Geochemical modeling of bacterially induced mineralization of schwertmannite and jarosite in sulfuric acid spring water

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ABSTRACT

Mineralogy and geochemistry of a sulfuric acid spring water with a pH of 3.37 to 2.89 were investigated to verify the formation processes of iron minerals and the effects of bacteria on their formation. To estimate the solubility of schwertmannite, experimental dissolution in 10.0 mM H₂SO₄ was conducted and this solubility data was used for geochemical modeling. Experimental incubation of the spring water containing bacteria was also performed and compared with a simulated abiotic system to evaluate the role of bacteria in the mineral formation. The spring water seeps through cracks of hydrothermally altered andesitic rocks containing pyrite, and precipitates schwertmannite and jarosite. Schwertmannite appears as a film-like thin layer floating on the water surface and composed of aggregates of spherical particles with diameters of 1 to 5 µm. Jarosite is produced as a precipitate on submerged rock surfaces. The precipitate contains well crystallized jarosite spheres 5 to 10 µm in diameter. Some ellipsoidal to rod shaped bacteria covered or decorated by poorly ordered iron minerals are also present in close association with the schwertmannite spheres. Results of the experimental incubation demonstrate that the oxidation rates of Fe²⁺ are 5.3×10^3 to 7.2×10^3 times greater than those of the simulated abiotic system, suggesting that the formation of the iron minerals is promoted by bacterial oxidation of Fe²⁺. The dissolution experiment indicates that the solubility product of the schwertmannite having an average chemical composition of $Fe_{s}O_{s}(OH)_{5,9}(SO_{4})_{1,05}$ is approximately log $K_s = 7.06 \pm 0.09$. Using this data, geochemical modeling reveals that the spring water is supersaturated with respect to schwertmannite and also goethite and jarosite, but undersaturated with respect to ferrihydrite. Additionally, it is confirmed that the bulk solution chemistry deviates slightly into the stability field of goethite rather than jarosite. This suggests that the aquatic environments in contact with the rock surfaces may be more acidic and/or enriched in SO_4^2 -relative to the bulk solution, which may eventually lead to the formation of jarosite instead of goethite.

INTRODUCTION

Microbiologically induced iron minerals are widely distributed in various geochemical environments, such as iron-silica minerals in various hot spring (Ferris et al. 1986) and ironoxides and iron-sulfates in acid mine drainages (Clarke et al. 1997; Bigham and Nordstrom 2000) and in acid sulfate soils (Fitzpatrick et al. 1992, 1996; Willett et al. 1992). In freshwater environments, various iron-aluminosilicates associated with bacteria have been reported from river and lake sediments (Konhauser et al. 1993, 1994, 1998) and from weathering environments of volcanic ash deposits (Kawano and Tomita 2001a, 2001b). Among these geochemical environments, the acid mine drainages have been most extensively investigated in terms of mineralogy, geochemistry, and geomicrobiology (Bigham and Nordstrom 2000). The acid mine drainages are commonly produced by biotic and/or abiotic oxidation of ironsulfides such as pyrite leading to the formation of sulfuric acid and the release of Fe2+ into aquatic environments (Kittrick et al. 1982). In such acid mine drainages, poorly ordered iron minerals such as schwertmannite and ferrihydrite are initially formed as a metastable phase resulting from bacterial oxidation of Fe2+, and jarosite and goethite are produced as thermodynamically stable phases by subsequent crystallization (Brady et al. 1986; Bigham et al. 1990, 1992, 1994, 1996a; Schwertmann et al. 1995; Hochella et al. 1999; Yu et al. 1999). Many field observations suggest that occurrences of these minerals are strongly dependent on solution chemistry, specifically the pH and SO₄²⁻ activity. For example, ferrihydrite normally occurs at near neutral pH and lower SO₄²⁻ activity conditions, but schwertmannite forms under acidic conditions with pH = 2.5-4.5 (Bigham et al. 1996a; Yu et al. 1999). On the other hand, goethite usually occurs from neutral pH to about pH = 3, whereas jarosite appears at about pH < 3 if the SO₄²⁻ activity is too high (Bigham et al. 1996b). In order to evaluate the formation conditions of these minerals, accurate estimates of their solubilities and thermodynamic stability relationships between these minerals are very important. However, there is no accu-

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rate information about the solubility product of schwertmannite. Two previous values, $\log K_s = 18.0 \pm 2.5$ (Bigham et al. 1996b) and $\log K_s = 10.5 \pm 2.5$ (Yu et al. 1999), were estimated from solution chemistry with no evidence of equilibrium. Therefore, more reliable values determined by a dissolution experiment are necessary to evaluate the solubility and stability relationships.

