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The solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$

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Abstract

Scorodite, $FeAsO_4 \cdot 2H_2O$, is an orthorhombic iron arsenate commonly associated with arsenic-bearing ore deposits as a weathering product. This study investigated the mode of formation and persistence of scorodite in nature, and suggests that its presence controls the arsenate levels in waters draining from oxidizing arsenic-rich ores. Solubility experiments give $K_{sp}\text{scor} = 10^{-21.7\pm0.5}$ and $\Delta G_f^\circ = -1263.52\pm0.28$ kJ mol^{-1}. Scorodite is metastable under most conditions and tends to dissolve incongruently, forming iron hydroxides and releasing arsenate to solution.

First-hand observations at the Brinton Arsenic Mine, Floyd County, VA, and observations by others at similar arsenopyrite deposits show a close spatial relationship between arsenopyrite and scorodite, suggesting that the reaction which forms scorodite is:

$$FeAsS(aspy) + 14Fe^{3+} + 10H_2O \rightarrow 14Fe^{2+} + SO_4^{2-} + FeAsO_4 \cdot 2H_2O(scor) + 16H^+ \quad (1)$$

This process is catalyzed by *Ferrooxidans* bacteria which oxidize Fe^{2+} to Fe^{3+}. The formation of scorodite involves the oxidation of arsenopyrite at low pH to give locally high arsenate and iron activities which lead to scorodite precipitation. After the arsenopyrite is consumed, scorodite dissolves incongruently to give goethite and aqueous arsenate. Scorodite has a stability field at pH values near 2 and arsenate activity greater than 0.01 molal. Analysis of the surface and ground waters at the Brinton Arsenic Mine site showed that scorodite seems to control maximum dissolved arsenate levels.

Introduction

Scorodite, orthorhombic $FeAsO_4 \cdot 2H_2O$, is isostructural with mansfieldite ($AlAsO_4 \cdot 2H_2O$), variscite ($AlPO_4 \cdot 2H_2O$), and strengite ($Fe^{3+}PO_4 \cdot 2H_2O$). Published chemical analyses of scorodite show little deviation from $FeAsO_4 \cdot 2H_2O$ (Foshag et al., 1930; Foshag, 1937; and Martens, 1924); however, in unusual geologic environments, intermediate compositions may form (Allen and Fahey, 1948; Yarosh, 1955; Shadlum and Nesterova, 1947). The formation of scorodite solid solutions is possible but their occurrence is limited by the unlikely coincidence of arsenic and phosphorus. Mansfieldite occurrence is unlikely because of the low activity of Al^{3+}in solution.

The low values of arsenic in waters draining from weathering sulfide/sulfarsenide deposits suggest that the buffering minerals have very low solubilities. Scorodite is a common weathering product of arsenic-bearing ore deposits (Boyle and Jonasson, 1973), and its persistence in nature suggests that its solubility may control the concentration of arsenate in natural waters. Scorodite is by far the most common natural arsenate; the only other common arsenates are annabergite, $Ni_3(AsO_4)_2 \cdot 8H_2O$ and erythrite, $Co_3(AsO_4)_2 \cdot 8H_2O$.

Figure 1 shows the Eh-pH relations of the As-H_2O system constructed from the thermodynamic data listed in the Appendix. The arsenate (As^{5+}) minerals predominate under oxidizing conditions found in the weathering environment. Arsenite (As^{3+}) minerals are much less common because of the narrower stability range of this oxidation state. Native arsenic and arsenide minerals form under the most reducing conditions in the H_2O stability field. The solubility product of scorodite determined by Chukhlantsev (1956) indicates that scorodite is stable only at geologically unreasonable iron and arsenate activities. The paragenesis of scorodite suggests that the solubility product determined by Chukhlantsev (1956) is too high.

Experimental design

Synthetic scorodite was prepared by mixing ferric chloride and sodium arsenate solutions (Dove, 1984). The resulting precipitate was aged 14 days in the mother liquor at 95–105°C and rinsed with distilled water to remove electrolytes and excess arsenate. The product was a light tan powder (1–7 μm diameter), showing a distinct X-ray diffraction pattern of scorodite with sharp peaks indicating good crystallinity.

