

UPDATING THERMODYNAMIC DATABASES TO INCLUDE  
SCHWERTMANNITE  $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4 \cdot n\text{H}_2\text{O}$

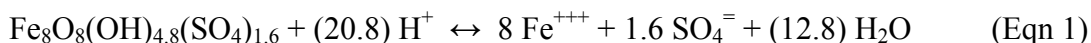
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Schwertmannite is a relatively recent addition to the lexicon of solid phases associated with acidic, sulfate-rich waters, in particular those associated with acid rock drainage (ARD) and acid mine drainage (AMD). It is now recognized as a key component to the ochreous formations in streams influenced by the oxidation of iron sulfide minerals (a.k.a, “yellow boy”). Earliest descriptions appear in (BIGHAM et al., 1994; BIGHAM et al., 1990). (BIGHAM and NORDSTROM, 2000) present a summary of literature as of 2000 and conclude that it is probably the “most common direct precipitate of Fe from acid sulfate waters in the range of pH 2 to 4” but that its “existence has been viewed with caution because it is poorly crystalline, is metastable and is commonly admixed with other nanophase Fe minerals”. Literature on this mineral continues to expand and is a testimony to its importance to the understanding of the formation of the most visible indication of the impact of mining on surface waters. The reference list here includes a sampling of the more relevant publications, but many more exist.

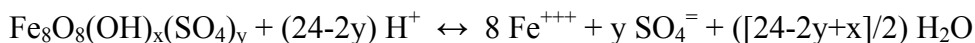
Unfortunately, some (perhaps most) of the more important thermodynamic databases associated with commonly-used geochemical modeling programs do not include schwertmannite. This is likely most true for older databases. The information needed to modify existing databases to include schwertmannite is presented here and discussed briefly. Most thermodynamic databases require either a  $\log K_{\text{equil}}$  constant or a Gibbs free energy of formation value ( $\Delta G^\circ_{f,298.15\text{K}}$ ).

BIGHAM et al., 1996b defines schwertmannite as  $\text{Fe}_8\text{O}_8(\text{OH})_x(\text{SO}_4)_y$  where  $8-x = y$  and  $1 \leq y \leq 1.75$ . The formula can be simplified to  $\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)$  for  $y = 1$ .

BIGHAM et al., 1996b initially proposed thermodynamic constants for schwertmannite based on solubility observations, and REGENSPURG et al., 2004 continues to cite those values, suggesting that nothing new has been introduced in the interim. A  $\log K_{\text{SP}} = +18.0 \pm 2.5$  was determined for  $\text{Fe}_8\text{O}_8(\text{OH})_{4.8}(\text{SO}_4)_{1.6}$  in the dissolution reaction:



Or, in terms of x and y:



This is equivalent to a  $\Delta G^\circ_{\text{rxn},298.15\text{K}} = -24.55 \pm 3.4 \text{ kcal}$  or  $-102.71 \pm 14.22 \text{ kJ}$ .

Using CODATA (WAGMAN et al., 1990) and USGS (ROBIE et al., 1979) data ( $\Delta G_{f298.15K}^{\circ} \text{Fe}^{+++} = -1.1 \text{ kcal}$ ,  $\Delta G_{f298.15K}^{\circ} \text{SO}_4^{--} = -177.97 \text{ kcal}$  and  $\Delta G_{f298.15K}^{\circ} \text{H}_2\text{O} = -56.687 \text{ kcal}$ ), the  $\Delta G_{f298.15K}^{\circ}$  Schwertmannite was calculated to be  $-994.59 \text{ kcal}$ .

Figure 1 was adapted from BIGHAM et al., 1996b (p. 2120, Fig. 10) and represents the stability (and meta-stability) field of schwertmannite relative to ferrihydrite, K-jarosite and goethite in Eh-pH space as described by BIGHAM et al. (op. cit)