In this study, we investigated the mineralogy and geochemistry of acidic spring water flowing down on the surfaces of hydrothermally altered andesitic rocks containing pyrite in southern Kyushu, Japan. In this water, schwertmannite and jarosite are predominately formed as a secondary phase, possibly induced by bacterial oxidation of Fe^{2+} . To elucidate the formation processes of these minerals, we estimated the solubility product of schwertmannite and evaluated the stability of schwertmannite, jarosite, and other related iron minerals. In addition, we examined the bacterial oxidation rates of Fe^{2+} , and compared them with those obtained from a simulated abiotic system. Although schwertmannite has been found in several similar anthropogenic environments, ours is the second reported occurrence of schwertmannite in nature.

MATERIALS

The hydrothermally altered Neogene formation consisting mainly of andesitic rocks are widely distributed in the Makurazaki area in southern Kyushu, Japan. This alteration is related to volcanic activity of Miocene-Pliocene age, which has produced several gold-bearing silicified ore deposits and alteration aureoles containing zonal sequences of various aluminous clay minerals such as kaolinite, illite, rectorite and smectite (Kawano and Tomita 1991). Such altered rocks are widely exposed in the eastern part of the city of Makurazaki, and in some cases springs seep through cracks or fractures in the rocks. Most of the springs produce orange to dark brown precipitates on the submerged rock surfaces; these normally have a thickness of <5 mm.

The samples used in this study were collected from spring water flowing down the altered andesitic rock surfaces in September, 2000 (Fig. 1). This spring water seeps through cracks in the altered rock and flows down slowly on the rock surfaces with a stream width of 1 to 1.5 m and a length of about 3 m. In this place, two distinct occurrences of orange to dark brown color precipitates are recognized. One is schwertmannite which occurs as film-like precipitates floating on the water surface, and sometimes exhibits an interference fringe similar to that of a thin oil film. The other is jarosite which occurs as thin coatings on the submerged rock surfaces with a thickness of <5 mm. This type is the most dominant secondary product in the acid water system. Three sampling points (A1 to A3) were selected along the water flow at intervals of 1.5 m. Four sets of samples including water, film-like precipitate, rock surface precipitate, and altered rock were collected from each sampling point. Temperature, pH, and Eh of the waters were also measured in the field. The samples were sealed in a plastic bottle, and then transported to the laboratory in a refrigerated cooler box to prevent oxidation of Fe2+. Chemical analyses of the water samples were carried out within 2 h of sample collection.



FIGURE 1. Map showing the location of the sampling points and a photograph of the sulfuric acid spring water flowing down the altered rock surface. The small photograph shows both film-like precipitate floating on the water surface and rock surface precipitate.

EXPERIMENTAL METHODS

Laboratory analyses

Both film-like and rock surface precipitates collected from the spring were examined with the following analytical methods: (1) X-ray powder diffraction analysis (XRD) for identification of material constituents; (2) scanning electron microscopy (SEM) with an energy dispersive X-ray spectrometer (EDX) for observation of micromorphology and associated chemical analysis; and (3) transmission electron microscopy (TEM) for observation of bacteria and their influence on mineral formation. The powder XRD experiments were done with a RIGAKU RU-200 diffractometer equipped with a graphite monochrometer and 0.5mm divergence scattering slits. The Cu X-ray tube was operated at 30 kV and 100 mA. Data were collected from 2 to $70^{\circ} 2\theta$ with a step size of 0.02° and a counting time of 0.6s. SEM was performed with a HITACHI S-4100 scanning electron microscope equipped with a LINK ISIS EDX spectrometer operated at an accelerating voltage of 15 kV. The EDX spectra were obtained using a spot size of approximately 1 to 2 µm, and a live time of 60 s. The samples used for SEM and EDX were washed 4 times with 80% ethanol and dried in air on a carbon holder, and then coated with carbon in a vacuum chamber. TEM was carried out with a HITACHI H-700H transmission electron microscope operated at an accelerating voltage of 200 kV using a carbon-coated sample deposited on a Cu grid covered with a collodion film. Selected area electron diffraction images were obtained using

a camera length of 1347 mm. Calibration of d spacings was done using a gold-coated collodion film. Samples for TEM were prepared by washing with sterilized-distilled water to remove excess salt after ultrasonic dispersion (30 s), and then one drop of the suspension was deposited on a Cu grid.

The mineralogy of the rock samples was examined by XRD using the same procedure described above. The chemical composition of the rock samples was determined with the EDX using a glass bead fused with $Li_2B_4O_7$. The water samples were filtered using 0.2 µm Minisart membranes, and the solutions were analyzed by colorimetric analysis for total dissolved Si, by atomic adsorption spectroscopy for total Fe, Al, Mn, Mg, Ca, Na, and K, and by ion chromatography for SO₄²⁻ and Cl⁻. The concentration of Fe²⁺ was determined using phenanthroline colorimetric methods. Eh, pH, and temperature were measured in the field with a digital pH meter.