Each solubility experiment consisted of three replicates. Thirty ml of distilled/deionized water was adjusted to initial pH values of 3.07, 5.57 or 10.38 with HCl or NaOH and combined with 1.0 g of the powdered synthetic scorodite. This mixture was placed in a 35 ml polyethylene bottle and incubated at 25±0.5°C for times up to 8 weeks before sampling. Sampled fluids were centrifuged at 800g for 20 minutes to remove any suspended solids prior to analysis for arsenic and iron. The pH of each sample was measured using an Orion model 811 pH meter.

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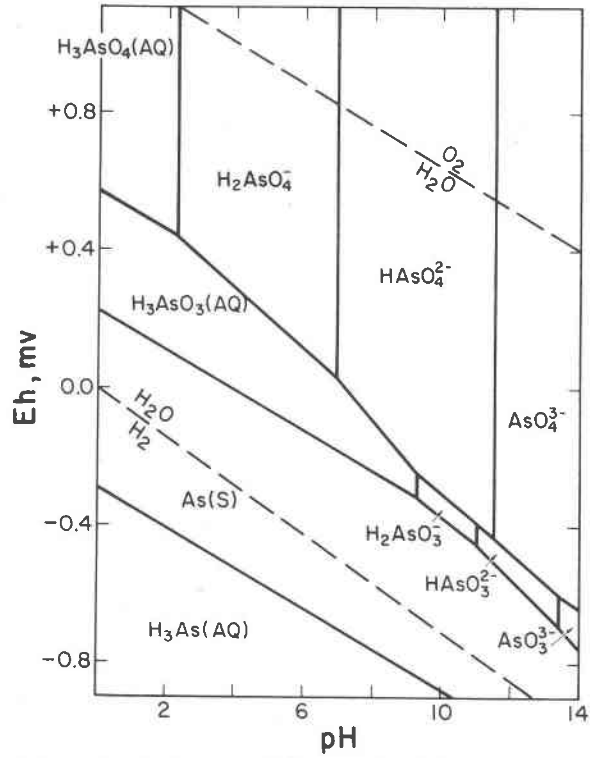

Fig. 1. Eh–pH diagram of the arsenic–H_2O system at $a_{As} = 10^{-3}$. Derived from the program SOLUPLOT (Bethke, 1978).

The arsenic analysis was modified from colorimetric procedures of Boltz and Mellon (1947), Kingsley and Schaffert (1951) and Haywood and Riley (1976). This procedure is based on the reaction of the arsenate ion with molybdate to form an arsenomolybdate blue complex. Details are given by Dove (1984). A linear relationship between absorbance at 840 nm and arsenate concentration was obtained when arsenic levels ranged between 0.10 μg and 2.0 μg per 1.0 ml of solution.

Iron analyses were done using both colorimetric (modified from Harvey et al. 1955; Wiersma and Rimstidt, 1984) and atomic absorption procedures. Details of this method which is based on the reaction of iron with 1,10 phenanthroline, are given in Dove (1984). Iron concentrations less than the colorimetric minimum sensitivity of 2.0 μg of iron per 1.0 ml were determined using a Perkin-Elmer 703 atomic absorption spectrophotometer.

Results

Only four of twenty experiments showed congruent dissolution of scorodite. In 16 of 20 experiments, scorodite dissolved incongruently (detailed data are given in Dove, 1984) by reaction (2):

$$FeAsO_4 \cdot 2H_2O + H_2O \rightleftharpoons H_2AsO_4^- + Fe(OH)_3(s) + H^+ \qquad (2)$$

