

Effect of Fe(II) and Cu(II) on the Transformation of Schwertmannite to Goethite under Acidic Condition

Sengpasith Houngaloune, Naoki Hiroyoshi, and Mayumi Ito

Abstract—Schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)_x$) is a critically important Fe(III) mineral in acid-mine drainage environments because of its widespread occurrence and high reactivity towards toxic oxyanions, such as arsenate. The present study investigates the effect of Fe(II) and Cu(II) on the transformation of schwertmannite to goethite. The transformation experiments were conducted by suspending schwertmannite in the solution containing various concentrations of Fe(II) and Cu(II) under acidic pH (3-4) at 65°C. Results indicate that Fe(II) has significant effect on the stability of schwertmannite; transformation of schwertmannite to goethite occurred within 1 h in the presence of >50 mM Fe(II). The transformation was retarded by the addition of Cu(II) concentration. When schwertmannite were suspended in solution containing 100 mM Fe(II) and >50 mM Cu(II), there was no transformation occurred. This indicates that Cu(II) has the ability to retard or inhibit the Fe(II)-catalyzed transformation of schwertmannite to goethite under such conditions.

Index Terms—Schwertmannite, transformation, Fe(II), Cu(II).

I. INTRODUCTION

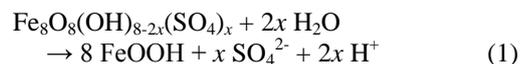
Schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_{8-2x}(\text{SO}_4)_x$ with x typically 1–1.75) is a poorly crystalline Fe(III)-oxyhydroxysulfate mineral, which commonly formed in acidic iron- and sulfate-rich (1000–3000 mg/L) environments [1], [2]. The occurrence of schwertmannite as an ochreous precipitate has been widely documented in acid-sulfate systems [3], including acid-mine drainage (AMD) streams [1], waters and sediments of mine-pit lakes [4], acid-sulfate soils and associated waterways [5], as well as bioleaching environments [6], and in the layers covering wetlands treating AMD [7]. Weathering of iron sulfide minerals (e.g. pyrite, FeS_2) leads to the formation of large amounts of secondary iron precipitates when Fe^{2+} is oxidized to Fe^{3+} , in a process that may be mediated by bacterial activity following exposure of the minerals to the atmosphere [2], [8]. The composition of these secondary iron precipitates is mainly determined by the composition of the aqueous phase, with pH and the SO_4^{2-} concentration as the main controlling variables [9]. Jarosite ($\text{K,Na,H}_3\text{O}[\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2]$) is formed at pH < 3 and at high SO_4^{2-} concentrations, ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot 1.8 \text{H}_2\text{O}$) and goethite ($\alpha\text{-FeOOH}$) are known to precipitate at neutral pH, and schwertmannite is commonly formed at pH 3.0–4.0 [2], [10].

Several authors have reported the structure of

schwertmannite as similar to that of akaganéite except that SO_4^{2-} instead of Cl occupies the parallel-extended square tunnels, with a unit cell of FeO_6 octahedra forming double chains and SO_4^{2-} ions present as both structural and adsorbed sulfate [11]–[13] found that the structural sulfate comprises both inner- and outer-sphere complexes; and the energetic stability if the outer-sphere complexes is lower than that of the inner-sphere sulfate complexes that may have an effect on the stability of schwertmannite.

There have been extensive studies of the reactivity of the schwertmannite with heavy metal and hazardous anions schwertmannite in natural AMD or wastewater under acid pH conditions [14]. Schwertmannite plays an important role as a naturally occurring attenuator for species such as arsenate and metals in AMD systems [8]. Because of its high specific surface area (e.g., 240–320 $\text{m}^2 \text{g}^{-1}$ for synthetic and 125–225 $\text{m}^2 \text{g}^{-1}$ for natural samples [11]) and its positive surface charge in these acid systems, schwertmannite can efficiently remove oxyanions from acid waters [15], [16]. Schwertmannite may delay the mobility of anions and cations present in these systems, by co-precipitation with the iron mineral oxide or by adsorption processes to the pre-existing schwertmannite [8]. It has been reported that extremely high arsenic concentrations in acid mine effluents was naturally decreased to background levels by incorporation into schwertmannite (adsorption capacity up to 60 mg g^{-1}) within meters downstream of effluent outlets [17]. The overall uptake of arsenic into schwertmannite is controlled by ligand exchanges with surface or structural SO_4^{2-} and/or surface precipitation [15].