Geochemical calculation

Geochemical equilibrium calculations were performed with the PHREEQC Ver.2 program (Parkhurst and Appelo 1999) to determine the activity of dissolved species and to evaluate the degree of saturation. The PHREEQC program is used to simulate chemical reactions and transport processes in natural or polluted water, and has three thermodynamic databases, i.e., PHREEQC.DAT, MINTEQ.DAT, and WATEQ4F.DAT. To perform these calculations, we used the MINTEQ.DAT database because it is the only one which contains thermodynamic data for ferrihydrite. However, this database has no solubility data for schwertmannite. Therefore, the solubility product of schwertmannite was determined by experimental dissolution and used for the geochemical calculation. The results of the PHREEQC calculations are presented in terms of the saturation index (SI) for each predicted mineral. SI is defined by SI = $log(IAP/K_{sp})$, where IAP is the ion activity product of the dissolved mineral constituents in a solubility reaction, and K_{sp} is the corresponding solubility product for the mineral. Thus, SI >0 implies supersaturation with respect to the mineral, whereas SI < 0 means undersaturation.

Solubility product of schwertmannite

To estimate the solubility product of the schwertmannite, experimental dissolution of the film-like precipitates collected from points A1 to A3 was performed using a batch-reaction system. Each sample was powdered in 80% ethanol using an agate mortar and passed through a 0.074 mm sieve, and then dried in vacuum after washing three times in 80% ethanol. XRD confirmed that the samples were composed of pure schwertmannite with no associated minerals. About 0.1 g of each powdered schwertmannite sample was placed in a pyrex glass flask with 100 mL of 10.0 mM H₂SO₄ solution. This flask was sealed with an aerated silicon cap, and then incubated at 30 °C for 60 days with no shaking. During incubation, pH and Eh were monitored every day with a digital pH meter, and concentrations of Fe3+ and SO2- were also analyzed daily by atomic adsorption spectroscopy and ion chromatography, respectively, using a diluted solution of 0.5 mL of extractant with 0.01 M HNO₃. To confirm phase transformation, about 0.01 g of schwertmannite sample was separated from each glass flask every 10 days and was examined by XRD after washing with 80% ethanol and air-drying on a glass slide. Using the solution data, the solubility products of schwertmannite were calculated with the PHREEQC geochemical code.

Bacterial oxidation rate

To evaluate bacterial oxidation rates of Fe²⁺, about 100 mL of each unfiltered spring water sample was transferred into a pyrex glass flask and a small fragment of film-like precipitate (approximately 1.0 mm × 1.0 mm) containing bacteria was also added. The flask was sealed with a aerated silicon cap and was placed in a thermostated incubator at 30 °C for 40 days. During incubation, pH, Eh, and concentrations of Fe²⁺, Fe³⁺, Si, Al, Mn, Mg, Ca, Na, K, SO₄²⁻, and Cl⁻ were measured daily by the same methods mentioned above. In order to compare bacterial and abiotic oxidation rates, 100 mL of sulfuric acid solution containing 2.0 mM FeSO₄ and 0.5 mM H₂SO₄ without bacteria was also incubated under the same conditions, and pH, Eh, and concentrations of Fe²⁺, Fe³⁺, and SO₄²⁻ were measured daily.

RESULTS

Mineralogy and chemistry of the altered rock

XRD analysis of the altered rocks collected from points A1 to A3 confirmed that they are composed of quartz, illite, pyrite, and feldspar. The chemical composition of altered rock from point A1 is listed in Table 1. This shows that the rock contains high levels of Fe and S, which may be attributed to the presence of pyrite. The chemistry of altered rocks from points A2 and A3 is almost the same as that from the point A1. The pyrite crystals display cubic and/or irregular shape, with a typical size of <0.1 mm, which can be observed on these rock surfaces with an optical microscope.

Water chemistry

The temperature, pH, Eh, and chemical composition of the spring water for each sampling point are presented in Table 2. The temperature increases from 24.5 to 31.8 °C as the distance from the seepage point increases from 0 to 3 m. The pH decreases from 3.37 to 2.89 along the water flow path, and this is accompanied by an increase in Eh from 214 to 253 mV (A3). The concentrations of Fe³⁺, Fe²⁺, and SO₄²⁻ ions are remarkably higher than those of natural water such as river and ground water (Berner and Berner 1987), which suggests that the acidic waters are produced by oxidative dissolution of pyrite through the following reaction (Kleinmann et al. 1981):

 TABLE 1. Chemical composition of altered rock collected from point A1

SiO ₂	46.94	
TiO ₂	1.26	
Al ₂ O ₃	22.82	
FeO	9.63	
MgO	4.61	
CaO	0.17	
Na ₂ O	0.01	
K ₂ O	2.05	
SO₃	12.51	
Total (%)	100.00	

Note: Total Fe as FeO. The wt% values were normalized to produce a total of 100 wt%.

