

Solubilities of synthetic schwertmannite and ferrihydrite

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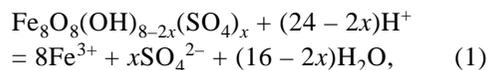
Schwertmannite, 2-line ferrihydrite, and 6-line ferrihydrite were synthesized at 25°C in the laboratory to determine their solubilities. Chemical and thermal analyses of the synthesized minerals show that schwertmannite has the chemical formula $\text{Fe}_2\text{O}_{3-x}(\text{SO}_4)_x \cdot n\text{H}_2\text{O}$ ($0.41 \leq x \leq 0.49$, $1.51 \leq n \leq 2.81$) and ferrihydrite $\text{Fe}_2\text{O}_{3-0.5y}(\text{OH})_y \cdot n\text{H}_2\text{O}$ ($0 \leq y \leq 1.96$, $0.82 \leq n \leq 1.14$). The solubility products (K) of the minerals were estimated from the activities of the corresponding species calculated with the computer program PHREEQC. The estimated $\log K$ values are 2.01 ± 0.30 for schwertmannite, 8.46 ± 1.40 for 2-line ferrihydrite, and 10.12 ± 0.74 for 6-line ferrihydrite. The solubility of schwertmannite seems to vary depending on the sulfate content, but more investigation is needed to quantify the relationship. The solubility of ferrihydrite does not show any significant correlation with the water content. The stability boundary between schwertmannite and ferrihydrite predicted in this study is biased to higher pH than that observed in nature, which also need further investigation.

INTRODUCTION

Schwertmannite and ferrihydrite are probably the two most frequently observed minerals precipitating from ferriferous aqueous systems, such as mine drainages, soil solutions and lake waters. Precipitation of these minerals not only controls the chemical conditions, but also removes many dissolved metals from the aqueous solution through coprecipitation and adsorption. Thus, the solubilities of schwertmannite and ferrihydrite should be known to describe the transport and fate of the metals and other chemicals in the systems.

The solubilities of schwertmannite and ferrihydrite need to be better defined. Both minerals are poorly crystalline and metastable with respect to goethite (Bigham *et al.*, 1990, 1996; Yu *et al.*, 1999), which might cause some difficulties in the solubility determination. The uncertainty in solubilities of the minerals also arises due to a few other reasons.

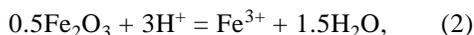
Schwertmannite is known to have variable chemical compositions. Bigham *et al.* (1994) suggested the chemical formula as $\text{Fe}_8\text{O}_8(\text{OH})_{8-2x}(\text{SO}_4)_x \cdot n\text{H}_2\text{O}$ ($1 \leq x \leq 1.75$). Later, Yu *et al.* (1999) reported the occurrence of schwertmannite having $x \geq 1.75$. The relation between the sulfate content and the solubility is not known. Bigham *et al.* (1996) pointed out that part of the analyzed sulfate in schwertmannite may be adsorbed sulfate, but it has not been distinguished from the structural sulfate yet. The solubility of schwertmannite has been reported only twice on the literature. For the following dissolution reaction



Bigham *et al.* (1996) and Yu *et al.* (1999) suggested 10^{18} and 10^{10} as the solubility product, respectively.

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Ferrihydrite has not only variable chemical compositions but also variable crystallinity. The chemical formula of ferrihydrite has been reported significantly diverse (Jambor and Dutrizac, 1998), and generally represented by a bulk chemical formula like $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ (Schwertmann and Taylor, 1989). Ferrihydrite may show up to 9 X-ray diffraction lines depending on its crystallinity, but 2- and 6-line ferrihydrite are most common (Towe and Bradley, 1967; Eggleton and Fitzpatrick, 1988; Martinez and McBride, 1998). Many investigators have tried to determine the solubility of ferrihydrite. However, significant discrepancies are still present among the reported solubilities and the relation among the solubility, chemical composition and crystallinity is yet to be more thoroughly investigated. For the following dissolution reaction



Nordstrom *et al.* (1990) summarized the reported values and gave the range of 10^3 to 10^5 for the solubility product.

The purpose of this study is to obtain more reliable solubilities of schwertmannite and ferrihydrite and examine the relationship among the solubilities, chemical compositions, and crystallinities of the minerals. Many of the reported solubilities have been determined from the natural waters or the solutions probably in a disequilibrium state. This study synthesized schwertmannite, 2-line ferrihydrite and 6-line ferrihydrite under various conditions and collected data from the analyses of the synthesized minerals and synthesis solutions.

METHODS

Mineral syntheses

Schwertmannite was synthesized from 1000 ml Na_2SO_4 + 1000 ml $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution of various concentrations. The concentrations were 0.02 M Na_2SO_4 + 0.02 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.0026 M Na_2SO_4 + 0.02 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.02 M Na_2SO_4 + 0.01 M

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.01 M Na_2SO_4 + 0.01 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 0.005 M Na_2SO_4 + 0.01 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. These solutions were hydrolyzed for 12 min. at 60°C right after the mixing, and then placed in a water bath at 25°C . We prepared two sets of the first mixture. The samples of one of the first mixture were collected after 1, 4, 8, 12, 18, 24, 30, 48, 60, 72, 84, 96, 108, 120, 132, 144, 168 hours passed since the experiment started. The samples of other first mixture and second one were collected after 1, 3, 7, and 14 days passed. The rest of the mixtures were sampled after 1, 4, 7, 14, 25 days passed.

2-line ferrihydrite was synthesized from $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solutions of various concentrations titrated with 1N NaOH to various pH. The concentrations of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were 0.025, 0.0165 and 0.005 M. The initial pH of 0.005 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ M solution was adjusted to approximately 5, 6 and 9. We prepared two 0.025 M solutions; one is used for sampling at a shorter time interval (1, 4, 7, 12, 17, 24, 31, 39, 48 hrs). The other 0.025 M and 0.0165 M solutions were sampled after 0, 3, 7, and 14 days passed. Samples of 0.005 M solutions were collected after 2, 4, 7, 12, 20, and 28 days passed.

6-line ferrihydrite was also synthesized from 0.025, 0.0125, and 0.005 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solutions prepared at 75°C . The solutions were allowed to be cooled for 13 min. at room temperature and then quenched with ice/water mixture. After the temperature of the solution recovers to 25°C , the solutions were titrated with 1 N NaOH. The sampling intervals of the solutions were the same as those for 2-line ferrihydrite.

The samples were always taken from the mixtures of solutions and precipitates homogenized by shaking and then filtered with $0.1 \mu\text{m}$ micropore membrane to separate the aqueous phase from the precipitates. Each filtrate were transferred to a presoaked 50 ml polyethylene bottle and acidified with c- HNO_3 . The precipitates were washed three times with deionized water, centrifuged 10,000 rpm for 5 min. and then dried at 50°C in an oven.

