Effect of schwertmannite ageing on Acid Rock Drainage geochemistry

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ABSTRACT

Schwertmannite is a common mineral formed from Acid Rock Drainage (ARD) and may become an efficient sink for some trace contaminants such as As. Is has been widely shown that schwertmannite is metastable and with time it recrystallizes into more stable phases. However, the influence of this transformation in the retention of trapped contaminants is a process insufficiently known.

In this study, the durability of natural schwertmannite precipitated in the acid discharge of the Monte Romero abandoned mine (SW Spain) and the related behaviour of associated trace contaminants was assessed in the field and in the laboratory. In both cases, the transformation with aging of schwertmannite into goethite plus jarosite was clearly observed by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

In the laboratory study, natural schwertmannite was kept in contact with its own acid water in a flask with a solid-liquid ratio 1:5 for 166 days. During this time, the pH of the solution dropped from 2.98 to 1.84 whereas the concentrations of SO_4, Fe and especially As, increased simultaneously to the transformation of the initial schwertmannite into goethite plus jarosite. However, the amount of As released to the solution is only a 0.06 % of the total As inventory in the solid phases.

INTRODUCTION

It is known that the water chemistry of Acid Rock Drainage (ARD) is controlled by several factors, such as mineralogy of the primary ores and enclosing rocks, weathering conditions and hydrological variability. Among these factors, precipitates newly formed from ARD may play a capital role in the removal of trace elements from solution (Bigham *et al*., 1994; Webster *et al*., 1998). To understand the chemistry of the water and to plan efficient remediation strategies, it is important to understand the mechanisms of removal of contaminants by the precipitates, and how the contaminants behave with the ageing of these solid phases.

Schwertmannite has been recognized in many localities as forming precipitates from ARD streams (Bigham *et al*., 1994, 1996; Yu *et al*., 1999), lakes receiving ARD (Schwertmann *et al*., 1995; Childs *et al*., 1998; Regenspurg *et al.,* 2004) or from wetlands receiving ARD (Gagliano *et al*., 2005). This mineral is a poorly crystalline oxyhydroxysulphate with an approximate formula of (Bigham *et al*., 1996) $Fe_8O_8(OH)_{8-2x}(SO_4)_x \cdot nH_2O$ ($1 \le x \le 1.75$) although higher SO_4^{-2} values ($1.75 \le x \le 1.86$) have also been described (Yu *et al*., 1999). The conditions more favorable for the formation of schwertmannite are acid waters with pH values between 2.8 and 4.5 and high sulfate concentrations (1000-3000 mg/l) (Bigham *et al*., 1994). The reaction proposed for schwertmannite to form is:

$$8Fe^{3+} + xSO_4^{2-} + (16-2x)H_2O = Fe_8O_8(OH)_{8-2x}(SO_4)_x(s) + (24-2x)H^+ \tag{1}$$

Among the different precipitates formed from AMD, schwermannite has been described as playing an important role in removal trace elements from water (Webster *et al*., 1994; Ball and Nordstrom; 1998). In particular, As concentration in water is described to drop from 200 to below 10 μg/L, in Nishinomaki mine, Japan (Fukushi *et al*., 2003) and in La Châtaigneraie district, France (Courtin-Nomade *et al*., 2005). In both cases schwermannite is the main solid phase to form.

Therefore, it appears that schwertmannite is an efficient sink for arsenic, which is attributed to its high reactive surface. However, schwertmannite is a metastable phase, and has been recognized to transform into goethite in weeks or months. Bigham *et al.* (1996) confirmed the metastable nature of schwertmannite in an aqueous equilibrium study in which a synthetic specimen of schwertmannite was placed in contact with distilled water and it was completely transformed to goethite over a period of 543 days, releasing SO_4, Fe and H^+ to the solution. The reaction proposed for the transformation is:

$$Fe_8O_8(OH)_{8-2x}(SO_4)_x(s) + 2xH_2O = FeOOH(s) + xSO_4^{2-} + 2xH^+ \tag{2}$$

Jönsson *et al.* (2005) found that the rate of the transformation was slower for high SO_4, low pH and low temperature. Gagliano *et al*. (2005) demonstrated the transformation from schwertmannite to goethite with the depth distribution of both minerals in a wetland. At the upper portion of the sediment column schwertmannite was predominant and so was goethite at the bottom. At middle portions of the column there was a transition zone, where the proportion of schwertmannite decreased as goethite increased with depth.