TABLE 2. Temperature and chemistry of the spring water

	A1	A2	A3
Distance (m)	0	1.5	3.0
T (°C)	24.5	29.5	31.8
pH	3.37	3.06	2.89
Eh (mV)	214	236	253
Si	4.98	5.03	6.30
Al	3.03	2.96	3.19
Fe ³⁺	0.12	0.23	0.74
Fe ²⁺	2.12	1.29	0.48
Mn	0.08	0.09	0.09
Mg	2.41	2.49	2.72
Ca	0.22	0.23	0.28
Na	2.68	2.71	2.93
К	0.24	0.24	0.26
SO ₄	9.69	9.84	10.77
CI	2.65	2.67	2.99

Notes: Units of solution chemistry are mM.

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$
(1)

The concentrations of Fe^{2+} decrease notably from point A1 to point A3, indicating that Fe^{2+} is progressively oxidized as the water flows downward on the rock surfaces. In addition, the total Fe concentration also decreases, from 2.24 mM at point A1 to 1.22 mM at point A3, indicating precipitation of some Fe minerals.

Mineralogy and chemistry of the precipitate

XRD analysis of the film-like precipitates collected from points Al to A3 reveals that they are composed of pure schwertmannite with no other crystalline phases (Fig. 2a). The XRD profiles display a pronounced broad 212 reflection at 2.55 Å and some broad diffraction peaks at about 3.5 and 1.5 Å, all of which are known to be typical reflections for schwertmannite (Bigham et al. 1994). With respect to the rock surface precipitates, XRD analysis verifies that they are composed mainly of jarosite with some contamination of quartz and illite from the altered rocks (Fig. 2b). The broad bulge at around 35° is probably due to small amounts of schwertmannite. Ferrihydrite and goethite were not found in these precipitates.

The SEM study showed that the film-like precipitates exhibit thin platy or film-like forms with a thickness <5 µm, and they are composed of aggregates of spherical particles of schwertmannite having a diameter of 1 to 5 µm (Fig. 3a). These schwertmannite particles consist mainly of Fe and S, and of small amounts of K, Si, and Al, with a variable S/Fe ratio ranging from 0.09 to 0.17 (Fig. 3b). Assuming that elements other than Fe and S are impurities, the average chemical formula obtained from the EDX data is Fe₈O₈(OH)_{5.36}(SO₄)_{1.32} for A1 and $\text{Fe}_8\text{O}_8(\text{OH})_{5.90}(\text{SO}_4)_{1.05}$ for A2 and A3. Some SO_4^{2-} may be adsorbed on the surfaces because the ZPC of Fe-hydroxide is about 9 which means that the schwertmannite surface has a positive charge in acidic solution (Bleam and McBride 1984). We found that the SO₄²⁻ ions may be extracted with a solution of higher pH value than the spring water, and they are almost completely removed by washing with a solution with pH = 10.

The SEM study also indicated that the rock surface jarosite is composed of highly aggregated spherical particles with diameters of 5 to 10 μ m (Fig. 3c). The jarosite spheres consist mainly of Fe and S, with trace amounts of K, Si, and Al (Fig 3d). The average S/Fe ratio of the particles is 0.314, which is



FIGURE 2. XRD profiles of film-like precipitates (**a**) and of rock surface precipitates (**b**) collected from points A1 to A3. The film-like precipitates are composed of poorly ordered schwertmannite. The rock surface precipitates contain jarosite and small amounts of schwertmannite with variable amounts of quartz and illite from the altered rocks.



FIGURE 3. SEM micrographs and EDX spectra of a film-like precipitate (a, b) and of a rock surface precipitate (c, d)collected from point A3. The film-like precipitate is composed of aggregates of spherical schwertmannite particles with diameters of 1 to 5 µm. The rock surface precipitate is composed mainly of spherical jarosite particles ranging in size from 5 to 10 µm.

lower than that of pure jarosite $[KFe_3(SO_4)_2(OH)_6]$; this could be due to contamination by significant amounts of schwertmannite as observed in the XRD profiles (Fig. 2b).

TEM images show that the suspensions of both film-like and rock surface precipitates are mainly composed of schwertmannite spheres <0.5 µm in diameter in irregular aggregates (Fig. 4a). The electron diffraction patterns of these particles display broad rings corresponding to 2.5 and 1.5 Å spacings. These d values are similar to the 212 (2.56 Å) and 004 (1.52 Å) reflections of schwertmannite (Bigham et al. 1994). In addition, TEM images confirm the presence of ellipsoidal- to rod-shaped bacteria about 1 to 2 µm in length in suspensions of both precipitates (Fig. 4b). Most of the bacteria are covered or decorated by variable amounts of poorly ordered precipitates of a mottled phase, possibly Fe-hydroxide. Electron diffraction patterns of these precipitates show a diffuse halo with no conspicuous spot or ring patterns. These precipitates exhibit irregular forms and unclear outlines with some spherical condensed parts as indicated by arrows on Figure 4b. This suggests that the poorly ordered materials are precipitated by bacterial interaction and the schwertmannite spheres are formed by subsequent crystallization processes. Surface precipitates of a needle-like schwertmannite phase are frequently found on bacterial cells in acidic environments (Bigham et al. 1994, 1996a; Schwertmann et al. 1995), but there is no report of the formation of such spherical schwertmannite precipitates by bacterial interaction.