Laboratory measurements and analyses

Temperature of the synthesis solutions was checked all the times and maintained at $25 \pm 1^\circ\text{C}$. The pH of each solution was measured right after the sampling and filtration with SUNTEX SP-701 pH/mV/ORP meter. The alkalinity measurement was performed only for the solutions having $\text{pH} > 4.5$ with Gran titration (Wetzel and Likens, 1991). Carbonate concentrations in aqueous phases were estimated from the alkalinities (Stumm and Morgan, 1996).

The concentrations of Si, Al, Fe, Ca, Mg and K in the aqueous solutions were determined with Perkin Elmer OPTIMA 3200XL ICP-AES at the Seoul Branch of Korea Basic Science Institute (SB-KBSI). Na was analyzed with flame AAS with Perkin Elmer Spectra AA-20 at the Department of Geosystem Engineering, Kangwon National University (KNU). When the solution has very low Fe and high Na contents, Na significantly interferes with the analysis of Fe. In this case, Fe was analyzed with standard addition method using the graphite furnace AES. The concentrations of anionic components, including Cl, NO_3 , and SO_4 in the aqueous phases were determined with Dionex 4500i IC at SB-KBSI and at the Department of Chemistry, KNU.

100 mg of each precipitate sample was dried at 120°C for 2 hrs in an oven and dissolved with 20 ml 5N HCl. This precipitate solution was diluted to 500 ml and then analyzed by the same method as in the aqueous solution analyses. X-ray diffraction (XRD) and thermal analyses of the precipitate samples were also conducted at the Industrial Mineral Bank, KNU. XRD profiles were obtained with Rigaku Umax 2200V X-Ray diffractometer, using a Co source with divergent-scattering-receiving slits of 1° - 1° -0.15 mm. Samples were continuously scanned from 5 to 100° with scan rate of $1^\circ/\text{min}$ and scan step of 0.02° in 2θ . Thermal analyses included differential thermal analysis (DTA), thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA), being performed with Rigaku TAS 100. These techniques were used to analyze 10 mg samples of precipitates in parallel with 10 mg

Al_2O_3 used as a reference material. The samples were dried at 60°C for 2 hours prior to the thermal analysis and then analyzed from room temperature to $1,000^\circ\text{C}$ with temperature increase rate of $10^\circ\text{C}/\text{min}$.

The amount of adsorbed sulfate on schwertmannite was attempted to be determined using the method of Rose and Ghazi (1997). The method is as follows; 0.75 g of schwertmannite was reacted with 7.5 ml (0.25M sodium oxalate : 1M sodium hydroxide = 1:1) of solution. The solutions were gently machine shaken in a 25°C water bath for 24 hours and were also vigorously hand shaken from time to time during this period. The supernatant was centrifuged and then filtered through a $0.1 \mu\text{m}$ micropore membrane. The filter cake was analyzed with XRD and the filtrate was analyzed with the methods described earlier for the aqueous solutions.

Chemical equilibrium calculation

The speciation of the dissolved component and the activities of the species were calculated from the chemical compositions of the aqueous solutions using the computer program PHREEQC (Parkhurst, 1995). The database used in the calculation was that of MINTQA2 (Allison *et al.*, 1991). No solid or gas was allowed to be in contact with the solution during the calculation.

RESULTS AND DISCUSSION

Chemical and mineralogical compositions

Tables 1, 2, and 3 list the chemical compositions of the aqueous solution and the mineralogical compositions of the precipitate samples collected during the syntheses of schwertmannite, 2-line ferrihydrite, and 6-line ferrihydrite, respectively. As expected, the aqueous phases mainly consist of Fe, Na, Cl, NO_3 , and SO_4 . The mineralogical compositions of the precipitates were determined from the XRD patterns. Figure 1 shows some typical XRD patterns of the precipitates. Many precipitates consists of schwertmannite, 2-line ferrihydrite, or 6-line ferrihydrite only. Some other precipitates, however, also contain goethite,

Table 1. The chemical compositions of the aqueous solutions and mineralogical compositions of the precipitates collected during the schwertmannite synthesis experiments

Starting solution	Collection time*	Sample No.	pH	Fe	Al	Mn	Ca	Mg	K	Na	Cl	NO ₃	SO ₄	Mineralogy**
0.02M Na ₂ SO ₄ + 0.02M FeCl ₃ ·6H ₂ O	1h	S1-1h	2.00	422	0.50	0.42	n.d.#	0.010	0.49	565	981	—	1007	S
	4h	S1-4h	2.03	405	0.64	0.33	n.d.	0.010	0.55	527	986	—	1009	S
	8h	S1-8h	2.02	446	0.59	0.64	n.d.	0.020	0.56	452	986	—	977	S
	12h	S1-12h	2.08	435	0.70	0.59	n.d.	0.010	0.50	494	962	—	961	S
	18h	S1-18h	2.02	435	3.32	0.87	n.d.	0.010	0.46	483	961	—	975	S
	24h	S1-24h	2.01	384	0.44	0.45	n.d.	0.010	0.47	561	953	—	1001	S
	30h	S1-30h	2.04	381	0.57	0.48	n.d.	0.010	0.51	529	968	—	988	S
	48h	S1-48h	2.05	418	0.69	0.56	n.d.	0.020	0.49	489	979	—	939	S
	60h	S1-60h	2.03	372	0.43	0.63	n.d.	0.010	0.52	475	957	—	934	S
	72h	S1-72h	2.00	367	0.52	0.42	n.d.	0.020	0.78	477	962	—	950	S
	84h	S1-84h	2.03	364	0.51	0.48	n.d.	0.010	0.50	476	1005	—	978	S
	96h	S1-96h	2.01	378	0.53	0.52	n.d.	0.020	0.50	498	972	—	964	S
	108h	S1-108h	2.01	364	0.51	0.64	n.d.	0.020	0.52	469	978	—	973	S
	120h	S1-120h	1.96	352	0.33	0.75	n.d.	0.020	0.52	466	1008	—	940	S
	132h	S1-132h	2.06	347	0.32	1.01	n.d.	0.020	0.56	482	1154	—	933	S
	144h	S1-144h	1.99	378	0.40	0.69	n.d.	0.010	0.53	448	1032	—	941	S
168h	S1-168h	2.05	385	0.37	0.99	n.d.	0.020	0.64	395	998	—	936	S	
0.02M Na ₂ SO ₄ + 0.02M FeCl ₃ ·6H ₂ O	1d	S2-1d	1.95	649	0.11	1.21	0.195	0.004	1.22	496	1246	—	963	S
	3d	S2-3d	1.88	594	0.13	1.22	0.355	0.007	0.88	488	1207	—	952	S
	10d	S2-10d	1.85	636	0.14	1.24	0.290	n.d.	1.01	498	1294	—	965	S
	14d	S2-14d	1.83	631	0.13	1.23	0.880	0.005	1.04	494	1237	—	962	S
0.0026M Na ₂ SO ₄ + 0.02M FeCl ₃ ·6H ₂ O	1d	S3-1d	1.76	542	0.13	1.21	0.175	0.009	0.45	59.4	1190	—	70.8	S+G
	3d	S3-3d	1.75	587	0.15	1.20	0.105	0.005	0.70	66.8	1264	—	70.8	S+G
	10d	S3-10d	1.74	521	n.d.	n.d.	n.d.	0.007	0.56	63.6	1280	—	70.2	S+G
	14d	S3-14d	1.66	505	0.19	1.24	0.445	0.015	0.48	60.9	1253	—	68.7	S+G
0.02M Na ₂ SO ₄ + 0.01M Fe(NO ₃) ₃ ·9H ₂ O	1d	S4-1d	2.13	231	0.09	0.29	0.025	0.003	2.28	528	—	759	876	S
	4d	S4-4d	2.14	218	0.09	0.29	0.026	0.003	2.22	547	—	806	849	S
	7d	S4-7d	2.11	207	0.09	0.28	0.038	0.005	1.99	531	—	796	830	S
	14d	S4-14d	2.14	195	0.08	0.29	0.036	0.005	3.12	532	—	806	852	S+G
	25d	S4-25d	2.09	166	0.11	0.28	0.052	0.011	1.85	527	—	812	896	S+G
0.01M Na ₂ SO ₄ + 0.01M Fe(NO ₃) ₃ ·9H ₂ O	1d	S5-1d	2.05	216	0.11	0.33	0.066	0.006	0.30	274	—	795	513	S
	4d	S5-4d	2.07	200	0.13	0.33	0.073	0.007	0.37	275	—	807	487	S
	7d	S5-7d	2.04	192	0.14	0.33	0.079	0.006	1.78	268	—	809	492	S
	14d	S5-14d	2.06	176	0.16	0.33	0.093	0.008	0.53	274	—	820	483	S+G
	25d	S5-25d	2.02	148	0.18	0.33	0.099	0.009	0.39	264	—	804	481	S+G
0.005M Na ₂ SO ₄ + 0.01M Fe(NO ₃) ₃ ·9H ₂ O	1d	S6-1d	1.98	161	0.09	0.40	0.023	0.002	n.d.	137	—	818	221	S
	4d	S6-4d	1.97	141	0.09	0.41	0.025	0.002	0.01	138	—	795	229	S+G
	7d	S6-7d	1.97	131	0.09	0.40	0.015	0.001	0.34	138	—	815	212	S+G
	14d	S6-14d	1.98	118	0.09	0.40	0.016	0.001	0.26	133	—	829	227	S+G
	25d	S6-25d	1.95	108	0.09	0.41	0.015	0.001	n.d.	133	—	829	236	S+G