These experiments showed one or more of the following effects: (1) Concentrations of total iron declined relative to total arsenic over the duration of the experiment. (2) Concentration changes were accompanied by systematic pH shifts. (3) Iron concentrations approached equilibrium with iron hydroxides. Figure 2 illustrates the difference between arsenic and iron concentration versus time for two groups of samples. Four samples that dissolved congruently had very small ($As_{total} - Fe_{total}$) differences that were random and on the order of $10^{-4.5}$ m. The remaining samples had much larger ($As_{total} - Fe_{total}$) values, resulting from a rapidly decreasing iron concentration accompanied by an increasing arsenic concentration. The samples that dissolved incongruently also showed a systematic pH change with time (Fig. 3). The pH shift over time for experiments with an initial pH of 10.4 can be best described by reactions (3) and (4). While the pH was greater than pK_2 of arsenate (6.86), reaction (3) was dominant and two hydrogen ions were released for each formula unit of scorodite dissolved. When the pH fell below 6.86, reaction (4) was predominant and one hydrogen ion was released per formula unit of scorodite dissolved.

$$FeAsO_4 \cdot 2H_2O + H_2O \rightleftharpoons HAsO_4^{2-} + Fe(OH)_3(s) + 2H^+ \quad (3)$$

$$FeAsO_4 \cdot 2H_2O + H_2O \rightleftharpoons H_2AsO_4^- + Fe(OH)_3(s) + H^+ \quad (4)$$

Incongruent reactions with an initial pH of 5.6 showed a small pH decrease over time (Fig. 3). This decrease can be explained by reaction (4) in which one hydrogen ion is released for each formula unit of scorodite dissolved. The pH shifts (Fig. 3) for the group of experiments with an initial pH of 3.1 are best described by reactions (5) and (4):

$$FeAsO_4 \cdot 2H_2O \rightleftharpoons H_2AsO_4^- + Fe(OH)^{2+} + OH^- \quad (5)$$

$$FeAsO_4 \cdot 2H_2O + H_2O \rightleftharpoons H_2AsO_4^- + Fe(OH)_3(s) + H^+ \quad (4)$$

Initially, congruent dissolution by reaction (5) was predominant causing a small pH increase with the release of one hydroxyl ion per formula unit of scorodite dissolved.

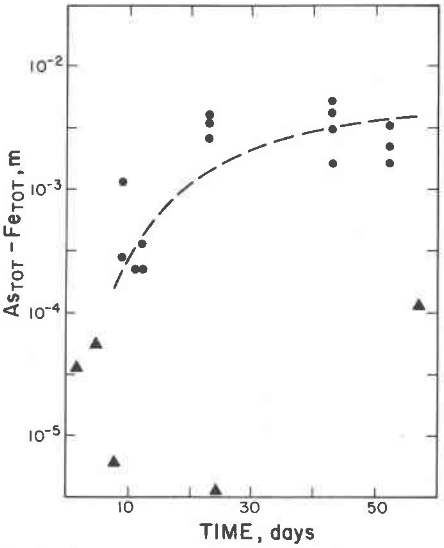

Fig. 2. Total arsenic concentration minus total iron concentration versus time for all experiments. Triangles denote experiments in which scorodite dissolved congruently. Dots represent experiments in which incongruent dissolution was predominant.

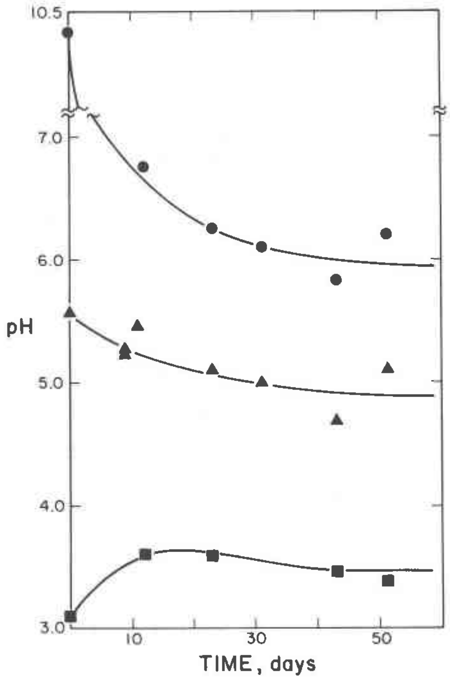

Fig. 3. pH versus time, showing the systematic pH change for experiments with three different initial pH conditions. Dots represent the high pH group, initial pH = 10.38; triangles represent the intermediate pH group, initial pH = 5.57; squares represent the low pH group, initial pH = 3.08. The reactions causing the systematic variations of pH with time are explained in the text. Data used in this diagram are from Dove (1984).