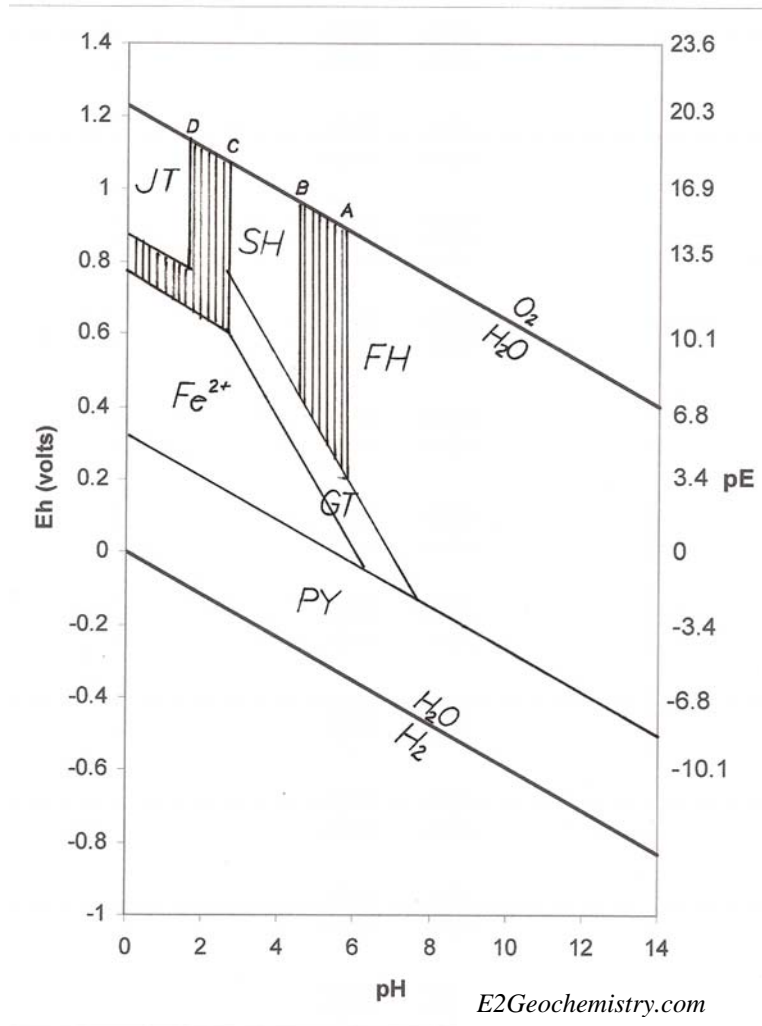


Fig. 1. Eh-pH diagram (after Bigham et al. 1996) showing the stability field of schwertmannite (SH) relative to ferrihydrite (FH), K-Jarosite (JT) and goethite (GT) for  $\log \Sigma \text{Fe} = -3.11$ ,  $\log \Sigma \text{SO}_4^{--} = -2.32$  and  $\log \Sigma \text{K}^+ = -3.78$ . SH stability is defined by  $K_{SP} = -18$  for Eqn 1. Vertical lines A and B represent the SH-FY boundary for ferrihydrite  $K_{SP}$  values of 5 and 4.5 (amorphous ( $pK = 37$ ) and crystalline ( $pK = 39$ )), respectively, as defined by  $\text{Fe}(\text{OH})_3 + 3\text{H}^+ = \text{Fe}^{+++} + 3 \text{H}_2\text{O}$ . The shaded area between A and B represents a field of SH metastability. Similarly C and D represent K-jarosite  $K_{SP}$  values of  $-12.51$  and  $-9.21$  for the reaction  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+ = \text{K}^+ + 2\text{SO}_4^{--} + 3\text{Fe}^{+++} + 6\text{H}_2\text{O}$

As a means of checking the accuracy of the database entry for schwertmannite, an attempt was made to reproduce the diagram of BIGHAM et al. (op. cit) as illustrated in Fig. 1. This effort was only partially successful but does confirm the accuracy of the schwertmannite entry as shown below for The Geochemist's Workbench. Using the following code in the Geochemist's Workbench thermodynamic database while suppressing K-jarosite, the A and B SH-FH boundaries in Fig. 1 could be reproduced. However, if the logK<sub>SP</sub> values for K-Jarosite suggested by Bigham et al. were used (i.e, -12.51 and -9.21) for the reaction



the resultant K-jarosite field obscured (was more stable than) the schwertmannite stability field. However, if log K<sub>SP</sub> values for more soluble, presumably less well-crystallized, K-jarosite (as tabulated by (BARON and PALMER, 1996) ) are used, a relatively small schwertmannite stability field emerges as shown in Fig. 2.

```
Schwertmannite          type= sulfate
formula= Fe8O8(OH)4.8(SO4)1.6
mole vol.= 153.200 cc   mole wt.= 810.108 g
4 species in reaction
 1.600 SO4--          8.000 Fe+++          12.800 H2O
-20.800 H+
 500.0000 18.0   500.0000 500.0000
 500.0000 500.0000 500.0000 500.0000
```