*Time passed since the synthesis started when the sample was taken. h = hours, d = days.

**Mineral compositions of the precipitates. S = schwertmannite, G = goethite.

#n.d. = not detected.

indicating that schwertmannite and ferrihydrite were transformed to more stable goethite during the experiments. It has been well known that metastable schwertmannite and ferrihydrite precipitate instead of stable goethite if pH is not too high, which would be gradually transformed to goethite (Chukrov *et al.*, 1974; Bigham *et al.*, 1996). There are many factors controlling this transformation, but this study focuses only on the solubilities of schwertmannite and ferrihydrite. Sample FII3 and FII6 consist only of goethite

which might be directly precipitated from the solution.

Tables 4 and 5 summarize the chemical compositions of some representative synthesized precipitates consisting of schwertmannite and ferrihydrite only, respectively. The thermal curves were used to determine the amount of H₂O(+) and H₂O(−) and to estimate the amount of the structural OH out of H₂O(+). Figure 2 shows typical thermal curves of the precipitates consisting only of schwertmannite (S2-3d), 2-line ferrihydrite

Table 3. The chemical compositions of the aqueous solutions and mineralogical compositions of the precipitates collected during the 6-line ferrrihydrite synthesis experiments

Starting solution	Collection time	Sample No.	pH	Fe	Al	Mn	Ca	Mg	K	Na	NO ₃	CO ₃	Mineralogy*
0.025M Fe(NO ₃) ₃ ·9H ₂ O (pH 4.92)	1h	FVII-1h	4.92	0.61	0.17	0.02	0.03	0.01	2.74	1398	3826	71.9	6F
	4h	FVII-4h	5.20	1.03	n.d.	0.53	0.03	0.01	2.75	1342	3788	—	6F
	7h	FVII-7h	5.06	1.94	0.26	n.d.	0.04	0.01	2.72	1323	3838	—	6F
	12h	FVII-12h	4.85	n.d.	n.d.	n.d.	0.12	0.02	3.10	1322	3794	—	6F
	17h	FVII-17h	4.97	0.66	0.15	n.d.	0.05	0.01	2.83	1311	3893	22.5	6F
	24h	FVII-24h	4.96	1.58	n.d.	n.d.	0.06	0.01	3.03	1210	3893	—	6F
	31h	FVII-31h	4.83	1.33	0.10	n.d.	0.05	0.02	2.87	1292	3869	—	6F
	39h	FVII-39h	4.80	1.48	n.d.	n.d.	0.08	0.02	2.94	1392	3921	—	6F
	48h	FVII-48h	4.93	1.12	0.51	n.d.	0.08	0.01	3.04	1318	3981	—	6F
0.025M Fe(NO ₃) ₃ ·9H ₂ O	0d	FVI2-1d	5.56	1.02	0.06	0.89	0.29	0.01	2.54	1505	4297	—	6F+G
	3d	FVI2-3d	4.80	1.05	0.04	0.98	0.21	0.01	2.33	1696	4284	—	6F+G
	7d	FVI2-7d	5.19	0.77	0.04	0.65	0.36	0.01	2.42	1511	4226	—	6F
	14d	FVI2-14d	4.61	1.35	n.d.	1.06	0.14	0.01	2.39	1631	4464	—	6F+G
0.0125M Fe(NO ₃) ₃ ·9H ₂ O	0d	FVI3-1d	9.63	0.86	n.d.	0.04	0.31	0.00	1.59	839	2231	8.09	6F+G
	3d	FVI3-3d	5.48	1.16	n.d.	0.56	0.17	0.01	1.45	817	2203	—	6F+G
	7d	FVI3-7d	5.10	1.37	0.03	0.55	0.12	0.01	1.57	858	2209	—	6F
	14d	FVI3-14d	6.59	0.68	0.05	n.d.	0.04	0.01	1.67	886	2337	22.9	6F+G
0.005M Fe(NO ₃) ₃ ·9H ₂ O Initial pH = 5.2	2d	FVI4-2d	4.87	13.5	0.02	0.23	0.06	0.01	0.94	393	931	30.6	6F
	4d	FVI4-4d	5.02	3.41	n.d.	0.24	0.05	0.00	0.64	403	935	14.8	6F
	7d	FVI4-7d	4.89	6.92	0.01	0.23	0.01	n.d.	0.58	408	911	41.9	6F
	12d	FVI4-12d	5.10	7.20	n.d.	0.24	0.02	n.d.	0.82	390	932	20.7	6F
	20d	FVI4-20d	5.16	7.51	0.01	0.24	0.03	0.00	1.11	414	921	19.6	6F
	28d	FVI4-28d	5.38	41.4	0.01	0.25	0.02	0.00	3.25	408	928	12.1	6F
0.005M Fe(NO ₃) ₃ ·9H ₂ O Initial pH = 6.9	2d	FVI5-2d	6.06	5.14	n.d.	0.04	0.02	n.d.	0.56	398	923	5.54	6F
	4d	FVI5-4d	6.15	6.80	0.00	0.04	0.03	n.d.	0.52	419	936	4.82	6F
	7d	FVI5-7d	6.08	5.53	0.01	0.04	0.03	n.d.	0.73	421	925	6.67	6F
	12d	FVI5-12d	6.25	4.43	0.01	0.04	0.04	n.d.	0.61	388	940	5.56	6F
	20d	FVI5-20d	6.30	6.06	n.d.	0.04	0.05	0.00	2.19	395	936	4.89	6F
	28d	FVI5-28d	6.62	4.72	n.d.	0.04	0.07	0.00	4.12	410	929	3.73	6F
0.005M Fe(NO ₃) ₃ ·9H ₂ O Initial pH = 9.0	2d	FVI6-2d	8.36	4.36	0.01	0.00	0.01	n.d.	0.80	372	924	8.55	6F
	4d	FVI6-4d	7.54	8.11	0.01	0.00	n.d.	n.d.	0.76	416	942	10.5	6F
	7d	FVI6-7d	6.95	9.54	0.02	0.00	n.d.	0.00	0.71	203	939	14.5	6F
	12d	FVI6-12d	7.17	4.26	0.02	0.00	0.01	0.01	0.67	373	951	13.8	6F
	20d	FVI6-20d	7.29	17.2	0.01	0.00	0.01	0.01	1.70	408	929	13.9	6F
	28d	FVI6-28d	7.42	6.32	0.02	0.00	0.02	0.01	3.31	409	930	15.0	6F