At approximately day 12, incongruent dissolution occurred by reaction (4). The release of one hydrogen ion per formula unit of scorodite dissolved again caused a decrease in pH.

Four experiments showed congruent dissolution. Their results were used to calculate the solubility product of scorodite. The solubility product defined by the congruent dissolution of scorodite is

$$FeAsO_4 \cdot 2H_2O(scor) \rightleftharpoons Fe^{3+} + AsO_4^{3-} + 2H_2O \qquad (6)$$

$$K_s = (a_{Fe^{3+}})(a_{AsO_4{}^{3-}}) \qquad (7)$$

The activity of Fe^{3+} was calculated using the equation

$$a_{Fe^{3+}} = \frac{Fe_{total}}{1 + \frac{K_1}{a_{H^+}} + \frac{K_1K_2}{(a_{H^+})^2} + \frac{K_1K_2K_3}{(a_{H^+})^3} + \frac{K_1K_2K_3K_4}{(a_{H^+})^4}} \qquad (8)$$

where $a_{H^+} = 10^{-pH}$ of the solution; Fe_{total} = concentration of iron in solution (molal); and K_1, K_2, etc. = hydrolysis constants of ferric iron species given in Table 1. Similarly, the activity of AsO_4^{3-} was calculated for total arsenic data as

$$a_{AsO_4{}^{3-}} = \frac{As_{total}}{1 + \frac{a_{H^+}}{K_3} + \frac{(a_{H^+})^2}{K_2K_3} + \frac{(a_{H^+})^3}{K_1K_2K_3}} \qquad (9)$$

Table 1. Hydrolysis constants of arsenate (Wagman et al., 1982) and ferric iron (Baes and Mesmer, 1976, p. 489) used to calculate the K_{sp} of scorodite.

	pK
Arsenate	
$H_3AsO_4 = H_2AsO_4^- + H^+$	2.24
$H_2AsO_4^- = HAsO_4^{2-} + H^+$	6.86
$HAsO_4^{2-} = AsO_4^{3-} + H^+$	11.49
Ferric iron	
$Fe^{3+} + H_2O = Fe(OH)_2^{2+} + H^+$	2.19
$Fe(OH)_2^{2+} + H_2O = Fe(OH)_2^+ + H^+$	3.48
$Fe(OH)_2^+ + H_2O = Fe(OH)_3 + H^+$	6.33
$Fe(OH)_3 + H_2O = Fe(OH)_4^- + H^+$	9.6

where $a_{H^+} = 10^{-pH}$ of the solution; As_{total} = arsenic concentration in solution (molal); and K_1, K_2, etc. = hydrolysis constants of arsenate species given in Table 1. Activity coefficients were rounded to 1.0 because calculated ionic strengths were always less than 10^{-4}.

The solubility product calculated for scorodite ($10^{-21.7 \pm 0.5}$ at 25°C) is approximately 1.5 log units lower than the K_{sp} reported by Chukhlantsev (1956). Based on this K_{sp} and the free energies given in the Appendix, the ΔG_f° of scorodite is -1263.52 ± 0.28 kJ mol^{-1}.