Schwertmannite is also known as a metastable compound that is transformed to stable crystalline goethite via dissolution and re-precipitation [3], [10], [18]. The overall reaction of the phase transformation can be expressed as [4], [10], [19], [20]:



The transformation is a relatively slow process requiring years or decades in acidic and oxic environments [4], [9], [21]. This transformation process is generally accelerated in higher pH environments, but requires more than 100 days under near-neutral, oxic conditions [4], [19], [22]. Kumpulainen *et al.* [23] reported an one-year duration for complete transformation of schwertmannite to goethite at pH-8. Schwertmann and Carlson [20] observed complete transformation of schwertmannite to goethite in deionized water at pH 7.2 after 100 days. In contrast, incomplete transformation at pH 6 after 543 days of ageing was reported

Manuscript received December 23, 2013; revised April 21, 2014.

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by Jönsson *et al.* [9]. Therefore, schwertmannite tends to accumulate and persist in oxic and acidic environments, such as within drained acid-sulfate soil (ASS) landscape [24]. Recently, it has been found that Fe(II)-catalyzed transformation of schwertmannite can be extremely rapid under near-neutral and anoxic conditions [3], [25].

Stability of schwertmannite has been extensively evaluated under acidic and oxidizing conditions [4], [9], [10], [21]-[23]; however less research has addressed the behavior of schwertmannite in the presence of Fe(II) and Cu(II) under acidic conditions. In natural mine waters, significant amount of iron ions may be existed due to the oxidation of iron sulfide minerals (e.g. pyrite, FeS_2) [26]. On the other hand, copper is a metal that is often found in areas affected by AMD [27]. The presence of iron and copper ions in such system may affect the stability of schwertmannite. This study investigates the effect of Fe(II) and Cu(II) on the transformation of schwertmannite to goethite under acidic (pH 3-4) condition at 65 °C.

II. MATERIALS AND METHODS

A. Synthesis of Schwertmannite

Schwertmannite was prepared as follows: 500 mL of solution containing 10 mM H_2SO_4 and 50 mM $\text{Fe}_2(\text{SO}_4)_3$ was prepared and heated to 65 °C in a beaker under magnetic stirring at 350 rpm. After discontinuing the magnetic stirring 1 M Na_2CO_3 was titrated to the solution to adjust the final pH to 3.0-4.0 (titration rate, 1500 $\mu\text{L}/\text{min}$). The resulting suspension was left to settle, and the supernatant was subsequently replaced with deionised water. This rinsing procedure was repeated 5 times to remove soluble ions. The precipitate in a beaker was then filtrated and dried at 40 °C in a vacuum oven for 24 hours, and subjected to X-ray diffraction (XRD) analysis. To identify the schwertmannite composition, the precipitates were dissolved in 1 M HCl (1 g L^{-1}) and the Fe and S contents were determined with inductively coupled plasma atomic emission spectroscopy (ICP-AES).

B. Transformation Experiment

Transformation experiments were conducted using the following procedure: 100 mg of dried synthetic schwertmannite and predetermined amounts of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and Na_2SO_4 powders were added to 100-mL of preheated (65 °C) distilled water in a glass bottle. Here, the total SO_4^{2-} concentrations were set to be the same in all solutions by the addition of Na_2SO_4 . Therefore, when comparing the results of the experiments, the effect of the SO_4^{2-} concentration on the transformation can be disregarded. The glass bottle was then placed into a dry stirring bath (HDBS-6) under magnetic stirring at 120 rpm and at 65 °C. At the completion of the 1 h reaction period, the suspension in the glass bottle was centrifuged (3500g, 5 min). After measurement for its pH and Eh, the supernatant was subsequently replaced 5 times with deionised water to remove soluble ions. The recovered solid, after being dried overnight in a vacuum dryer, was ground in an agate mortar, and subjected to XRD analysis. 10 mg of the dried solid was dissolved in 10 mL of 1 M HCl and S content was determined

with ICP-AES. The amount of released SO_4^{2-} was calculated from the differences between the initial amount and final (remaining) amount of SO_4^{2-} in the solid phase. The use of SO_4^{2-} release in combination with mineralogical characterization by XRD has been previously applied by several authors to quantify schwertmannite transformation rates in the absence/presence of Fe(II) [3], [4]. It should be noted that the quantitative transformation rates obtained from SO_4^{2-} release data assume that retention of SO_4^{2-} within the newly formed goethite is negligible [3].