*6F = 6-line ferrrihydrite, G = goethite.

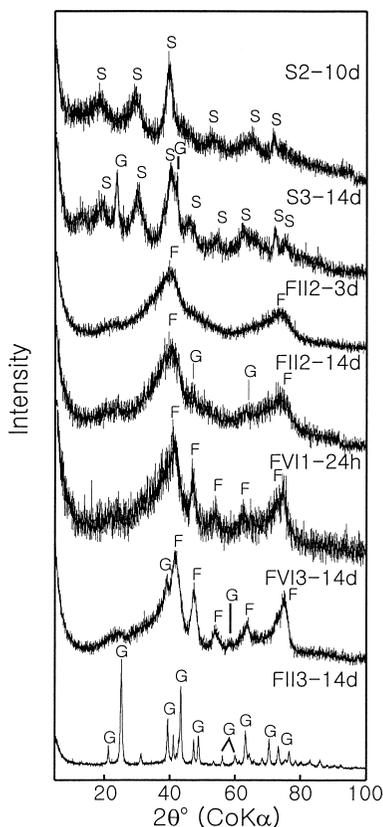


Fig. 1. X-ray diffraction profiles of some representative precipitate samples collected during the syntheses. Abbreviations; S = schwertmannite, F = ferrihydrite, G = goethite.

(FII2-3d), and 6-line ferrihydrite (FVI2-1d). The amount of $\text{H}_2\text{O}(-)$ was calculated from the weight loss on TGA curve before temperature (T) reaches 120°C . The amount of $\text{H}_2\text{O}(+)$ was estimated from the total weight loss except that by SO_3 gas release after T passes 120°C . The release of SO_3 is due to the SO_4 in schwertmannite and occurs around 600°C . The amount of the structural OH was determined from the weight loss corresponding to the second endothermic peak around $200\text{--}300^\circ\text{C}$. The amount of structural OH is denoted as $\text{H}_2\text{O}(\text{str})$ and the rest of $\text{H}_2\text{O}(+)$ as $\text{H}_2\text{O}(\text{cry})$ in Table 5.

Schwertmannite was first named by Bigham *et al.* (1994), who gave the chemical formula of

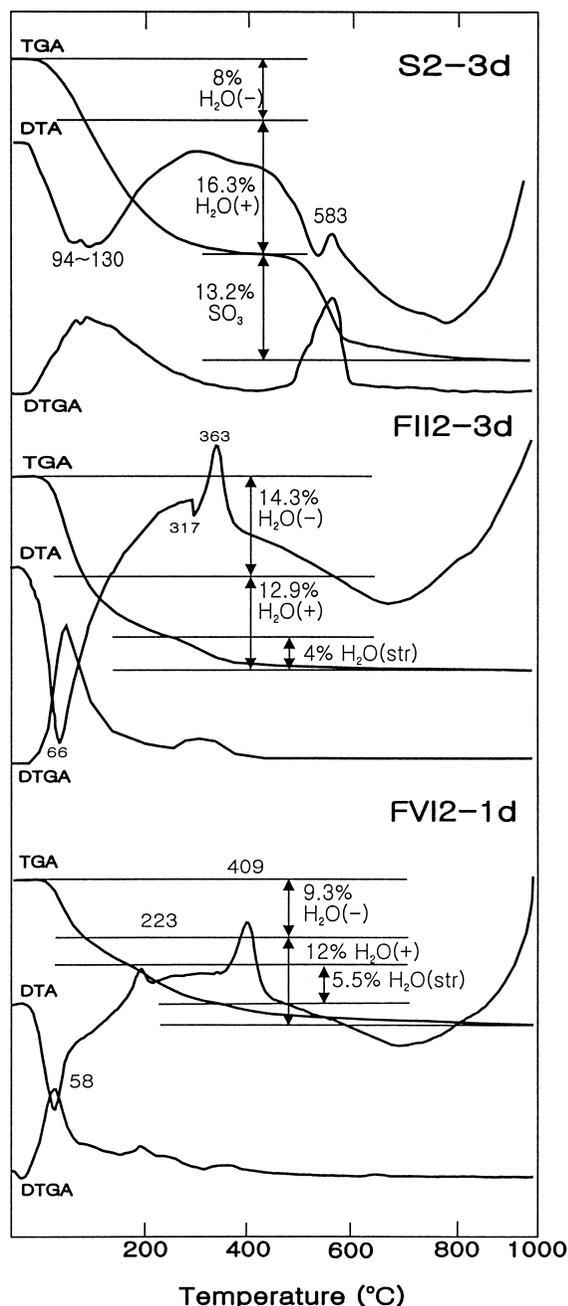


Fig. 2. Typical thermal curves of the precipitate consisting purely of schwertmannite (sample S2-3d), 2-line ferrihydrite (FII2-3d), and 6-line ferrihydrite (sample FVI2-1d).