The question of how schwertmannnite recrystallisation into goethite affects to the trapped contaminants remains unclear. It is suggested that the more crystallized is a mineral (goethite compared to schwertmannite), the less it can include trace elements in its structure, especially anions (Houben, 2003). Therefore, the progressive transformation which can occur for the As-bearing poor crystalline Fe-oxyhydroxides into more crystalline Fe oxides leads to the release of significant amounts of As to the solution (Courtin-Nomade *et al.*, 2003). Schroth and Parnell (2005) studied this point only from the composition of precipitates (schwermannite and goethite) found in a waste pile from Alta mine, Montana, USA. No primary water in equilibrium with minerals was available. Differently from the previously mentioned authors, they concluded that recrystallisation into goethite did not significantly affect the amount of trace elements retained into schwermannite.

For schwermannite to be considered an efficient trace element sink, metals removed from solution by means of reaction (1) must be retained in the solid phase throughout reaction (2).

The main goals of this study on schwertmannite durability are to characterize the evolution of the natural precipitates found in the studied acid discharge from pure schwertmannite to other more stable mineral phases and also to ascertain the behaviour of trace metals, especially As, related to this transformation.

With the aim of clarifying this interesting issue, two types of studies were planned, field sampling of acid waters and characterization of its corresponding fresh and aged precipitates and a laboratory experiment consisting of aging monominerallic natural schwertmannite under controlled conditions.

For the field study, samples of waters, fresh and aged precipitates were taken and characterized in different sampling points in the Monte Romero AMD (Iberian Pyritic Belt, SW Spain) in order to link, if possible, the evolution of the acid mine waters to the aging of the precipitates. Schwertmannite durability was also assessed under controlled laboratory conditions by keeping a sample of fresh schwertmannite in contact with acid water taken at the same time and in the same field sampling point for 166 days and monitoring the evolution of the precipitate and its related waters in this closed system.

MATERIALS AND METHODS

Analytical techniques

The acidified water samples described in this paper were analyzed for Fe, Cu, Zn, Na, Al, Ca, Mg, and S by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and for As, Sr, Cd, Pb, Ni and Co by inductively coupled plasma atomic mass spectroscopy (ICP-MS).

A Crison meter and combined electrode with temperature compensation was used to measure pH and was calibrated regularly in the laboratory and in the field with standard 2, 4 and 7 buffer solutions. Eh was measured with the same meter using a Pt Eh combination electrode that was calibrated with standard buffer solutions. Measurements were corrected to standard hydrogen electrode. Electric Conductivity was performed by a Myron Ultrameter with a Pt cell calibrated with standard solutions.

Ferrous and total dissolved iron (following reduction with hydroxylamine hydrochloride) determinations were carried out by colorimetry using the ferrozine method (To *et al.* 1999) in a UV-VIS HP Spectrophotometer.

X-ray Diffraction (XRD) was used in an attempt to identify the mineralogy of minerals observed in each precipitate sample using Cu $K\alpha$ radiation. Powdered samples were run over a 2θ range from 0 to 60 degrees using a scan speed of 0.025º/18 s.

Select Au-Pd coated mineral samples were examined by Scanning Electron Microscopy to examine if changes in the mineralogy of precipitates were associated to major changes in the morphology of the mineral phases.

Field site and sampling description

All the samples of ochreous sediments and waters used in this study were collected in the acid discharge of the Monte Romero abandoned mine, SW Spain, (fig. 1). The site is placed in the Pyritic Belt, which is one of the main world reservoirs of sulfide minerals. The samples of precipitates were all collected in January 2004, but previous water sampling and characterization has been carried out in the discharge in several occasions.