C. Analytical Methods

A pH-meter and combined electrode with temperature compensation was used to measure the pH and was calibrated regularly with standard buffer solutions of pH 1.68, 4.01, and 6.86. The redox potential was measured using an ORP combined electrode consisting of Pt and Ag/AgCl reference electrodes. The concentrations of iron and sulfur in the aqueous phase were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Seiko instruments SPS7800. Solid samples were ground to a homogeneous powder in a mortar and subsequently analyzed by X-ray diffraction (XRD) using a RIGAKU powder diffractometer with $\text{CuK}\alpha$ radiation (40 kV and 30 mA) to identify the minerals present in the samples. Peak maxima were read from the diffractogram and minerals were identified by comparison with a schwertmannite standard from an XRD pattern identical to that of the schwertmannite described by Bigham *et al.* [11].

III. RESULTS AND DISCUSSION

A. Characterization of Schwertmannite

Examination by XRD of the schwertmannite prepared in the present study confirmed that schwertmannite was the only mineral detectable (Fig. 1).

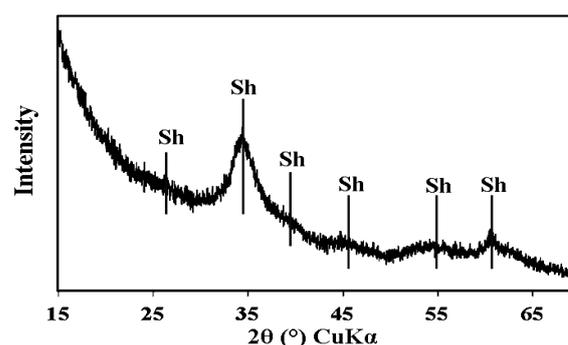


Fig. 1. XRD patterns showing that Schwertmannite (denoted as "Sh") was the only detectable mineral in the initial synthesized Schwertmannite.

As mentioned above schwertmannite is described by the formulation $\text{Fe}_8\text{O}_8(\text{OH})_{8-2x}(\text{SO}_4)_x$, with x ranging between 1 and 1.75. The amount of Fe and S measured after complete dissolution of synthesized schwertmannite in 1 M HCl were $8.6 \pm 0.3 \text{ mmol g}^{-1}$ and $1.62 \pm 0.06 \text{ mmol g}^{-1}$, respectively. The molar Fe/S ratio, determined from the Fe and S molar proportions, is 5.3 ± 0.35 which agrees with the molar values suggested previously for schwertmannite (molar Fe/S ratio = 4.5-8.0, [1], [11]). On this basis, the synthesized

schwertmannite composition can be represented as $\text{Fe}_8\text{O}_8(\text{OH})_{4.98}(\text{SO}_4)_{1.51}$. This composition is very close to the average value reported in [9], [10], [28].

B. Effects of Fe(II) on Transformation of Schwertmannite

To investigate the effects of Fe(II) on transformation of schwertmannite to goethite, the synthesized schwertmannite was suspended in solution containing 0, 1, 10, 50, or 100 mM Fe(II) at 65 °C at pH 3-4 for 1 h. As mentioned previously, schwertmannite is metastable with respect to goethite [9], [11] and the transformation of schwertmannite to goethite releases significant amounts of SO_4^{2-} (Eq. 1). The SO_4^{2-} released from schwertmannite after suspension in solution containing various Fe(II) concentrations are shown in Fig. 2. Results show that about 5.7% of total solid phase SO_4^{2-} was released in the case of schwertmannite suspended in the absence of Fe(II). The release of SO_4^{2-} was increased toward the addition of Fe(II) concentrations. The fraction of released SO_4^{2-} is approximately 15.3%, 54.8%, 81.7%, and 90.4% for schwertmannite suspended in 1, 10, 50, and 100 mM Fe(II) solutions, respectively.