Table 4. Chemical compositions of the precipitates consisting of schwertmannite only and the chemical formulae of schwertmannite calculated with the chemical compositions

Chemical compositions:									
Sample No.	S1-12h	S1-48h	S1-96h	S1-132h	S1-168h	S4-4d	S4-7d	S5-4d	S5-7d
Fe ₂ O ₃	62.27	56.88	61.14	60.02	56.85	54.06	55.38	53.29	53.30
Na ₂ O	0.03	0.28	0.09	0.30	0.20	3.80	2.20	5.36	4.82
K ₂ O	0.37	0.08	0.16	0.18	0.08	0.76	0.44	1.25	0.97
SO ₃	13.40	13.30	12.70	12.90	13.00	13.40	12.60	12.90	12.90
H ₂ O(-)	6.00	6.70	7.30	12.50	7.00	10.50	10.00	10.10	10.80
H ₂ O(+)	15.80	15.80	15.20	10.20	16.00	17.00	15.50	16.90	16.50
Total (%)	97.87	93.04	96.59	96.10	93.13	99.52	96.12	99.80	99.29
Chemical formula: Fe ₈ O ₈ (OH) _{8-2x} (SO ₄) _x ·nH ₂ O									
x	1.72	1.87	1.66	1.71	1.82	1.98	1.82	1.93	1.93
n	6.71	7.71	6.47	3.74	7.80	9.13	7.74	9.18	8.91
Chemical formula: Fe ₂ O _{3-x} (SO ₄) _x ·nH ₂ O									
x	0.43	0.47	0.41	0.43	0.46	0.49	0.45	0.48	0.48
n	2.25	2.46	2.20	1.51	2.49	2.79	2.48	2.81	2.74

Table 5. Chemical compositions of the precipitates consisting of ferrihydrite only and the chemical formulae of ferrihydrite calculated with the chemical compositions

Chemical compositions:							
Sample No.	2-line ferrihydrite			6-line ferrihydrite			
	FIII-12h	FIII-24h	FIII-48h	FVII-4h	FVII-12h	FVII-24h	FVII-48h
Fe ₂ O ₃	66.93	63.21	65.61	74.87	65.57	77.25	71.93
MgO	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	0.75	0.99	1.01	1.14	0.36	0.07	0.60
K ₂ O	0.23	0.21	0.20	0.14	0.24	0.14	0.24
H ₂ O(-)	11.50	13.30	12.70	12.00	11.20	11.00	8.60
H ₂ O(cry)*	8.60	7.70	7.20	7.80	7.20	7.30	6.70
H ₂ O(str)**	5.50	7.00	6.30	4.70	4.20	4.30	4.20
Total (%)	93.52	92.41	93.02	100.66	88.76	100.06	92.26
Chemical formula: Fe ₂ O _{3-y/2} (OH) _y ·nH ₂ O							
y	1.46	1.96	1.70	1.11	1.14	0.99	1.04
n	1.14	1.08	0.97	0.92	0.97	0.84	0.83

*H₂O(+) – H₂O of structural OH⁻.

**Structural OH⁻.

Fe₁₆O₁₆(OH)_y(SO₄)_z·nH₂O (16 – y = 2z and 2 ≤ z ≤ 2.5) with other physicochemical parameters of the mineral. Later, Bigham *et al.* (1996) and Yu *et al.* (1999) investigated the stability of schwertmannite in an aqueous solution using the same form of the chemical formula. However, the thermal curves not only from Bigham *et al.* (1996),

and Yu *et al.* (1999) but also from this study indicate that schwertmannite has little structural OH. The shapes of the DTA and TG curves due to water loss from schwertmannite (sample S2-3d in Fig. 2) rather resemble that of so-called “zeolitic or colloidal water” (Todor, 1976). Bigham *et al.* (1990) already recognized it and noted “similar

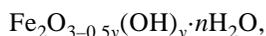
results were achieved by Margulis *et al.* (1975) from a synthetic gel with composition $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot m\text{H}_2\text{O}$ ". Thus, we think that schwertmannite has little or no structural OH and propose a new chemical formula for schwertmannite as below:



Table 4 compares the calculated x and n values according to the formula suggested by Bigham *et al.* (1994) with that by this study.

The sulfate contents in the synthesized schwertmannite in Table 4 are considerably higher than those originally reported by Bigham *et al.* (1994). Bigham *et al.* (1996) pointed out that some of the sulfates analyzed may be present not as the structural but as the adsorbed form. We tried to determine the amount of the adsorbed sulfate on schwertmannite using the method of Rose and Ghazi (1997), but failed because most of schwertmannite was transformed to goethite during the desorption experiment.

Many investigators have proposed the chemical formula of ferrihydrite, but no single formula is widely accepted (Jambor and Dutrizac, 1998). The disagreement among the reported formulae lies in the amount of structural OH and crystallization water. For example, Towe and Bradley (1967) gave $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$, but Chukrov *et al.* (1974) gave $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$. Eggleton and Fitzpatrick (1988) reported generalized bulk chemical formulae of $\text{Fe}_4(\text{O},\text{OH},\text{H}_2\text{O})_{12}$ for synthetic 2-line ferrihydrite and $\text{Fe}_{4,6}(\text{O},\text{OH},\text{H}_2\text{O})_{12}$ for synthetic 6-line ferrihydrite. It is not very clear, however, that how the electrical neutrality is satisfied between Fe, O, and OH. This study proposes a revised general chemical formula of ferrihydrite as below:



which may be easy to formulate and balance the electrical charges of Fe with O and OH. Table 5 lists the calculated y and n values in the above formula for some 2- and 6-line ferrihydrites.

The solubilities of schwertmannite and ferrihydrite

Figure 3 shows the variation of the Fe and SO_4 concentration in the aqueous solutions as a function of time. The concentrations of the constituent components of schwertmannite and ferrihydrite in the solutions become more or less steady after at least 60 and 20 hours, respectively. Thus, the solubility of schwertmannite was calculated only with the data obtained from the samples collected after 60 hours passed among those consisting of schwertmannite only, while the solubility of ferrihydrite being estimated from the samples collected after 20 hours among those consisting of ferrihydrite only.

The solubility of each mineral usually expressed with the solubility product for the corresponding dissolution reaction. If the dissolution reaction achieves an equilibrium state, the solubility product equals to the equilibrium constant for the reaction. The calculated solubility products of schwertmannite and ferrihydrite in this study, however, are highly improbable to be the equilibrium constants, because the dissolution reactions of the minerals seem irreversible. This study actually examines the precipitation reactions of the minerals and the dissolution experiments of the minerals have not been attempted. The results from work of Kim (2001) and the SO_4 desorption experiment of this study indicate that schwertmannite and ferrihydrite show incongruent dissolution to goethite in alkaline or dilute solutions.

Although the minerals are both metastable with respect to goethite, they may experience instantaneous dissolution and precipitation back and forth and achieve a kind of "pseudo-equilibrium" for a finite amount of time. The XRD patterns (Fig. 1) of the precipitates indicating only schwertmannite or ferrihydrite suggest that this may actually happen, but again we really do not know if these XRD patterns resulted from the true absence of goethite or from the presence of insufficient amount of goethite due to very slow transformation of the minerals to goethite.