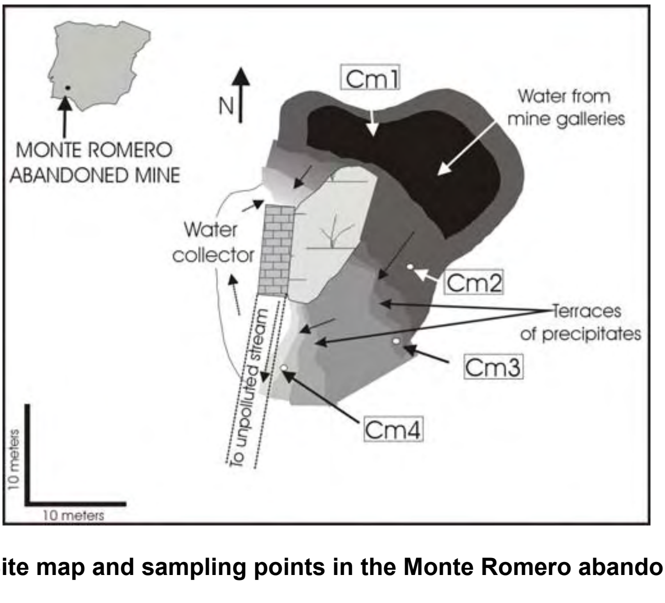

Figure 1: Site map and sampling points in the Monte Romero abandoned mine.

This acid discharge is represented by waters with pH values ranging from 2.6 to 3.3 depending on seasonal variations and actual sampling sites and exhibits high iron, sulphate and zinc concentrations (see table 1). Its main channel runs for less than 300 meters before joining an unpolluted stream. The discharge bed is covered with some centimeters of fresh and soft precipitates of ochreous sediments lying on thick layers of crusty and reddish material, creating three different levels of terraces.

Table 1: Major and trace elements concentrations in water sampled during three different sampling campaigns at the 4 sampling points marked in fig. 1.

Date	Sampling point	T	pH	Eh	EC	Cu	Zn	Na	Al	Ca	Mg	SO_4^{-2}	Fe	Fe(II)	As	Ni	Co	Cd	Pb
		(°C)		(mV)	(µS cm^{-1})	(mg l^{-1})								(%)	(µg l^{-1})				
February 2003	CM1	20.1	2.92	-	4698	17	495	19	147	212	237	3697	395	61	467	1044	764	792	84
	CM2	18	2.65	-	4713	18	504	19	147	214	238	3724	377	56	346	946	768	752	79
	CM3	16.2	3.03	-	4633	17	490	19	145	209	234	3642	363	53	265	744	734	714	91
	CM4	15.7	3.00	-	4604	17	495	19	145	209	234	3641	347	48	219	876	724	748	101
June 2003	CM1	23	3.24	535	4629	12	434	20	137	212	265	3784	368	80	152	790	840	88	24
	CM2	23	3.20	599	4540	12	435	20	137	208	265	3766	342	68	55	400	840	84	20
	CM3	23.8	2.82	689	4810	13	459	21	145	217	278	3958	263	63	22	260	900	87	26
	CM4	25.2	2.64	708	5084	13	473	21	150	227	288	4056	252	60	24	400	900	98	27
January 2004	CM1	19	3.27	581	3922	12	383	19	132	185	218	3095	291	77	562	838	605	787	96
	CM2	18.3	3.17	616	4045	13	398	19	135	192	228	3194	291	74	453	895	670	849	92
	CM3	15.9	3.07	637	3968	13	393	19	133	189	224	3143	274	64	348	815	582	779	92
	CM4	15.4	2.99	633	3946	12	386	19	131	186	221	3077	258	57	283	781	568	786	95

In each field sampling point shown in fig. 1, two water samples were taken and pH, Eh, temperature and electric conductivity was measured. One of the water samples was filtered at 0.45 µm and acidified with HNO_3 for major cations, sulfur and trace elements analysis and the other one was filtered at 0.1 µm and acidified with HCl, adjusting its pH to less than one for Fe(II)/Fe(III) determination. All the samples were preserved at 4^0C until analyses.