The solubility product of schwertmannite

Changes in pH, Eh, and concentrations of Fe³⁺ and SO₄²⁻ during experimental dissolution of schwertmannite in 10 mM H₂SO₄ solution are shown in Figure 5. The pH increases rapidly from 1.56 to 1.84-1.87 within approximately 20 days, and then decreases gradually to 1.75-1.83 depending on the samples. Simultaneously, the Eh decreases rapidly from 310 to 288-292 mV. Similarly, the Fe3+ concentration increases rapidly to 3.3-3.9 mM within 20 days and decreases slowly after about 30 days. The SO₄²⁻ content also increases from 10 to a level of 11 mM within 10 days, and remains almost constant up to 60 days. XRD analyses confirm the formation of trace amounts of goethite after 20 days in A1, and after 40 days in A2 and A3. This indicates that transformation of schwertmannite into goethite proceeds more rapidly in A1 than in A2 and A3, and the transformation decreases Fe³⁺ concentration in solutions. Therefore, solution data for A2 and A3 were used to calculate a solubility product for schwertmannite because these data are more likely to be in equilibrium than those of A1. The equilibrium equation for schwertmannite and solu-



FIGURE 4. TEM micrographs of the spherical schwertmannite particles (**a**) of the rock surface precipitate collected from the point A3. This sample contains variable amounts of ellipsoidal- to rod-shaped bacteria (**b**) covered or decorated by irregular aggregates of poorly ordered materials with some spherical particles as indicated by the arrows; this may be schwertmannite.

tion is as follows:

$$Fe_8O_8(OH)_{5.90}(SO_4)_{1.05} + 21.9H^+ \rightarrow 8Fe^{3+} + 1.05SO_4^{2-} + 13.9H_2O$$
 (2)

The solubility product of the schwertmannite $(\log K_s)$ in this reaction system is defined as

$$\log K_{\rm s} = \log [{\rm Fe^{3+}}]^8 [{\rm SO_4^{2-}}]^{1.05} / [{\rm H^+}]^{21.9}$$
(3)



FIGURE 5. Changes in solution pH, Eh, and concentrations of Fe³⁺ and SO₄²⁻ during experimental dissolution of schwertmannite in 10.0 mM H₂SO₄ solution at 30 °C. The schwertmannite samples used were 0.1 g of powdered film-like precipitates collected from the points A1 to A3. The chemical compositions of the schwertmannites are A1: Fe₈O₈ (OH)_{5.36}(SO₄)_{1.32}, A2: Fe₈O₈(OH)_{5.90}(SO₄)_{1.05}, and A3: Fe₈O₈(OH)_{5.90} (SO₄)_{1.05}. Their XRD profiles are illustrated in Figure 3a.

According to the above equation, the solubility product of the schwertmannite is approximately $\log K_s = 7.06 \pm 0.09$ at 30 °C. The geochemical calculation confirms that there is no significant difference between $\log K_s$ at 25 °C and this value. Two previous values for the solubility product of schwertmannite determined using solution chemistry are presented in Table 3 together with this one. Notably, $\log K_s$ obtained by the present dissolution experiment is slightly smaller than the previous values (Bigham et al. 1996a; Yu et al. 1999).

Bacterial oxidation rate

The experimental incubation of spring waters with bacteria demonstrated rapid oxidation of Fe^{2+} and precipitation of

Mineral	Reaction	log K	Ref.
ferrihydrite	$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$	4.891	1
schwertmannite (1)	$Fe_{B}O_{B}(OH)_{5.9}(SO_{4})_{1.05} + 21.9H^{+} = 8Fe^{3+} + 1.05SO_{4}^{2-} + 13.9H_{2}O_{5.0}$	7.06 ± 0.09	2
schwertmannite (2)	$Fe_8O_8(OH)_{4.4}(SO_4)_{1.8} + 20.4H^+ = 8Fe^{3+} + 1.8SO_4^{2-} + 12.4H_2O_6$	10.5 ± 2.5	3
schwertmannite (3)	$Fe_8O_8(OH)_{4.8}(SO_4)_{1.6} + 20.8H^+ = 8Fe^{3+} + 1.6SO_4^{2-} + 12.8H_2O_4^{-}$	18.0 ± 2.5	4
goethite	$FeOOH + 3H^+ = Fe^{3+} + 2H_2O$	0.5	1
jarosite	$KFe_{3}(SO4)_{2}(OH)_{6} + 6H^{+} = K^{+} + 3Fe^{3+} + 2SO_{4}^{2-} + 6H_{2}O$	-14.8	1
Notos: 1 - Parkburst and	Appelo (1999) $2 = \text{this study} = 2 = \text{Visited} (1999) = 4 = \text{Righam et al.} (1996) \text{The}$	a chamical composition	of cohwortmannit