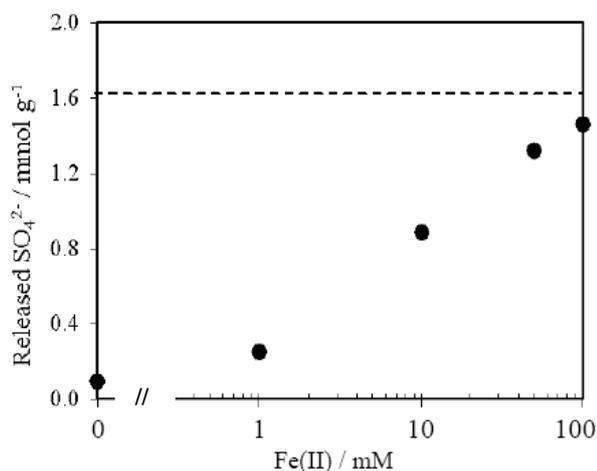


Fig. 2. Fraction of SO_4^{2-} released from schwertmannite suspended with the presence of various Fe(II) concentrations at 65 °C, at pH 3-4 for 1 h. The total amount of initial SO_4^{2-} in the solid (1.62 mmol g^{-1}) is indicated by a dashed line.

Previous research has shown that SO_4^{2-} is associated with schwertmannite both through bonding in the internal structure and through adsorption onto the surface, which can make up to 35% of the total SO_4^{2-} content [9], [11]. For schwertmannite suspended in the solution without Fe(II), the SO_4^{2-} released most likely reflects desorption of loosely bound surface SO_4^{2-} from relatively weak sites of electrostatic attraction [9], [22]. The release of >50% SO_4^{2-} observed in the present study for schwertmannite suspended in the solution containing 10, 50 or 100 mM Fe(II) indicates a contribution of SO_4^{2-} from both the internal structure and the surface of schwertmannite.

The XRD data demonstrate that SO_4^{2-} released following the addition of Fe(II) can be attributed to the transformation of schwertmannite to goethite (Fig. 3). The XRD results show schwertmannite peaks and there is no formation of other phases in the solid suspended in solution without Fe(II). Schwertmannite remains the dominant mineral for solid suspended in 1 mM Fe(II) solution. Some goethite (αFeOOH) peaks appear with 10 mM Fe(II), and the goethite

contribution continues to increase with Fe(II) concentration. At the initial Fe(II) concentration of 50 and 100 mM, goethite is the main mineral phase detected. This indicates that Fe(II) has a significant effect on the stability of schwertmannite even at acidic (pH 3-4) condition.

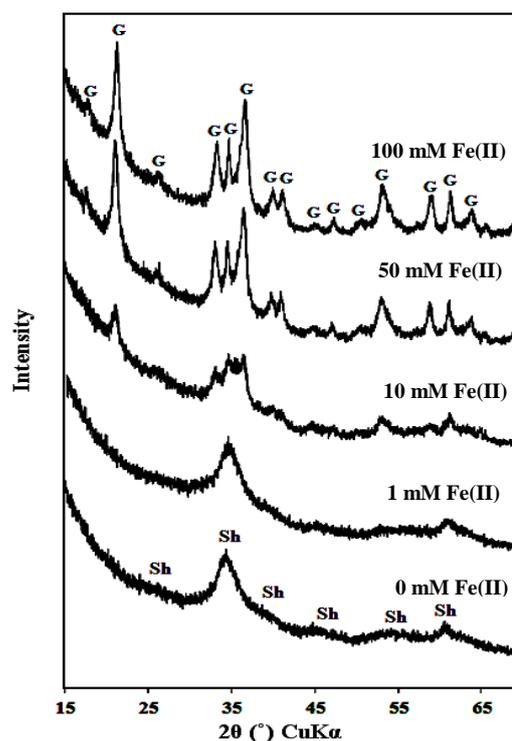


Fig. 3. XRD patterns for schwertmannite suspended in solutions containing various Fe(II) concentrations at 65 °C, at pH 3-4 for 1 h. Schwertmannite is denoted as “Sh” and goethite as “G”.

Burton *et al.* [3] investigated factors affecting the transformation rate of schwertmannite to goethite in a chloride solution at 25 °C under anoxic condition. Here, the transformation rate is increased in the presence of Fe(II) and at pH > 5; and complete conversion of schwertmannite to goethite occurred within hours at pH > 6 and $\text{Fe(II)} \geq 5 \text{ mM}$. Such Fe(II)-catalyzed transformation of iron minerals also occurs for other minerals than schwertmannite. Yee *et al.* [29], and Hansel *et al.* [30] reported that the transformation of ferrihydrite to goethite phase is catalyzed by Fe^{2+} , and used isotopes to confirm that electron transfer between Fe(II) adsorbed from the solution phase and structural Fe(III) in the ferrihydrite lattice during the transformation process. Referring to these studies, Burton *et al.* [3] had proposed a model of the Fe(II)-catalyzed transformation of schwertmannite to goethite.