In any case, it is obvious that the precipitation-dissolution reactions of schwertmannite and

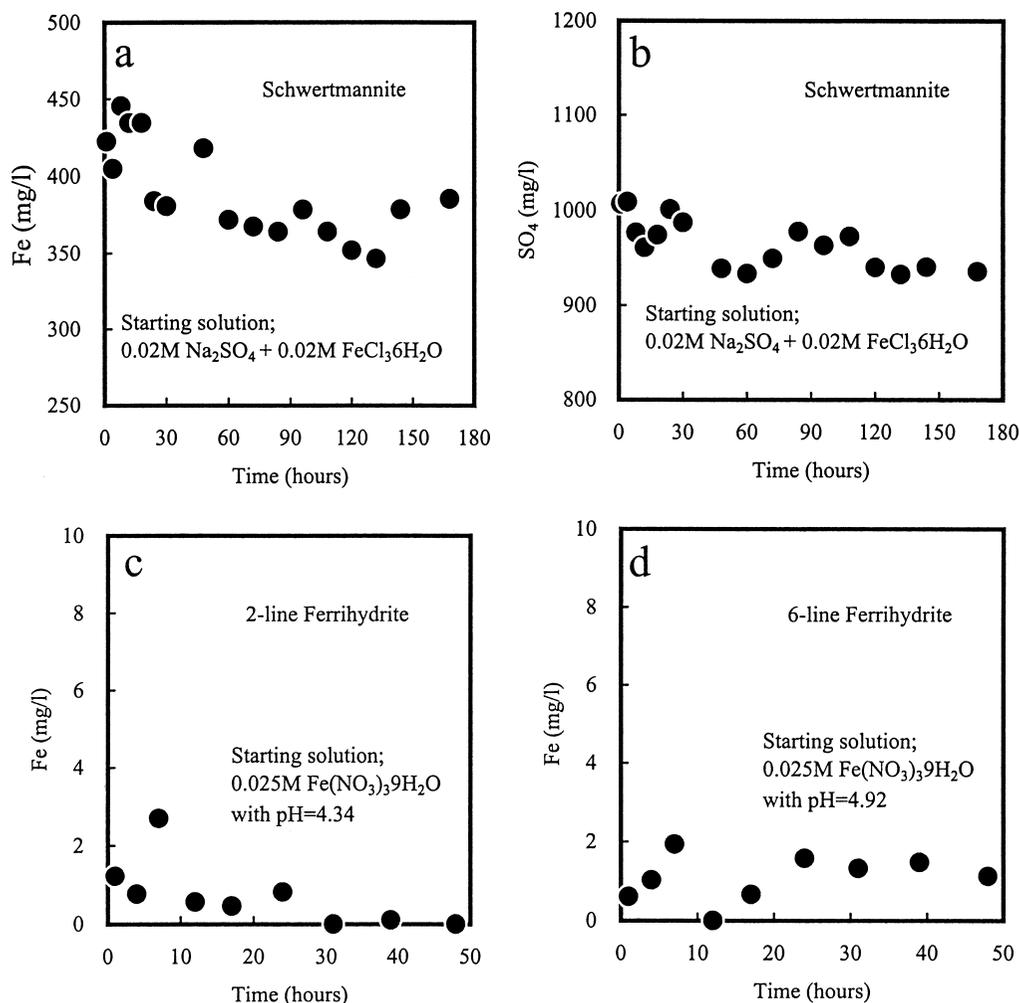
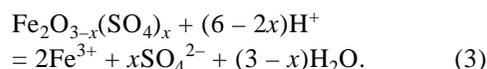


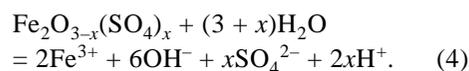
Fig. 3. Concentration variation of the dissolved Fe and SO₄ in the aqueous solutions as a function of time passed since the experiment started.

ferrihydrite are irreversible and the calculated solubility products in this study should not be considered as the equilibrium constants. In this sense, using the term “apparent solubility product” instead of “solubility product” would be more appropriate. In the followings, however, we simply use of the term “solubility product” for convenience. The concentrations of Fe and SO₄ in Figs. 3a and 3b show a little fluctuation, which may also indicate the disequilibrium between the mineral and solution.

The dissolution reaction of schwertmannite may be represented as



As expressed as reaction (3), however, the variation in sulfate concentration among the samples causes difficulties in representing the solubility product K_s on a solubility diagram. Slight modification of reaction (3) as below can circumvent this problem:



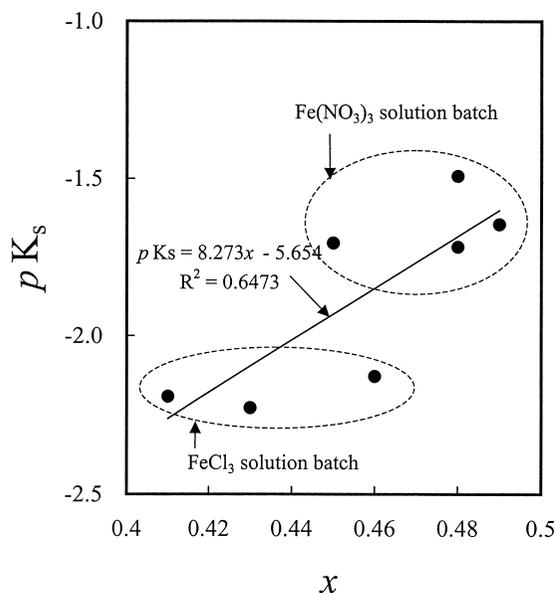


Fig. 4. Variation of the equilibrium constant of schwertmannite dissolution reaction as a function of the sulfate content (x) in the mineral. The solid line represents the linear regression line for the whole data. The broken ellipses represent separate solution batches.

If the solubility product for reaction (4) is K'_s , then

$$\log K'_s = 2(\log a_{\text{Fe}^{3+}} + 3 \log a_{\text{OH}^-}) + x(\log a_{\text{SO}_4^{2-}} + 2 \log a_{\text{H}^+}) \quad (5)$$

or

$$pK'_s = pK_s + pK_w = 2(p\text{Fe} + 3p\text{OH}) + x(p\text{SO}_4 + 2p\text{H}), \quad (6)$$

where K_w is the dissociation constant of water and p means $-\log_{10}$. Equation (6) represents a line on a $(p\text{SO}_4 + 2p\text{H})$ versus $(p\text{Fe} + 3p\text{OH})$ diagram whose slope depends on the sulfate content in schwertmannite.