The higher solubility product reported by Chukhlantsev (1956) is probably due to grain size effects. The effect of grain size on solubility measurements is given by Enustun and Turkevich (1960).

$$\ln (C_r/C_{eq}) = [(2/3)\sigma V\alpha]/[2.303\nu RT(2r)] \qquad (10)$$

where C_r = apparent solubility at a given radius r (m); C_{eq} = bulk solubility; σ = surface free energy (mJ m^{-2}) from equation (12); V = molar volume of scorodite (6.99×10^{-5} m^3 mol^{-1} calculated from cell dimensions given in Kitahama et al.; 1975); α = geometric factor (6.0 for spheres was used here); $\nu = 2$ (ions contributed to solution per formula unit of scorodite dissolved); $R = 8.314$ J mol^{-1} K^{-1} and T = temperature (K). The surface free energy of scorodite was estimated using a relationship developed by Sohnel (1982).

$$\sigma = -17.8 \log C_{eq} + 34.8 \qquad (11)$$

Table 2. Results of experiments showing congruent dissolution used to calculate solubility product of scorodite. From these data, ΔG_f° scorodite = -1263.52 ± 0.28 kJ mol^{-1}.

TIME ELAPSED DAYS	INITIAL pH	FINAL pH	TOTAL pAs,m	TOTAL pFe,m	SCOR pKsp
5	5.57	5.97	4.15	4.84	21.88
8	5.57	6.36	4.27	4.32	21.71
25	5.57	6.23	4.61	4.50	22.14
57	5.57	5.53	3.86	4.69	21.32
		Average			21.7±0.5

where σ = surface free energy (mJ m^{-2}) and C_{eq} = bulk solubility (molal). The scorodite solubility determined in this study (2×10^{-5} m) was used for C_{eq} in equation (12) to give $\sigma = 118$ mJ m^{-2}. Figure 4 shows the solubility of scorodite as a function of grain size at 25°C. Grain size affects solubility only when the grain diameter is less than about 2.0 μm. The material used in this study had diameters of 1.0–7.0 μm, and thus the measured solubility product is very close to that of the bulk solid. Synthetic scorodite prepared by the procedure of Chukhlantsev (1956) contained much smaller grains with many below the measurable limit of 0.5 μ.

Scorodite occurrence

The Brinton Arsenic Mine site (Dietrich, 1959) in Floyd County, Virginia, provided a site to observe the formation and breakdown of natural scorodite. The mine site consists mainly of two waste piles, one of roasted ore and the other of arsenopyrite-bearing, quartz sericite schist. The coarse sandy soils of the mine site contain up to 42,000 ppm total arsenic (Rocovich and West, 1975); microscopic examination of dump samples showed arsenopyrite to be the most abundant ore mineral with chalcopyrite present in small amounts (Craig, pers. comm.).

The presence of scorodite in the mine waste was confirmed by X-ray diffraction. Scorodite occurs as thin yellow-green, botryoidal layers on the surface of arsenopyrite-bearing rocks.

Several water samples were collected from the mine area on September 19, 1983, near the end of a dry summer. During collection, pH was measured in the field using a Beckman portable meter (model H5). The samples were collected in polyethylene bottles that had been leached in 10% nitric acid. Samples were protected from direct sunlight during transport. Within a few hours of collection the samples were filtered and acidified with 2% nitric acid to give a pH of less than 2.0. Total arsenic and iron were determined by atomic absorption. The results are given in Table 3.

Table 3. Field data and calculated solubility quotient, Q, from waters collected at Brinton Arsenic Mine, Floyd County, VA.

SITE	pH	TOTAL pAs,m	TOTAL pFe,m	pQ
1. About 100m upstream from mine site in small perennial stream.	5.80	6.57	6.05	25.45
2. Shallow spring near mine entrance.	5.50	5.06	5.39	23.21
3. Seep at base of waste pile.	4.20	3.95	5.90	22.61
4. About 5 m downstream from mine site in same perennial stream as site 1.	4.72	4.83	5.84	23.39

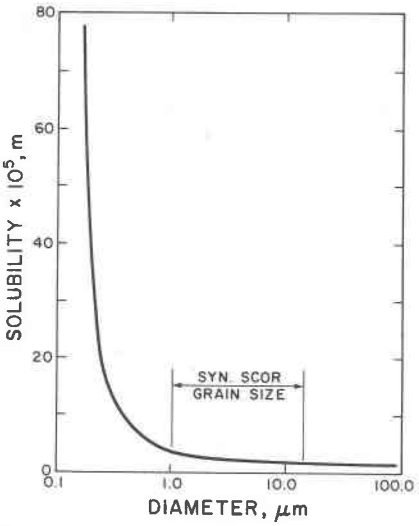

Fig. 4. Scorodite solubility as a function of grain diameter, as calculated from equation (10).