In this model, the phase transformation involves the adsorption of Fe(II) to the schwertmannite surface. Schwertmannite has a point of zero charge (PZC) of 7.2 [9], and its surface is positively charged in the acidic region, Fe(II) also with a positive charge, causing the repulsion between Fe(II) and schwertmannite surface. Under higher pH conditions, the schwertmannite surface becomes negatively charged, enabling Fe(II) to adsorb on the surface of schwertmannite by electrostatic attraction, so increasing the amount of adsorption. An electron transfer subsequently occurs between the adsorbed Fe(II) (acting as an electron donor) and the structural Fe(III) at the mineral-water

interface via overlapping d-orbitals [31]. The surface layer of schwertmannite is destabilized due to the presence of this nascent structural Fe(II), causing a reductive dissolution and the release of the adsorbed Fe(III), structural Fe(II), SO_4^{2-} , and OH⁻. Finally, the desorbed Fe(III) rapidly hydrolyzes and precipitates as a thermodynamically more stable phase mainly as goethite [30].

The experimental conditions of the present study (sulphate solution, 65 °C, pH 3-4) are different from those of previous studies, for instance Burton *et al.* [3] (Chloride solution, 25 °C, pH > 5). Therefore, it is difficult to subject the results of the present study to a quantitative description by the above model, however qualitatively the processes involved are similar.

The transformation of schwertmannite to goethite in the present study occurred at lower pH values (3-4) than reported by Burton *et al.* [3]. This may be due to the higher Fe(II) concentration (100 mM) and high temperature (65 °C), which could accelerate the transformation rate. It has been reported that the transformation rate of schwertmannite to goethite is slower at lower temperatures [9]. In addition, Yee *et al.* [29] found that in the presence of Fe(II), the transformation of poorly ordered ferrihydrite into crystalline goethite is significantly faster at 60 °C than at 21 °C. This indicates that the transformation rate is dependent on temperature. Furthermore, it has also been reported that the PZC values of iron oxide/hydroxide decrease with increase in temperature [32]. This may cause Fe(II)-catalyzed transformation of schwertmannite to goethite at lower pH (3-4).

To clarify this phenomenon, the synthesized schwertmannite was suspended at 25 °C and at pH 3-4 for 1 h. Results indicate that there was no significant change in SO_4^{2-} released following the addition of various Fe(II) concentrations (Fig. 4). The XRD data (Fig. 5) also confirm negligible degrees of schwertmannite transformation, even suspended with 100 mM Fe(II); suggesting the possibility that the PZC of schwertmannite shift to a lower pH values at higher temperature.

In addition, schwertmannite was also suspended at 25 °C and at pH 3-4 for 24 h to observe the kinetic transformation of schwertmannite. However, the results show that no transformation occurred even suspended in 100 mM Fe(II) solution.

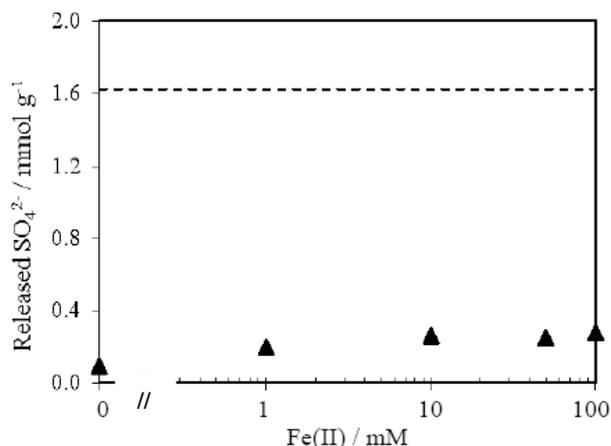


Fig. 4. Fraction of SO_4^{2-} released from schwertmannite suspended with the presence of various Fe(II) concentrations at 25 °C, at pH 3-4 for 1 h. The total amount of initial SO_4^{2-} in the solid (1.62 mmol g^{-1}) is indicated by a dashed line.