TABLE 3. Reactions and solubility products of schwertmannite and related iron minerals

Notes: 1 = Parkhurst and Appelo (1999), 2 = this study, 3 = Yu et al. (1999), 4 = Bigham et al. (1996). The chemical composition of schwertmannite (1) is an average value for material from points A2 and A3. The chemical compositions of schwertmannite (2) and (3) are shown as mean values.



FIGURE 6. Changes in solution pH, Eh, and concentrations of Fe^{2+} , Fe^{3+} , and SO_4^{2-} during experimental incubation of waters collected from points A1 to A3 at 30 °C. The initial solution chemistry of the spring waters is presented in Table 2.

schwertmannite within a few days. Figure 6 illustrates the changes in pH, Eh, and concentrations of Fe²⁺, Fe³⁺, and SO₄²⁻ during incubation up to 40 days. The pH decreases rapidly at the beginning of the incubation with precipitation of small amounts of schwertmannite, and also decreases continuously after about 5 days. This is accompanied by a simultaneously large increase in Eh. The concentration of Fe²⁺ (2.12–0.48 mM) also drops to <0.01 mM within 5 days. This rapid oxidation leads to increased concentration of Fe³⁺ in the early stages

(within 2 or 3 days), but this decreases slowly during subsequent incubation through precipitation of schwertmannite. The SO_4^{2-} concentration remains almost constant over a period of 40 days. XRD analyses confirm the precipitation of schwertmannite without goethite within a few days, while the 4.19 Å peak of goethite can be detected after 20 days. The oxidation of Fe²⁺ to Fe³⁺ consumes protons, which increases solution pH. However, formation of schwertmannite releases protons resulting in a rapid decrease in solution pH. Additionally, the transformation of schwertmannite to goethite releases protons, which also lowers solution pH.

The oxidation rates of Fe^{2+} in these reaction systems were calculated in accordance with the first-order reaction:

$$k = \ln \left(a_0 / a_t \right) / t \tag{4}$$

where k is a rate constant and a_0 and a_t are concentrations of Fe²⁺ before and after reaction for a period of t seconds. The rate constants obtained using the solution data over a period of 3 days are A1: 2.4×10^{-5} s⁻¹, A2: 2.3×10^{-5} s⁻¹, and A3: 1.7×10^{-5} s⁻¹. On the other hand, no significant changes in solution chemistry are observed in the abiotic system containing 2.0 mM FeSO₄ and 0.5 mM H₂SO₄ without bacteria. The pH and Eh of the abiotic system remain constant at about 2.95 and 222 mV throughout the incubation period. The Fe²⁺ concentration is also unchanged up to 40 days. These results indicate that the rapid oxidation of Fe²⁺ in the spring waters should be caused by bacterial interaction rather than abiotic reaction.

DISCUSSION

Bacterial oxidation and mineralization

The spring waters contain relatively high contents of total Fe and SO_4^2 supplied from pyrite in altered rocks. The Fe²⁺ ions released into the waters are subsequently oxidized and precipitate as iron minerals when saturation is achieved. The oxidation reaction of Fe²⁺ can be written as follows:

$$Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$
 (5)

This oxidation reaction is thermodynamically favored and proceeds rapidly if the environment is oxidizing and near neutral conditions, but the reaction is inhibited and negligible in reducing or acidic environments. Such abiotic oxidation rate of Fe^{2+} is given by (Singer and Stumm 1970):

$$dm_{\rm Fe^{2+}}/dt = -(2.91e - 9 + 1.33e 12 a_{\rm OH}^2 P_{\rm O_2})m_{\rm Fe^{2+}}$$
(6)