The solubility of schwertmannite may depend on x , the sulfate content in schwertmannite. Figure 4 shows pK_s against x . Taking account of the whole data, pK_s seems increase as x increases

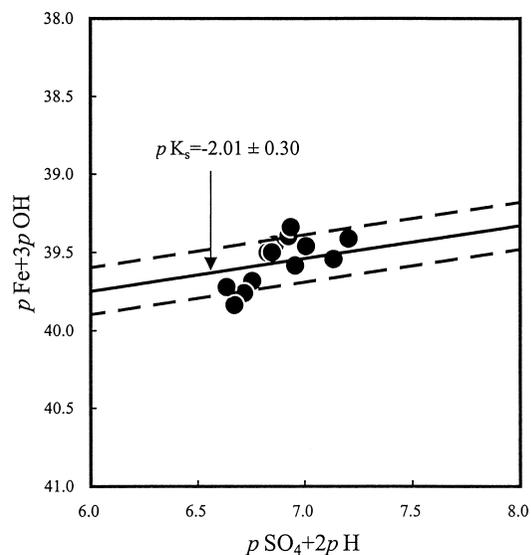
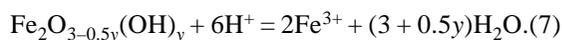


Fig. 5. Plot of $(p\text{Fe} + 3p\text{OH})$ versus $(p\text{SO}_4 + 2p\text{H})$ for the aqueous phases of the samples precipitating pure schwertmannite. The solid line represents the solubility line with $pK_s = -2.01$ and the broken lines represent the confidence limit defined by the ± 0.30 .

(solid line in Fig. 4). However, examining the data of FeCl_3 solution batch separately from those of $\text{Fe}(\text{NO}_3)_3$ solution batch (Table 1) reveals that pK_s may be independent of x (broken ellipses in Fig. 4). For the time being, it is difficult to clearly understand the relationship between pK_s and x with the given data. More data and through investigation on them is required for and the quantification of the relation. Figure 5 plots $(p\text{SO}_4 + 2p\text{H})$ versus $(p\text{Fe} + 3p\text{OH})$ of the samples precipitating pure schwertmannite. pK_s of schwertmannite, calculated with Eq. (6), is -2.01 ± 0.30 on 95% confidence level. The solid line in Fig. 5 represent the solubility lines defined by Eq. (6) when $pK_s = -2.01$ and $x = 0.42$. The broken lines show the confidence limit. The calculated value is fairly close to $pK_s = -2.68$ which is the value recalculated from pK_s given by Yu *et al.* (1999) for reaction (1) between 10 and 15°C.

The dissolution reaction of ferrihydrite may be expressed as



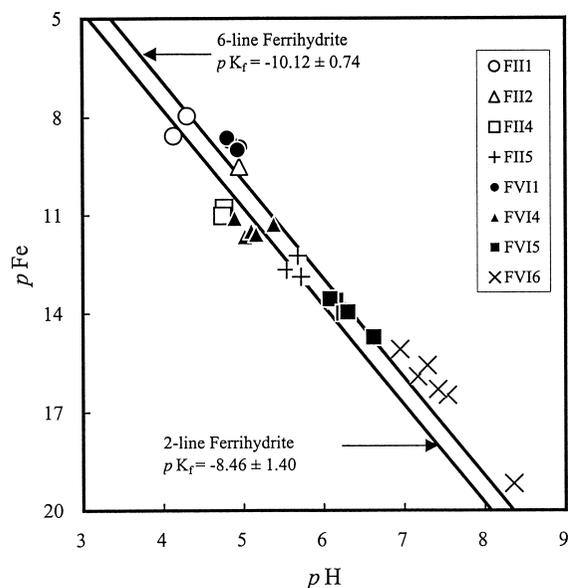


Fig. 6. Plot of $p\text{Fe}$ versus $p\text{H}$ for the aqueous solutions of the samples precipitating pure ferrihydrite. The solid lines are the solubility lines of 2- and 6-line ferrihydrite.

If the solubility product for reaction (7) is K_f ,

$$\log K_f = 2 \log a_{\text{Fe}^{3+}} - 6 \log a_{\text{H}^+} \quad (8)$$

or

$$p\text{Fe} = 3p\text{H} + \log K_f/2. \quad (9)$$

Equation (9) represents a line on a $p\text{Fe}$ - $p\text{H}$ diagram.

Figure 6 plots $p\text{Fe}$ versus $p\text{H}$ of the aqueous solutions in equilibrium with the precipitates of pure ferrihydrite. pK_f of 2- and 6-line ferrihydrite, calculated from these data with Eq. (9), were -8.46 ± 1.40 and -10.12 ± 0.74 , respectively. These values are within the range, 6 to 10, suggested by Nordstrom *et al.* (1990), but a little higher than the value estimated by Yu *et al.* (1999) based on the stability relation between schwertmannite and ferrihydrite. Yu *et al.* (1999) suggested $pK_f = -8.6 \pm 0.5$ for 6-line ferrihydrite. It may be worth noting that more poorly crystal-

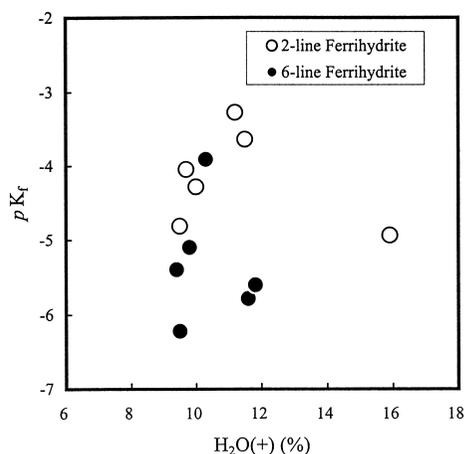
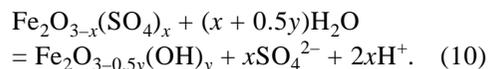


Fig. 7. The solubility versus the water content of ferrihydrite.

line 2-line ferrihydrite has a lower solubility than 6-line ferrihydrite of better crystallinity. We currently do not understand why the ferrihydrite having poorer crystallinity has lower solubility, and it may deserve further investigation. The solubility of ferrihydrite may depend on the content of $\text{H}_2\text{O}(+)$ or structural OH as well as crystallinity. Figure 7, however, shows that the solubility and water content does not have any correlation.

The stability boundary between schwertmannite and ferrihydrite can be expressed in terms of the equilibrium constant, K_r , of the following transformation reaction:



The relative stabilities between schwertmannite and ferrihydrite may be determined with the apparent solubility products as accurate as with true thermodynamic equilibrium constants. If this is the case, the stability boundary is given by the equation

$$p\text{SO}_4 = -2p\text{H} + \frac{pK_r}{x} = -2p\text{H} + \frac{pK_s - pK_f}{x}. \quad (11)$$

Figure 8 shows the stability boundaries of differ-

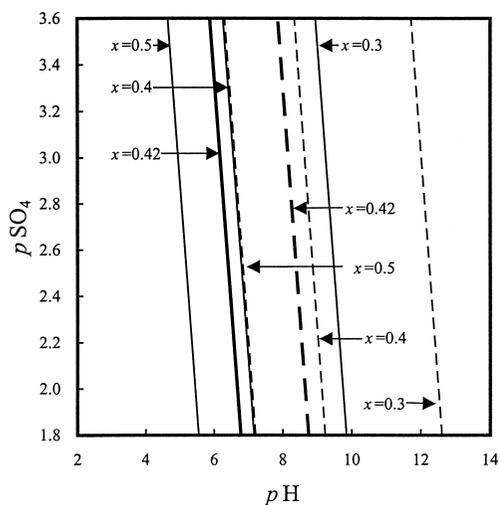


Fig. 8. Stability boundaries between schwertmannite and ferrihydrite at different x values. The solid and broken lines are for 2- and 6-line ferrihydrite, respectively.

ent x values on pH - pSO_4 diagram. The boundary between schwertmannite and 2-line ferrihydrite when $x = 0.42$ (thick solid line in Fig. 8) is pertinent to what we observe in nature. However, the natural ferrihydrite is mostly 6-line ferrihydrite. The boundary between schwertmannite and 6-line ferrihydrite when $x = 0.42$ (thick broken line in Fig. 8) is considerably biased to the higher pH than the boundary observed in nature. This may be due to determining the stability boundary with apparent solubility products, due to the solubility change of schwertmannite as a function of sulfate content, or due to other reasons that we have not recognized. If the solubility of schwertmannite increases as the chemical condition approaches to the stability boundary, the boundary can be shifted much to the lower pH than that predicted with constant solubility. It also requires further investigation.