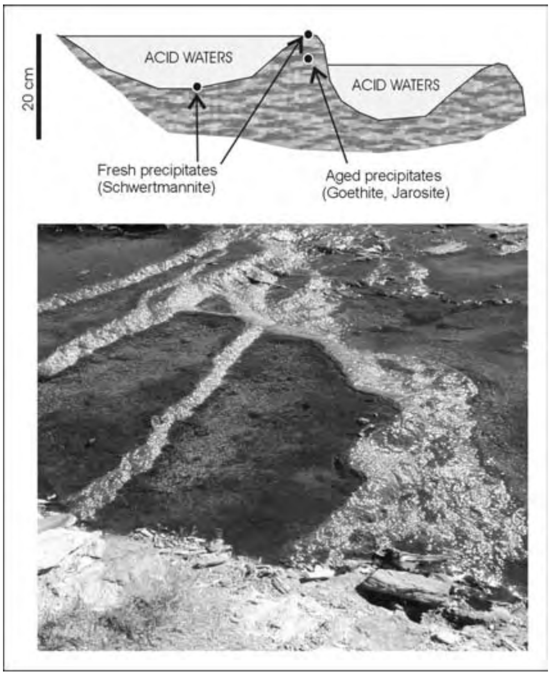

Figure 2: Typical view of one of the sampling points and position of the points for sampling precipitates in the terraces of the Monte Romero abandoned mine.

During the sampling carried out on January 2004, fresh and aged precipitates were taken for XRD and SEM characterization in different sampling points. Samples of 200 g (approx.) of fresh ochreous precipitates were also taken in polyethylene bottles in the sampling point CM3 together with 1L of the acid water in contact with them. The mixed precipitates-liquid samples were stored in the darkness at 4°C for some weeks until being used in the laboratory durability experiment. A typical view of one of the sampling points and the position in the terraces of the points for sampling precipitates is shown in fig. 2.

RESULTS AND DISCUSSION

Field study on schwertmannite formation and ageing

The analyses of the waters in the natural discharge of Monte Romero abandoned mine (table 1) in three different sampling campaigns, including the one in which precipitates were taken, show generally a decrease in pH together with a general decrease in the As concentrations from point 1 to 4, whereas the concentration of the rest of trace elements remains almost constant. This fact is probably due to the ability, described in many previous works, of precipitating schwertmannite to act as a sink for the As present in the coexisting waters.

Fresh and aged precipitates were taken and characterized in different sampling points in the field. All the fresh precipitates corresponded to monomineralic schwertmannite whereas, in the aged precipitates underneath, goethite or goethite plus jarosite were the sole phases detected by the XRD examination of powdered solid samples. It is worth noting the clear presence of both goethite and jarosite in the aged precipitate sampled in the same point as the fresh precipitated sample taken for the laboratory durability experiment. The morphology of the precipitates is also clearly different depending on whether they are fresh, in which the typical pin-cushion morphology of the aggregates can be observed, or aged precipitates, with much more planar crystals densely aggregated.

Laboratory durability study

In order to assess the durability of schwertmannite under controlled laboratory conditions, a sample of fresh schwertmannite sampled on January 2004 from point CM3, whose purity was proved by XRD, was kept in contact, in a solid:liquid ratio of 1:5, with acid water taken at the same time and in the same field sampling point at laboratory room temperature (25 ± 2°C), in contact with atmospheric oxygen and in the presence of light for 166 days.

This mixed sample was stirred on a regular basis and small volumes of water (8 ml) were taken every 6-20 days for analysis, pH and temperature determination. One precipitate sample was also taken every month, dried at room temperature and stored for XRD and SEM characterization. A summary of the general results in the waters and solid samples in the laboratory durability experiment is shown in table 2.

Table 2: Major and trace elements evolution in waters and corresponding mineralogy of precipitates, as deduced from XRD spectra, in the laboratory experiment on schwertmannite durability.