\* (see Bingham et al 1996b)

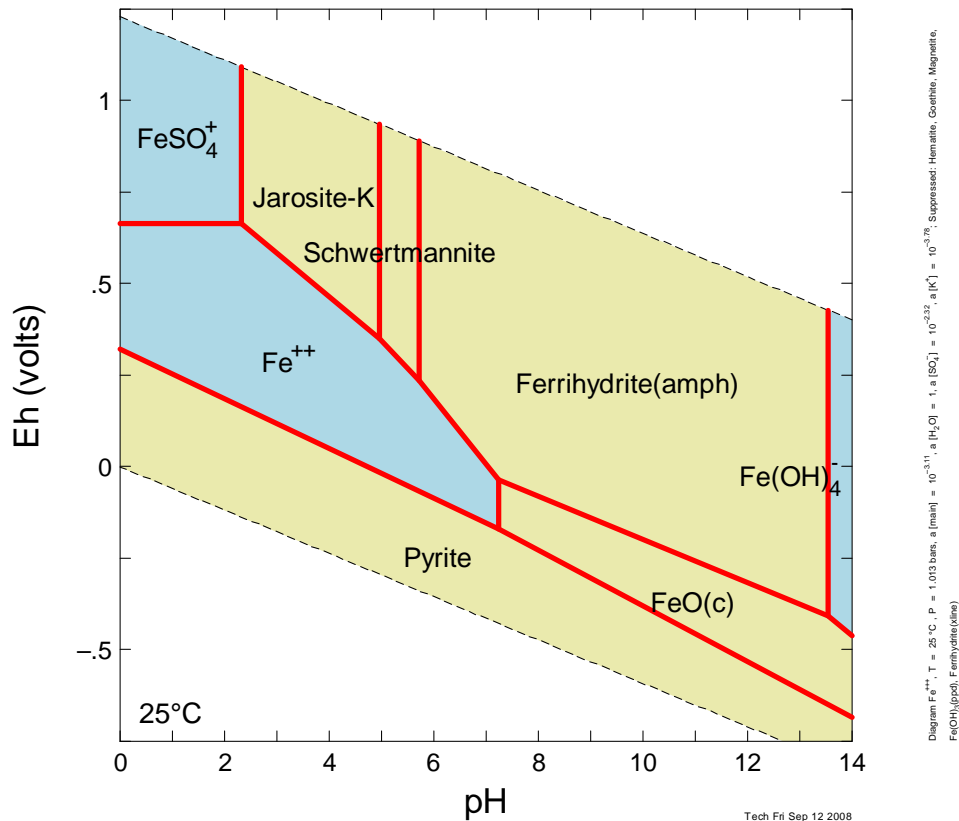
```
Ferrihydrite(amph)      type= hydroxide
formula= Fe(OH)3
mole vol.= 20.820 cc   mole wt.= 106.868 g
3 species in reaction
-3.000 H+             1.000 Fe+++          3.000 H2O
 500.0000  5.0   500.0000 500.0000
 500.0000 500.0000 500.0000 500.0000
```

\* represents pK = -37 as FeOH3 -> Fe+++ + 3OH-

```
Ferrihydrite(xline)    type= hydroxide
formula= Fe(OH)3
mole vol.= 20.820 cc   mole wt.= 106.868 g
3 species in reaction
-3.000 H+             1.000 Fe+++          3.000 H2O
 500.0000  4.5   500.0000 500.0000
 500.0000 500.0000 500.0000 500.0000
```

\* represents pK = -39 as FeOH3 -> Fe+++ + 3OH-

Note that the 500.0000 entries indicate no available data for temperatures other than 25°C.



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Fig. 2 Eh-pH diagram created for the same conditions as Fig. 1 using Th Geochemist's Workbench.  $\log K_{SP}$  for ferrihydrite(amph) = 5 (equivalent to line A in Fig. 1),  $\log K_{SP}$  for K-jarosite = -9.21

It is apparent from the literature that great care is required in applying modeling to the interpretation of precipitates from acid-sulfate waters. The effects of particle size, crystallinity and aging on the free energy of the various solids involved result in profound meta-stability and changes over time subsequent to initial precipitation.

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