where t is time in seconds, a_{OH} - is the activity of hydroxyl ions, P_{02} is the oxygen partial pressure, and $m_{\rm Fe^{2+}}$ is the total molarity of Fe2+ ions. The A1 to A3 samples contain 2.12 to 0.48 mM of Fe^{2+} , and their pH values range from pH = 3.37 to 2.89. Assuming that the spring waters are at equilibrium with oxygen partial pressure, the abiotic oxidation of Fe²⁺ in these waters for up to 20 years was simulated by PHREEQC as illustrated in Figure 7. In this simulation, the reaction temperature was kept at 30 °C and solution chemistry of the original spring waters was used for the initial solutions. It can be seen that the abiotic oxidation of Fe²⁺ proceeds very slowly and more than 15 years are required to reduce the Fe2+ concentration of A1 to that of A3. The rate constants calculated using first-order reaction equation are A1: $3.58 \times 10^{-9} \text{ s}^{-1}$, A2: $3.18 \times 10^{-9} \text{ s}^{-1}$, and A3: 2.97×10^{-9} s⁻¹. This indicates that the oxidation rates of Fe²⁺ in the experimental systems are 5.3×10^3 to 7.2×10^3 times greater than those of the simulated abiotic systems. It is well known that some bacteria such as Thiobacillus ferrooxidans promote Fe²⁺ oxidation to gain chemical energy for their metabolism, which results in formation of Fe-oxide and/or hydroxide minerals on their cell surfaces(Ehrlich 1990). These bacterial oxidation rates have been estimated to be 10⁵ to 10⁶ times faster than those of abiotic conditions (Lacey and Lawson 1970; Nordstrom 1982), and the rates are known to be strongly influenced by various factors such as Fe²⁺ and O₂ concentrations, and bacterial activity (Kirby et al. 1999). The oxidation rates in the experimental systems are slightly lower than this, possibly due to low bacterial activity, however it is apparent that the oxidation of Fe2+ is promoted by iron-oxidizing bacteria.

TEM observations confirm the presence of bacteria in close association with both film-like and rock surface precipitates (Fig. 4). Most bacteria are covered by noncrystalline and/or poorly ordered precipitates, possibly formed by Fe^{2+} oxidation



FIGURE 7. Changes in concentration of Fe^{2+} during abiotic oxidation processes of the spring waters simulated by the PHREEQC program. The reaction temperature was kept at 30 °C and solution chemistry of the original spring waters (Table 2) was used for initial solutions.

and precipitation. The TEM results also show transformation of the cell surface precipitates into a spherical schwertmannite. These observations suggest that the film-like precipitates consisting of spherical schwertmannite may be produced by bacterial interaction with the spring water. Similar bacterial oxidation and microbial mineralization have frequently been reported in various sulfuric acid environments such as acid mine drainages (e.g., Mann et al. 1992; Ghiorse and Ehrlich 1992), acid sulfate soils (e.g., Fitzpatrick et al. 1992), and hydrothermal sea-vents (Fortin et al. 1997, 1998).

Solubility and saturation index

Schwertmannite and jarosite were produced as primary secondary products in the spring water. In many acid mine drainages, however, ferrihydrite and goethite are produced instead of schwertmannite and jarosite, respectively (Bigham and Nordstrom 2000). In order to understand the formation of these iron minerals, accurate estimates of the equilibrium relationship between each mineral and the solution chemistry are essential. It is well known that Fe^{3+} ions in near neutral environments are readily hydrolyzed and precipitated as ferrihydrite. The aqueous equilibrium for ferrihydrite can be written as following reaction:

$$Fe(OH)_3 + 3H^+ \rightarrow Fe^{3+} + 3H_2O \tag{7}$$

The solubility relation becomes

$$\log K_{\rm f} = \log[{\rm Fe}^{3+}] + 3\rm{pH} \tag{8}$$

where, $\log K_{\rm f}$ is the solubility product of ferrihydrite which has previously been reported as $\log K_{\rm f} = 4.891$ (Parkhurst and Appelo 1999). In the spring water, schwertmannite is widely produced as a film-like precipitate instead of ferrihydrite. The equilibrium reaction of schwertmannite is

The A2 and A3 samples have an average chemical composition of $Fe_8O_8(OH)_{5.90}(SO_4)_{1.05}$. The equilibrium for this schwertmannite can be expressed as shown in Equation 2, and the solubility product obtained by the experimental dissolution is log $K_s = 7.06 \pm 0.09$. In sulfuric acid solution, Fe³⁺ ions frequently produce goethite and/or jarosite depending on solution chemistry. The dissolution reactions of these minerals can be described as

$$FeOOH + 3H^+ \rightarrow Fe^{3+} + 2H_2O \tag{10}$$

$$KFe_3(SO_4)_2(OH)_6 + 6H^+ \rightarrow 3Fe^{3+} + K^+ + 2SO_4^{2-} + 6H_2O$$
 (11)

The solubility products of goethite $(\log K_g)$ and jarosite $(\log K_j)$ are then defined as follows:

 $log K_g = log[Fe^{3+}] + 3pH$ $log K_j = 3log[Fe^{3+}] + log[K^+] + 2log[SO_4^{2-}] + 6pH$ (12)
(13)