Time (d)	pH	Mineralogy precipitates	Fe	Cu	Zn	Na	Al	Ca	Mg	SO_4^{-2}	As	Ni	Co	Cd	Pb
			($mg\ l^{-1}$)								($\mu g\ l^{-1}$)				
0	2.98	Sch	1057	11	442	24	100	200	254	4668	21	1100	670	907	183
6	2.65		792	12	451	23	100	200	261	4542	*b.d.l.*	870	680	871	212
19	2.61		1385	9	446	24	54	203	266	5563	*b.d.l.*	680	660	918	182
26	2.71		2756	5	424	23	23	199	254	7514	*b.d.l.*	860	720	894	143
34	2.60	Sch, (Gt)	3494	4	440	24	11	211	270	9021	*b.d.l.*	990	740	897	107
47	2.56		3458	3	401	23	7	202	256	9239	*b.d.l.*	900	740	844	62
61	2.55		4187	3	388	23	13	203	254	10593	*b.d.l.*	1190	750	860	54
77	2.42	Sch, Gt, Jt	4744	3	370	23	36	206	259	11864	4	1080	690	868	48
93	2.39		5445	5	388	25	77	220	273	13955	14	900	700	941	32
112	2.27	Gt, Jt, (Sch)	5444	6	379	24	131	213	264	14964	148	890	750	911	26
128	2.17		5422	6	377	23	152	212	264	15752	442	870	740	795	12
149	2.00		5527	7	382	23	157	217	270	16765	738	870	790	928	15
166	1.84	Gt, Jt	5572	6	377	18	160	213	266	17184	791	850	720	870	17

b.d.l. : below etection limit. Sch: schwertmannite; Gt: Goethite; Jt: Jarosite

As can be observed in table 2, pH in the water dropped throughout the experiment from 2.98 to 1.84, whereas iron and sulphate concentrations increased from 1057 to 5572 mg l^{-1} and from 4668 to 17184 mg l^{-1}, respectively. The rest of major ions remained almost unchanged in the water during the experiment except Al, which increased from 100 to 160 mg l^{-1}, and Cu, which dropped from 11 to 6 mg l^{-1}. Trace elements present in the waters in detectable concentrations remained generally unchanged during the experiments except Pb, which dropped from 183 to 17 µg l^{-1} and especially As, which increased from 21 µg l^{-1} in the initial water to 791 µg l^{-1} at the end of the experiment.

The evolution of precipitates can be clearly observed in fig 3, in which the XRD spectra corresponding to successive precipitate samples have been ordered in time and put together. The presence of noticeable amounts of goethite is confirmed by XRD as early as 34 days after the beginning of the experiment. After 77 days of experiment, the presence of goethite and also jarosite is evident in the XRD spectrum, coincidently in time with the first water sample in which an As increase is detected. The XRD spectrum of the last sample, taken after only 166 days of experiment does not show any evidence of the presence of schwertmannite.

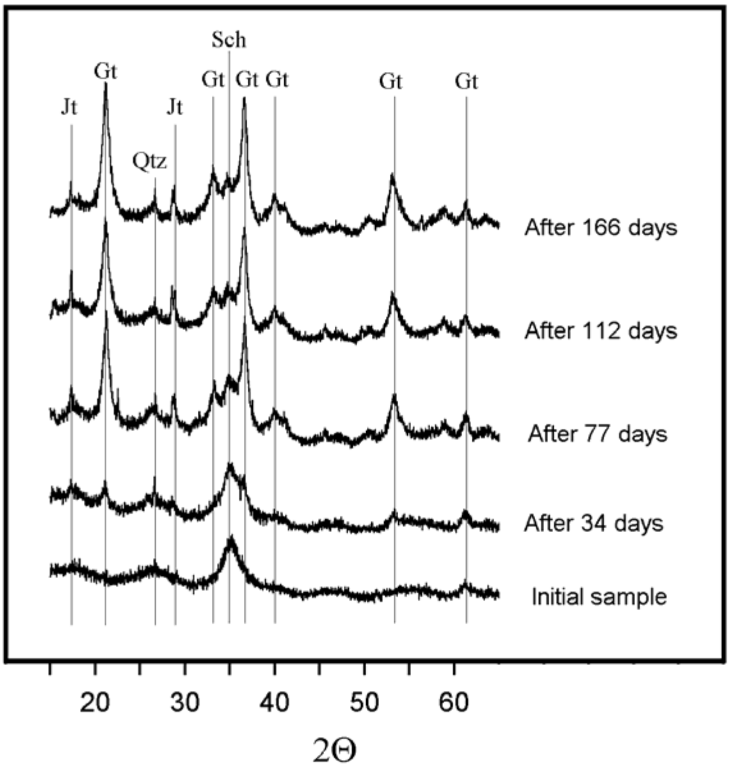

Figure 3: X-ray diffraction patterns for samples taken at different times during the evolution of the precipitates in the laboratory experiment on schwertmannite durability, showing a progressive change from pure schwertmannite (at the beginning of the experiment) to goethite plus jarosite (at the end).