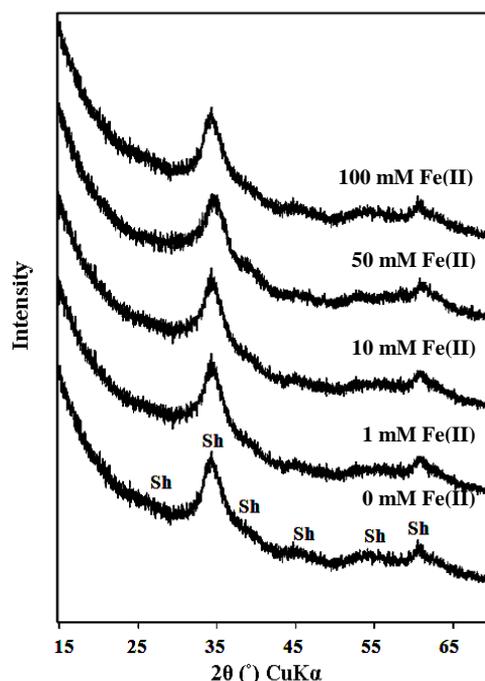


Fig. 5. XRD patterns for schwertmannite suspended in solutions containing various Fe(II) concentrations at 25 °C, at pH 3-4 for 1 h. Schwertmannite is denoted as “Sh” and goethite as “G”.

C. Effects of Cu(II) on Fe(II)-Catalyzed Transformation of Schwertmannite to Goethite

In general, copper is a metal that is often found in areas affected by AMD [27]. The inclusion of copper ions in such system may have an important effect on the stability of schwertmannite. Antelo *et al.* [27] found that the incorporation of Cu(II) ions into the crystalline structure of schwertmannite affect its stability of and delay its transformation to a more crystalline phase like goethite. Therefore, the effect of Cu(II) on Fe(II)-catalyzed the transformation of schwertmannite to goethite was investigated in the present study.

As mentioned above, Fe(II) influences the stability of schwertmannite, especially at high Fe(II) concentrations. Thus the transformation experiments were carried out by suspending schwertmannite in solutions containing 100 mM Fe(II) and 0-100 mM Cu(II) at 65 °C at pH 3-4 for 1 h.

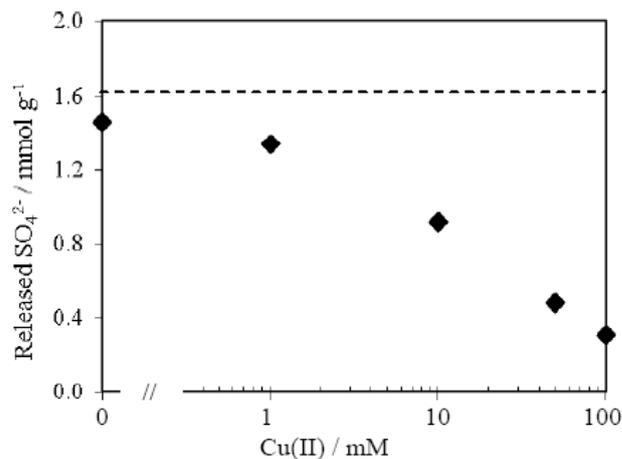


Fig. 6. Fraction of SO_4^{2-} released from schwertmannite suspended with the presence of 100mM Fe(II) and various Cu(II) concentrations at 65 °C, at pH 3-4 for 1 h. The total amount of initial SO_4^{2-} in the solid (1.62 mmol g^{-1}) is indicated by a dashed line.

Results (Fig. 6) show that significant amount (90.4%) of SO_4^{2-} was released from schwertmannite suspended in solution containing 100 mM Fe(II) and with the absence of Cu(II). The release of SO_4^{2-} was decreased toward the addition of Cu(II) concentrations. The amount of released SO_4^{2-} is approximately 82.7%, 56.7%, 29.7%, and 19.2% for schwertmannite suspended with the addition of 1, 10, 50, and 100 mM Cu(II), respectively. The release of <30% SO_4^{2-} observed in schwertmannite suspended in solution containing 50 and 100 mM Cu(II) may indicate a contribution of SO_4^{2-} from the surface of schwertmannite only, not from the internal structure. Therefore, it may be expected that no transformation of schwertmannite occurred for solids suspended with the presence of 100 mM Fe(II) and 50 and 100 mM Cu(II). These results were further confirmed by XRD.