From the measured pH, total arsenic and total iron data, a solubility quotient, Q, was calculated for each sample site using

$$Q = (a_{Fe^{3+}})(a_{AsO_4^{3-}}) \quad (12)$$

The value of Q for each sample location is given in Table 3. The calculated Q value from site 1 showed the stream water entering the area to be undersaturated with respect to scorodite by approximately four orders of magnitude. This is reasonable as this water is upstream from the high arsenic environment. Sites 2, 3 and 4 were unsaturated with respect to scorodite by approximately 1 to 1.5 orders of magnitude. The observed undersaturation is probably the result of: (1) dilution by streamwater, surface and groundwater; (2) slow equilibration rates of the waters with scorodite. It is important to note that none of the sample locations have Q values exceeding the scorodite solubility product. This suggests that scorodite controls the maximum arsenate levels in solution.

The formation of scorodite at the Brinton Arsenic Mine involves the oxidation of arsenopyrite to give locally low pH and high arsenate and iron activities. After the arsenopyrite has been depleted, iron and arsenate concentrations decline and/or the pH increases. This allows scorodite to dissolve incongruently, precipitating goethite and releasing aqueous arsenate.

$$\text{ASPY} \rightarrow \text{SCOR} \rightarrow \text{GOE} + \text{Arsenate(aq)} \quad (13)$$

It is likely that arsenopyrite is oxidized by ferric iron (in a manner analogous to pyrite oxidation in mine wastes (Wiersma and Rimstidt, 1984)) to give ferrous iron, arsenate, sulfate and a large quantity of hydrogen ion.

$$\text{FeAsS(aspy)} + 13Fe^{3+} + 8H_2O \rightarrow$$
$$14Fe^{2+} + SO_4^{2-} + H_3AsO_4 + 13H^+ \quad (14)$$

The ferric iron is regenerated by *Ferrooxidans* bacteria which oxidize ferrous iron using O_2.

$$Fe^{2+} + 1/4O_2 + H^+ \xrightarrow{\text{bugs}} Fe^{3+} + 1/2H_2O \quad (15)$$

Ehrlich (1964) showed that these bacteria persist in high arsenic environments and catalyze arsenopyrite oxidation. The iron is thus recycled to react with more arsenopyrite according to equation (15). Scorodite precipitates quickly from the acidic, highly concentrated solutions of Fe^{3+} and AsO_4^{3-}:

$$Fe^{3+} + H_3AsO_4 + 2H_2O \rightleftharpoons FeAsO_4 \cdot 2H_2O(scor) + 3H^+ \qquad (16)$$

Figure 5 shows that scorodite has a stable field at pH values near 2.0 when $a_{Fe^{3+}} = 10^{-3}$ and $a_{AsO_4^{3-}}$ is greater than 0.1. When the rate of arsenopyrite oxidation declines, the pH increases and the arsenate activity may increase as the scorodite breaks down to goethite and aqueous arsenate:

$$FeAsO_4 \cdot 2H_2O(scor) \rightarrow FeOOH(goe) + H_2AsO_4^-(aq) + H^+ \qquad (17)$$

Thus, the final products of arsenopyrite weathering are goethite and arsenate (aq).

A listing of selected scorodite occurrences is given by Dove (1984). At most localities, scorodite is associated with the oxidation of arsenopyrite-bearing sulfide deposits. Scorodite has also been reported associated with geothermal systems and in a pegmatite. In most of these cases, scorodite has formed under conditions of low pH and high activities of iron and arsenic. Emmon's (1917) report that scorodite eventually alters to goethite is consistent with scorodite stability as predicted from the experiments reported here.