This mineralogical change corresponds to a change in the morphology of the precipitates from the typical pin-cushion shape of schwertmannite precipitates to a morphology in which the sphericity of the aggregates is preserved but the individual crystals are less rounded and more planar (see fig. 4).

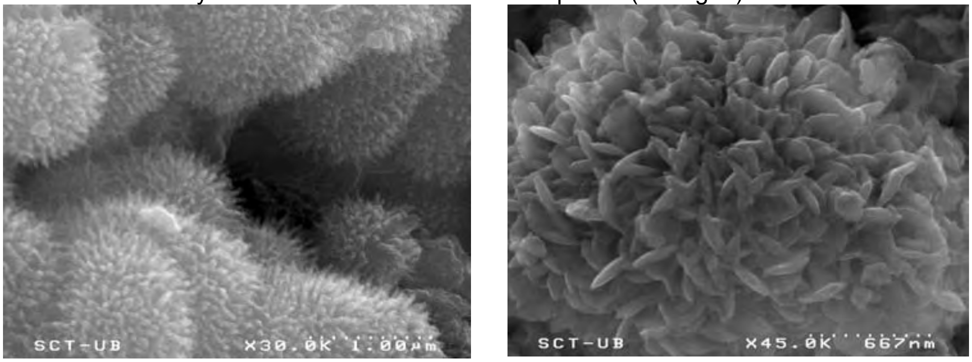

Figure 4: Scanning Electron Microscopy images of the precipitates at the beginning (left) and at the end (right) of the laboratory experiment on schwertmannite durability.

The chemical composition of the precipitates at the beginning of the laboratory durability experiment was determined by analyses of the leachates obtained in total acid digestion. From these results, the stoichiometry for the Monte Romero schwertmannite is deduced to $Fe_8O_8(OH)_{4.32}(SO_4)_{1.84}$, which is in very good agreement with the stoichiometry proposed by Yu *et al.* (1999). The amount of As associated to this initial solid sample is around 0.6% wt. of the total solid mass. A comparison between this amount and the concentration of As released to the solution during the laboratory durability experiment shows that only a 0.06 % of the As initially present in the fresh precipitate has been yielded to the acid water as a consequence of the schwertmannite ageing.

Putting together the information about the observed mineralogical change from schwertmannite to goethite plus jarosite and its related change in the pH, and in the Fe and SO_4^{-2} concentrations in the acid waters in contact with the precipitates, and taking into account the deduced stoichiometry for the Monte Romero schwertmannite, the general reaction that summarizes the process seems to be

$$\begin{gathered} Fe_8O_8(OH)_{4.32}(SO_4)_{1.84}(s)+2.55H_2O\rightarrow \\ \rightarrow 5.72FeOOH(s)+0.68Fe_3(SO_4)_2(OH)_5+0.54SO_4^{2-}+0.33Fe^{3+}+0.08H^{+} \end{gathered} \tag{3}$$

CONCLUSIONS

The durability of natural schwertmannite precipitated in the acid discharge of the Monte Romero abandoned mine (SW Spain) and the related behaviour of associated trace contaminants has been assessed in the field and in the laboratory.

In both cases, the transformation with aging of schwertmannite into goethite plus jarosite was clearly observed by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

In the laboratory study, it has been proved that the recrystallisation in closed system of natural schwertmannite into goethite plus jarosite produces a drop in the pH along with an increase in the SO_4, Fe and As concentrations in the coexistent aqueous solutions. On the contrary, other trace metals, such as Cu and Pb, seem to be much more efficiently incorporated into the newly-formed goethite or jarosite.

The general reaction deduced for the transformation of the schwertmannite used in this study into goethite plus jarosite seems to be

$$\begin{gathered} Fe_8O_8(OH)_{4.32}(SO_4)_{1.84}(s)+2.55H_2O\rightarrow \\ \rightarrow 5.72FeOOH(s)+0.68Fe_3(SO_4)_2(OH)_5+0.54SO_4^{2-}+0.33Fe^{3+}+0.08H^{+} \end{gathered}$$

Although the yield of As from the solid to the solution as a result of this transformation can be important for the geochemistry and potential toxicity of the of the acid waters, the amount of As released is negligible compared to the total inventory of this element in the solid phases.