SUMMARY

Synthesized schwertmannite and ferrihydrite have the chemical formula of $Fe_2O_{3-x}(SO_4)_x \cdot nH_2O$ ($0.41 \leq x \leq 0.49$, $1.51 \leq n \leq 2.81$) and

$Fe_2O_{3-0.5y}(OH)_y \cdot nH_2O$ ($0 \leq y \leq 1.96$, $0.82 \leq n \leq 1.14$). The aqueous solutions for schwertmannite and ferrihydrite synthesis reach steady states after 60 and 20 hours passed since the synthesis starts, respectively. The measured solubility of schwertmannite is in good agreement with the value reported by Yu *et al.* (1999), but that of ferrihydrite is a little higher than the value suggested by Yu *et al.* (1999). The solubility products for the dissolution reactions of schwertmannite, 2-line ferrihydrite, and 6-line ferrihydrite are $10^{2.01 \pm 0.30}$, $10^{8.46 \pm 1.40}$, and $10^{10.12 \pm 0.74}$, respectively.

The synthesis experiments of this study reveal a few important problems which should be solved to accurately estimate the solubilities of schwertmannite and ferrihydrite and understand the system including these minerals. The solubility of schwertmannite seems to be a function of sulfate contents, but we need more data to quantify the relation. The stability boundary between schwertmannite and ferrihydrite predicted with the above solubility products is in disagreement with that observed in natural system when the solubility of schwertmannite is assumed constant. The explanation of the disagreement may be possible only after the solubilities of schwertmannite and ferrihydrite are fully understood. The solubility of 2-line ferrihydrite is turned out to be lower than 6-line ferrihydrite of better crystallinity. In most cases, polymorphs of better crystallinity have lower solubilities. These problems may be of great importance in dealing with ferrihydrite systems in near surface environments and expected to be solved near future.

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REFERENCES

- Allison, J. D., Brown, D. S. and Novo-Gradac, K. J. (1991) MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual. EPA/600/3-91/021, EPA, Athens.
- Bigham, J. M., Schwertmann, U., Carlson, L. and Murad, E. (1990) A poorly crystallized oxyhydroxysulfate of iron formed by bacterial oxidation of Fe(II) in acid mine waters. *Geochim. Cosmochim. Acta* **54**, 2743–2758.
- Bigham, J. M., Carlson, L. and Murad, E. (1994) Schwertmannite, a new iron oxyhydroxysulfate from Physalmi, Finland and other localities. *Mineral. Mag.* **58**, 641–648.
- Bigham, J. M., Schwertmann, U., Traina, S. J., Winland, R. L. and Woolf, M. (1996) Schwertmannite and the chemical modeling of iron in acid sulfate waters. *Geochim. Cosmochim. Acta* **60**, 2111–2121.
- Chukrov, F. V., Zvyagin, B. B., Gorshkov, A. I., Yermilova, L. P. and Balashova, V. V. (1974) Ferrihydrite. *Int. Geol. Rev.* **10**, 1131–1143.
- Eggleton, R. A. and Fitzpatrick, R. W. (1988) New data and revised structural model for ferrihydrite. *Clays Clay Miner.* **36**, 111–124.
- Jambor, J. L. and Dutrizac, J. E. (1998) Occurrence and constitution of natural and synthetic ferrihydrite, a widespread iron oxyhydroxide. *Chem. Rev.* **98**, 2549–2585.
- Kim, J. (2001) Transformation of Synthetic Schwertmannite and Ferrihydrite to Goethite. M.S. Thesis, Kangwon National University, Chuncheon, 64 pp. (in Korean with English abstract).
- Margulis, E. V., Savchenko, L. A., Shokarev, M. M., Beisekeeva, L. I. and Vershinina, F. I. (1975) The amorphous basic sulphate $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot m\text{H}_2\text{O}$. *Russian J. Inorg. Chem.* **20**, 1045–1048.
- Martinez, C. E. and McBride, M. B. (1998) Coprecipitates of Cd, Cu, Pb and Zn in iron oxides: Solid phase transformation and metal solubility after aging and thermal treatment. *Clays Clay Miner.* **46**, 537–545.
- Nordstrom, D. K., Plummer, L. N., Langmuir, D., Busenberg, E., May, H. M., Jones, B. F. and Parkhurst, D. L. (1990) Revised chemical equilibrium data for major water-mineral reactions and their limitations. *Chemical Modeling in Aqueous System II* (Melchior, D. C. and Bassett, R. L., eds.), A.C.S. Symposium Series, 416, 398–413.
- Parkhurst, D. L. (1995) User's Guide to PHREEQC—A Computer Program for Speciation, Reaction-Path, Advective Transport, and Inverse Geochemical Calculations. USGS Water Res. Invest. Rep. 95-4227.
- Rose, S. and Ghazi, M. (1997) Release of sorbed sulfate from iron oxyhydroxides precipitated from acid mine drainage associated with coal mining. *Environ. Sci. Technol.* **31**, 2136–2140.
- Schwertmann, U. and Taylor, R. M. (1989) Iron oxides. *Minerals in Soil Environments*, 2nd ed., Chap. 8, 379–438, Soil. Sci. Soc. Amer.
- Stumm, W. and Morgan, J. J. (1996) *Aquatic Chemistry*. 3rd ed., Wiley, New York, 1022 pp.
- Todor, D. N. (1976) *Thermal Analysis of Minerals*. Abacus Press, Turnbridge Wells, 256 pp.
- Towe, K. M. and Bradley, W. F. (1967) Mineralogical constitution of colloidal hydrous ferric oxides. *J. Coll. Interface Sci.* **24**, 384–392.
- Wetzel, R. G. and Likens, G. E. (1991) *Limnological Analysis*. 2nd ed., Springer Verlag, 391 pp.
- Yu, J.-Y., Heo, B., Cho, J.-P. and Chang, H.-W. (1999) Apparent solubilities of schwertmannite and ferrihydrite in natural stream waters polluted by mine drainage. *Geochim. Cosmochim. Acta* **63**, 3407–3416.