Conclusions

Scorodite is metastable under most conditions and tends to break down to form iron hydroxides and aqueous arsenate. In many of our experiments, nucleation of iron hydroxide caused iron concentrations to decline to levels that approach equilibrium with amorphous $Fe(OH)_3$, while the arsenate concentrations increased. This produced arsenic concentrations that were as much as 10^3 times greater than iron concentrations. In only four cases did iron hydroxides fail to nucleate and scorodite dissolved congruently. The results of these experiments were used to calculate K_{sp} scorodite and ΔG_f° (Table 2). Figure 5 shows the Eh–pH stability field of scorodite when iron activity is 10^{-3} and arsenate activity is 1.0 and 0.1. Scorodite is not stable for arsenate activities less than 0.01; thus it persists only metastably at lower arsenate concentrations. Figure 6 illustrates scorodite and goethite solubilities as a function of pH; scorodite is stable only when pH is less than 1.5 or arsenate concentrations are greater than 0.01 molal.

Although scorodite is metastable under most conditions, it does form in areas where arsenopyrite is oxidizing rapidly. The close spatial relationship between these minerals in natural occurrences suggests that the reaction forming scorodite is:

$$FeAsS(aspy) + 14Fe^{3+} + 10H_2O \rightarrow 14Fe^{2+} + SO_4^{2-} + FeAsO_4 \cdot 2H_2O(scor) + 16H^+ \qquad (18)$$

The process is catalyzed by *Ferrooxidans* bacteria which oxidize Fe^{2+} to Fe^{3+}. Scorodite is stable during this oxidation process because arsenate activities are high and the pH is low. After arsenopyrite oxidation ceases, arsenate activities decline and pH increases, causing scorodite to

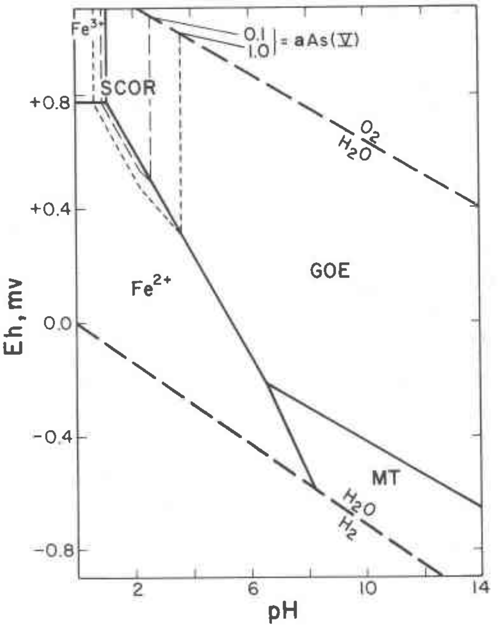

Fig. 5. Eh–pH relations for the Fe–H_2O system at $a_{Fe} = 10^{-3}$ (solid lines). The arsenate–H_2O system is superimposed on this diagram. Scorodite is stable when arsenate activities are greater than or equal to $10^{-1.29}$.

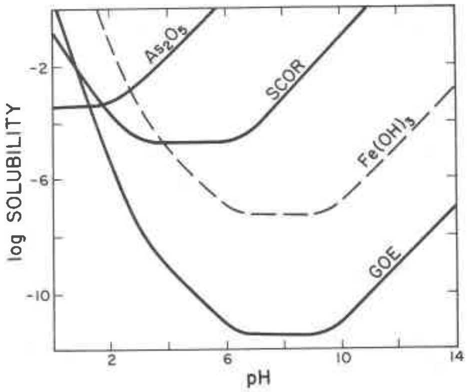

Fig. 6. Logarithm of solubility versus pH for As_2O_5, scorodite, amorphous $Fe(OH)_3$ and goethite. The goethite and $Fe(OH)_3$ curves were derived from data given in Stumm and Morgan (1981, p. 780). The As_2O_5 curve was derived from data given by Naumov (1974). The scorodite curve was derived from the K_{sp} determined in this study.

dissolve incongruently, to iron hydroxide and arsenate ion solutions. Such a process was also observed in this laboratory study.