REFERENCES

Ball, J.W. and Nordstrom, D.K. (1998). Final revised analyses of major and trace elements from acid mine waters in the Leviathan mine drainage basin. Water-resources investigations report: 89-4138, U. S. Geological Survey.

Bigham, J.M., Carlson, L. and Murad, E.(1994). Schwertmannite, a new iron oxyhydroxy-sulphate from Pyhäsalmi, Finland, and other localities. Mineralogical Magazine, 58 (393): 641-648.

Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L. and Wolf, M. (1996). Schwertmannite and the chemical modeling of iron in acid sulfate waters. Geochimica et Cosmochimica Acta, 60 (12): 2111-2121.

Childs, C.W., Inoue, K. and Mizota, C. (1998). Natural and anthropogenic schwertmannites from Towada-Hachimantai National Park, Honshu, Japan. Chemical Geology, 144 (1-2): 81-86

Courtin-Nomade, A., Bril, H., Neel, C. and Lenain, J.F. (2003). Arsenic in iron cements developed within tailings of a former metalliferous mine - Enguiales, Aveyron, France. Applied Geochemistry, 18 (3): 395-408.

Courtin-Nomade, A., Grosbois, C., Bril, H. and Roussel, C. (2005). Spatial variability of arsenic in some iron-rich deposits generated by acid mine drainage. Applied Geochemistry, 20 (2): 383-396.

Fukushi, K., Sasaki, M. and Sato, T. (2003). A natural attenuation of arsenic in drainage from an abandoned arsenic mine dump. Applied Geochemistry, 18 (8): 1267-1278.

Gagliano, W.B., Brill, M.R., Bigham, J.M., Jones, F.S. and Traina, S.J. (2005). Chemistry and mineralogy of ochreous sediments in a constructed mine drainage wetland. Geochimica et Cosmochimica Acta, 68(9): 2119-2128.

Houben, G. J. (2003). Iron incrustations in wells. Part 1: genesis, mineralogy and geochemistry. Applied Geochemistry, 18: 927-939.

Jönsson, J., Persson, P., Sjoberg, S. and Lovgren, L. (2005). Schwertmannite precipitated from acid mine drainage: phase transformation, sulphate release and surface properties. Applied Geochemistry, 20 (1): 179-191.

Regenspurg, S., Brand, A. and Pfeiffer, S. (2004). Formation and stability of schwertmannite in acidic mining lakes. Geochimica et Cosmochimica Acta, 68 (6): 1185-1197.

Schroth A.W. and Parnell R.A.Jr (2005) Trace metal retention through the schwermannite to goethite transformation as observed in a field setting, Alta Mine, MT. Applied Geochemistry, 20 (5): 907-917.

To T.B., Nordstrom D.K., Cunningham K.M., Ball J.W. and McCleskey R.B. (1999). New method for the direct determination of dissolved Fe(III) concentration in acid mine waters. Environmental Science and Technology,33. 807-813.

Schwertmann, U., Bigham, J.M., Murad, E. (1995). The 1st occurrence of schwertmannite in a natural stream environment. European Journal of Mineralogy, 7 (3): 547-552.

Webster, J.G., Nordstrom, D.K. and Smith, K.S. (1994). Environmental geochemistry of sulfide oxidation: transport and natural attenuation of Cu, Zn, As and Fe in the acid mine drainage of Leviathan and Bryant Creeks. In: D. Alpers and D.K. Nordstrom (Eds.). Environmental Geochemistry of Sulfide Oxidation, ACS Symposium Series, 550. pp. 244-260.

Webster, J.G., Swedlund, P.J. and Webster, K.S. (1998). Trace metal adsorption onto an acid mine drainage iron(III) oxy hydroxy sulfate. Environmental Science and Technology, 32 (10): 1361-1368.

Yu, J.Y., Heo, B., Choi, I.K., Cho, J.P. and Chang, H.W. (1999). Apparent solubilities of schwertmannite and ferrihydrite in natural stream waters polluted by mine drainage. Geochimica et Cosmochimica Acta, 63 (19-20): 3407-3416.