Using the solubility product data listed in Table 3, solubility lines for ferrihydrite, schwertmannite, goethite, and jarosite are generated and are shown in Figure 8. In addition, stability lines for schwertmannite generated using log $K_s = 10.5 \pm 2.5$ (Yu et at. 1999) and $\log K_s = 18.0 \pm 2.5$ (Bigham et al. 1996a) are shown in Figure 8. The Fe³⁺ activities of samples A1 to A3 were also plotted on this solubility diagram. This diagram suggests that the spring waters are undersaturated with respect to ferrihydrite, and are supersaturated with respect to schwertmannite, goethite, and jarosite. Table 4 shows a list of saturation indices for ferrihydrite, schwertmannite, goethite, and jarosite calculated with the PHREEQC program using the solubility products presented in Table 3. These indices also show that the spring waters are supersaturated with respect to these iron minerals, except for ferrihydrite. Therefore, schwertmannite tends to precipitate as a initial phase by bacterial oxidation of Fe²⁺, and is subsequently transformed into goethite or jarosite as a final stable phase depending on stability relationship of these materials.

Equilibrium between jarosite and goethite

As is well known, goethite is a common and widespread secondary mineral in acidic conditions where pH < 4 (Brady et al. 1986; Bigham et al. 1996a; Yu et al. 1999), and jarosite is stable rather than goethite at very low pH and sufficiently high sulfate concentration (Stahl et a. 1993; Baron and Palmer 1996). In samples A1 to A3, jarosite is a predominant secondary mineral in the rock surface precipitates and there is no goethite. The equilibrium relation of these minerals can be described as follows:

$$3FeOOH + K^+ + 2SO_4^{2-} + 3H^+ \rightarrow KFe_3(SO_4)_2(OH)_6 \quad (14)$$



FIGURE 8. Plots of pH and Fe^{3+} activity of the spring waters on a stability diagram of schwertmannite and other related iron minerals. The stability boundary lines of these minerals were calculated using the equilibrium reactions and solubility products shown in Table 3.

 TABLE 4.
 Saturation indices of iron minerals calculated by using PHREEQC

Mineral	A1	A2	A3
ferrihydrite	-0.62	-1.18	-1.15
schwertmannite (1)	17.46	13.63	14.21
schwertmannite (2)	14.02	10.19	10.77
schwertmannite (3)	6.52	2.69	3.27
goethite	3.76	3.37	3.48
jarosite	8.83	8.44	9.26

Note: The solubility products presented in Table 3 were used in this calculation.

The equilibrium constant log K_{gi} for this reaction is

$$\log K_{gj} = 3pH - \log[K^+] - 2\log[SO_4^{2-}]$$
(15)

Using Equations 12 and 13, the equilibrium constant log $K_{\rm gi}$ can be simplified to

$$\log K_{\rm gi} = 3\log K_{\rm g} - \log K_{\rm i} = 16.3 \tag{16}$$

The stability boundary between jarosite and goethite is then given by:

$$pH = 5.43 + 1/3 \log[K^+] + 2/3 \log[SO_4^{2-}]$$
(17)

Figure 9 shows the SO_4^{2-} and K⁺ activities of the spring waters on a stability diagram calculated using Equation 17. From this diagram it is apparent that the solution chemistry of the spring waters coincides with the stability field of goethite rather than jarosite. However, jarosite is predominantly formed on the submerged rock surfaces but goethite is not. The possible reason for this discrepancy may be lower pH and/or higher SO₄²⁻



FIGURE 9. Plots of SO_4^{-} and K⁺ activities of the spring waters on a stability diagram of jarosite and goethite. The boundary lines of these minerals were calculated using the equilibrium reactions and solubility products presented in Table 3, and can be expressed as pH = $5.43 + 1/3 \log[K^+] + 2/3 \log[SO_4^{-}]$.

activities in the aquatic environments in contact with the rock surfaces than in the bulk spring water. If the pH of the rock surface environment is lower than about pH = 2.56 or if the SO_4^{2-} activity is higher than about $log[SO_4^{2-}] = -1.2$, the stable phase changes to jarosite as illustrated in Figure 9. Such chemical differences in aquatic environments between the rock surfaces and the bulk spring waters are likely to occur because the acidification of the spring waters is attributed to the formation of sulfuric acid on the rock surfaces by oxidation of pyrite as described in Equation 1. In addition, there is no apparent evidence of the influence of bacteria on the formation of jarosite in this aquatic system. Consequently, the formation of jarosite may be controlled by its inherent thermodynamic properties without the influence of bacteria. Bigham et al. (1996b) demonstrated that jarosite formation is favored in acidic conditions below pH = 2.5 with relatively high SO_4^{2-} concentrations, whereas goethite increases in abundance above pH = 3.3 and at lower SO₄²⁻ concentrations. Similar mineralogical differences which depend on solution chemistry have also been reported in a field study of coal mine drainage (Bigham et al. 1996a). The results of the present study agree well with these experimental and field observations.

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