Measurements of the pH, m_{Fe} and m_{As} of surface and ground waters at the Brinton Arsenic Mine site showed that scorodite solubility probably sets an upper limit for dissolved arsenate levels in the ground and surface waters.

Acknowledgments

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Appendix
Critically Evaluated Arsenic Thermodynamic Data

	$\Delta H_f°$ kJmol^{-1}	$\Delta G_f°$ kJmol^{-1}	S° Jmol^{-1} K^{-1}	Ref.
As(s)	0.0	0.0	35.69 ±0.84	(1)
AsO^{*}(aq)		-163.80		(2)
As_2O_3(arsn)	-656.97 ±1.67	-575.96 ±1.88	107.41 ±0.13	(1)
As_2O_3(cld)	-654.79 ±1.71	-575.55 ±1.05	113.33 ±0.13	(1)
AsO_3^{3-}(aq)	-663.71	-447.69	-186.61	(3)
AsO_4^{3-}(aq)	-888.14	-648.52	-162.76	(2)
$HAsO_3^{2-}$(aq)	-689.10 ±12.55	-524.25 ±20.92	-15.06	(3)
$HAsO_4^{2-}$(aq)	-906.34	-714.11	-1.67	(2)
$H_2AsO_3^{-}$(aq)	-714.79	-587.22	110.26	(2)
$H_2AsO_4^{-}$(aq)	-909.56	-753.29	117.15	(2)
H_3AsO_3(aq)	-742.24	-639.90		(2)
H_3AsO_4(aq)	-902.49	-766.09	184.10	(2)
H_3As(aq)	49.37	90.55	92.80	(4)[1]
H_3As(v)	66.44	68.91	222.76	(2)
AsS(real)	-37.94	-35.76	59.88	(5)[2]
As_2S_3(orp)	-96.08	-95.29	161.49	(6)[3]
$Pb_3(AsO_4)_2$(s)		-3482.34		(3)
$AlAsO_4 \cdot 2H_2O$(mans)		-1708.75		(3)
$Zn_3(AsO_4)_2 \cdot 5H_2O$(legr)		-2611.23		(3)
$Cu_3(AsO_4) \cdot 6H_2O$(s)		-2731.73		(3)
$Ni_3(AsO_4)_2 \cdot 8H_2O$(anna)		-3482.34		(3)
$Co_3(AsO_4) \cdot 8H_2O$(ery)		-3530.46		(3)
$FeAsO_4 \cdot 2H_2O$(scor)		-1263.52		(7)
FeAsS(aspy)	-111.75	-125.70	113.96	(6)[4]
$FeAs_2$(loel)	-46.44	-66.68	138.16	(6)
$Mn_3(AsO_4)_2 \cdot 8H_2O$(s)		-4055.13		(3)
$Ca_2(AsO_4)_2 \cdot 4H_2O$(s)		-4018.73		(3)

References: (1) Robie et al. (1978); (2) Wagman et al. (1982); (3) Naumov et al. (1974); (4) Barton (1969); (5) Barton and Skinner (1979); (6) Barton (1979); (7) Dove (1984) This study.

Footnotes: [1] Tabulated values obtained from Barton (1969) and Wilhelm et al. (1977) for the reaction $H_3As(v) = H_3As(aq)$. Consistent with Wagman et al., 1982. [2] Agrees with Barton (1969). These values selected because they are internally consistent with observed phase equilibria. Values of Robie et al. (1978) and Wagman et al. (1982) are approximately twice these and were determined calorimetrically. [3] Agrees with Barton (1969). These values selected because they are internally consistent with observed phase equilibria values of Robie et al. (1978) and Wagman et al. (1982) are approximately twice these and were determined calorimetrically. [4] Consistent with Barton (1969).