OH), 6: $\upsilon_4$ ($SO_4^{2-}$), 7: $\tau$(OH).

oxidized by *T. ferrooxidans* is dependent on the cations, though argentojarosite was not reported. The present results suggest that argentojarosite is more readily automorphic than other jarosite-group minerals.

The distinctive IR absorbance frequencies of jarosite are the $\upsilon_3$ mode of $SO_4^{2-}$ at 1190 to 1200 and 1090 to 1100 $cm^{-1}$, the $\upsilon_1$ mode of $SO_4^{2-}$ at 1010 to 1030 $cm^{-1}$, the $\upsilon_4$ mode of $SO_4^{2-}$ at 640 to 650 $cm^{-1}$, the OH stretch at 3300 to 3400 $cm^{-1}$, $\sigma$(OH) at 1000 to 1010 $cm^{-1}$, and $\tau$(OH) at 470 to 480 $cm^{-1}$ (Lazaroff *et al.* 1982, Tuovinen & Carlson 1979). The FTIR spectra of products show all these peaks (Fig. 4). Plots of the intensity at 1190 and 1090 $cm^{-1}$ (the $\upsilon_3$ mode of $SO_4^{2-}$) against the mass percent of standard argentojarosite (Fig. 5) indicate a linear relationship over the two orders of magnitude in range of concentration (correlation coefficients, r = 0.998 for both). On the basis of the calibration curves in Figure 5, the relative IR purity of the $\upsilon_3$ mode of $SO_4^{2-}$ to the standard was calculated as shown in Table 3. It is clear that the IR purity of the chemical products is much higher than

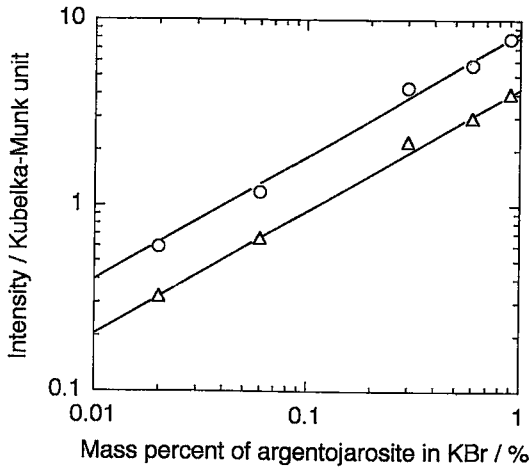



FIG. 5. Dependence of intensity at two bands of $\upsilon_3$ ($SO_4^{2-}$) in DRIFTS on concentration of standard argentojarosite, Δ, at 1190 $cm^{-1}$, ○, at 1090 $cm^{-1}$.

that of the biological products. The difference is too large to be attributed to experimental errors. It may be that S–O bondings in biologically formed argentojarosite are strained owing to the state of aggregation, whereas those in chemical products are normal. The differences, however, did not appear in the FWHM of the 113 peak in the XRD patterns (Table 1).

Two different explanations of the contribution of *T. ferrooxidans* to the formation of jarosite-group minerals have been reported: one is a kind of biomineralization by *T. ferrooxidans* (Lazaroff *et al.* 1982, Tazaki *et al.* 1990, Tazaki 1991), and the other does not support the biomineralization hypothesis (Tuovinen & Carlson 1979). Lazaroff *et al.* (1982) reported that ammoniojarosite was formed from biologically oxidized $Fe^{3+}$ ions, whereas it was not formed from chemically oxidized ions.

It must be noted here that there is no description of changes in pH during chemical or biological oxidation of $Fe^{2+}$ to $Fe^{3+}$ ions in the report of Lazaroff *et al.* although the initial pH was noted to be 2.5. The oxidation of $Fe^{2+}$ ions by $H_2O_2$ is a proton-consuming reaction, and values of pH should increase quickly after addition of $H_2O_2$. Simple equilibrium calculations indicate that $Fe^{3+}$ ions precipitate as FeOOH at a pH close to 2.5. It is possible that precipitation of $Fe^{3+}$ oxyhydroxides led to the absence of jarosite formation in the experiments by Lazaroff *et al.* (1982). In the present work, the initial and the final pH were 2.00 and 2.10. Based on the IR and XRD data, Tuovinen & Carlson (1979) reported that iron-oxidizing bacteria do not participate directly in the formation of jarosite, but that the bacteria catalyze the production of $Fe^{3+}$ ions, which is a prerequisite for the basic ferric sulfate reaction. They did not carry out chemical analyses of the biological and chemical products, however. It is evident from the present work that *T. ferrooxidans* itself makes no direct contribution to the crystallization of argentojarosite, but extracellular substances may take part in the aggregation of argentojarosite. Natural jarosite could be formed not only biologically but chemically.

TABLE 3. INTENSITIES AT TWO $\upsilon_3$ ($SO_4^{2-}$) BANDS OF DRIFTS FOR BIOLOGICALLY AND CHEMICALLY PRODUCED ARGENTOJAROSITE

| Sample | Intensity / Kubelka-Munk unit | | IR purities / % | |
|---|---|---|---|---|
| | 1090 $cm^{-1}$ | 1190 $cm^{-1}$ | 1090 $cm^{-1}$ | 1190 $cm^{-1}$ |
| Standard | $4.3_1$ | $2.2_2$ | | |
| Biological 1 | $1.0_2 \pm 0.02_8$ | | $13._7$ | |
| | | $0.7_2 \pm 0.00_7$ | | $21._0$ |
| Biological 2 | $0.4_7 \pm 0.03_8$ | | $4._0$ | |
| | | $0.7_4 \pm 0.00_5$ | | $23._3$ |
| Chemical 1 | $3.0_4 \pm 0.11_4$ | | $70._0$ | |
| | | $1.9_6 \pm 0.24_7$ | | 100 |
| Chemical 2 | $4.1_8 \pm 0.54_5$ | | 110 | |
| | | $2.4_5 \pm 0.01_4$ | | 136 |

Each sample was diluted to 0.3 (w/w) % in KBr and mean values and standard deviations in four times measurements are shown.

## CONCLUSIONS

Argentojarosite was formed at ambient temperatures without by-product by the addition of stoichiometric amounts of $Ag^+$ ions to bacterially formed $Fe^{3+}$ sulfate solutions. Biologically formed $Fe^{3+}$ complexes are precursors to jarosite-group minerals and similar to chemically formed ones. It was concluded that neither *T. ferrooxidans* itself nor extracellular substances make any direct contribution to the crystallization of argentojarosite. However, biologically formed argentojarosite, with or without bacterial cells during aging, shows an aggregated morphology and weaker FTIR intensities for S–O bondings than chemically formed products. These findings suggest that extracellular substances may take part in the aggregation.

## ACKNOWLEDGEMENTS

We express our appreciation to Dr. J.E. Dutrizac at CANMET, Canada, for supplying the standard jarosite compounds, and also thank Dr. T. Furusaki at Hokkaido University for performing the SEM observations of argentojarosite. The authors also thank Dr. D.A.C. Manning and an anonymous reviewer for their constructive comments.

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*Received April 4, 1995, revised manuscript accepted September 14, 1995.*