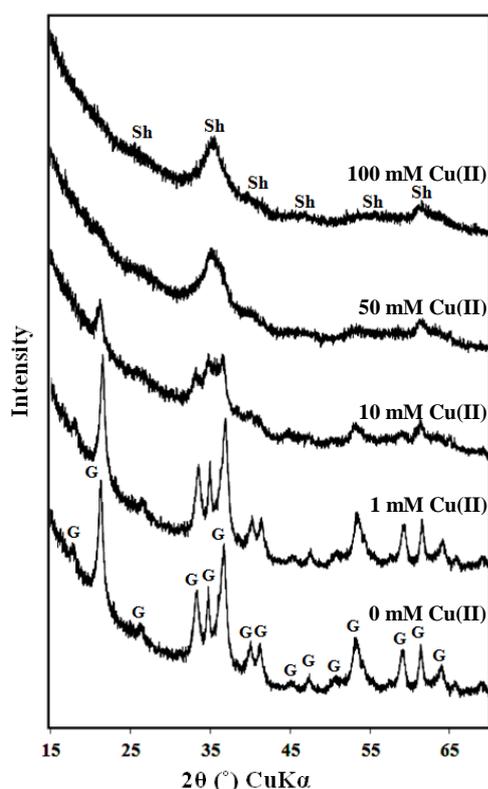


Fig. 7. XRD patterns for schwertmannite suspended in solutions containing 100mM Fe(II) and various Cu(II) concentrations at 65 °C, at pH 3-4 for 1 h. Schwertmannite is denoted as “Sh” and goethite as “G”.

The XRD patterns (Fig. 7) demonstrate that goethite is the dominant phase detected for the solid suspended in solution containing 100 mM Fe(II) and without Cu(II). Some goethite peaks become absent and some schwertmannite is detected for the sample suspended in the solution containing 10 mM Cu(II). Schwertmannite becomes the prominent mineral with no goethite phase detected in the presence of 50 and 100 mM Cu(II). This indicates that Cu(II) has the ability to retard or inhibit the Fe(II)-catalyzed transformation of schwertmannite to goethite.

Assuming the model proposed by Burton *et al.* [3] to hold, the transformation may be described as: (1) adsorption of Fe(II) and Cu(II) onto the schwertmannite surface; (2) reductive dissolution of schwertmannite by the absorbed Fe(II), a process that may involve two steps: both Fe(II) and

Cu(II) are positively charged and these ions may affect the electrostatic attraction to the schwertmannite surface, the Cu(II) would prevent the adsorption of Fe(II) onto the surface. Further, Cu(II) functions as an oxidizing agent (electron acceptor), whereas Fe(II) is a reducing agent (electron donor). When Fe(II) supplies electrons to schwertmannite, some of these electrons are consumed by the Cu(II), and the reductive dissolution rate of schwertmannite can be expected to decrease. However, further investigation is required to establish the details of these phenomena.

IV. CONCLUSION

Schwertmannite is a critically important Fe(III) mineral in acid-sulfate soil and acid-mine drainage environments because of its widespread occurrence and high reactivity towards toxic oxyanions, such as arsenate. Schwertmannite is also known as a metastable iron oxide that is transformed to goethite under oxic conditions. Transformation of schwertmannite to goethite may strongly affect the mobility of these toxic oxyanions. The present study has investigated the effect of Fe(II) and Cu(II) on the transformation of schwertmannite to goethite under oxic and acidic pH (3-4) at 65 °C. The results confirm that Fe(II) has significant effect on the stability of schwertmannite. The transformation of schwertmannite to goethite occurred within 1 h in the presence of >50 mM Fe(II). The transformation was retarded toward the addition of Cu(II) concentration. When schwertmannite were suspended in solution containing 100 mM Fe(II) and >50 mM Cu(II), there was no transformation occurred. This indicates that Cu(II) has the ability to retard or inhibit the Fe(II)-catalyzed transformation of schwertmannite to goethite. These findings have important implications for understanding the stability of schwertmannite under Fe(II)- and Cu(II)-rich environments.

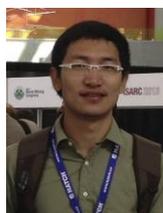
ACKNOWLEDGMENT

This work is supported by a collaborative research program between Hokkaido University and Sumitomo Metal Mining Co., LTD.

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