

Solubility products of amorphous ferric arsenate and crystalline scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) and their application to arsenic behavior in buried mine tailings

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Abstract

Published solubility data for amorphous ferric arsenate and scorodite have been reevaluated using the geochemical code PHREEQC with a modified thermodynamic database for the arsenic species. Solubility product calculations have emphasized measurements obtained under conditions of congruent dissolution of ferric arsenate ($\text{pH} < 3$), and have taken into account ion activity coefficients, and ferric hydroxide, ferric sulfate, and ferric arsenate complexes which have association constants of 10^{404} ($\text{FeH}_2\text{AsO}_4^{2+}$), 10^{986} (FeHAsO_4^+), and 10^{189} (FeAsO_4). Derived solubility products of amorphous ferric arsenate and crystalline scorodite (as $\log K_{sp}$) are -23.0 ± 0.3 and -25.83 ± 0.07 , respectively, at 25 °C and 1 bar pressure. In an application of the solubility results, acid raffinate solutions (molar $\text{Fe}/\text{As} = 3.6$) from the JEB uranium mill at McClean Lake in northern Saskatchewan were neutralized with lime to pH 2–8. Poorly crystalline scorodite precipitated below pH 3, removing perhaps 98% of the As(V) from solution, with ferric oxyhydroxide (FO) phases precipitated starting between pH 2 and 3. Between pH 2.18 and 7.37, the apparent $\log A_p^\wedge$ of ferric arsenate decreased from -22.80 to -24.67 , while that of FO (as Fe(OH)_3) increased from -39.49 to -33.5 . Adsorption of As(V) by FO can also explain the decrease, in the small amounts of As(V)(aq) that remain in solution above pH 2–3. The same general As(V) behavior is observed in the pore waters of neutralized tailings buried for 5 yr at depths of up to 32 m in the JEB tailings management facility (TMF), where arsenic in the pore water decreases to 1–2 mg/L with increasing age and depth. In the TMF, average apparent $\log K_{IV}$ values for ferric arsenate and ferric hydroxide are -25.74 ± 0.88 and -37.03 ± 0.58 , respectively. In the laboratory tests and in the TMF, the increasing crystallinity of scorodite and the amorphous character of the coexisting FO phase increases the stability field of scorodite relative to that of the FO to near-neutral pH values. The kinetic inability of amorphous FO to crystallize probably results from the presence of high concentrations of sulfate and arsenate.

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1. Introduction

Scorodite is the least soluble arsenate phase in many mine tailings systems, and as such understanding and controlling its solubility is of special relevance in efforts to limit arsenic releases to tailings pore waters and to the environment. Published solubility products for amorphous and crystalline scorodite have generally been computed from

solubility measurements without properly taking into account the chemical composition and thermodynamic properties of the solutions at equilibrium. Also, the solubility of both crystalline and amorphous scorodite has usually been measured in solutions where equilibrium was approached from undersaturation only.

Published solubility data for amorphous ferric arsenate (AFA) to crystalline scorodite (scorodite(cr)) measured in starting solutions without dissolved Fe or As, are plotted versus pH in Fig. 1. The solubility data of Chukhlantsev (1956), Makhmetov et al. (1981), Dove and Rimstidt

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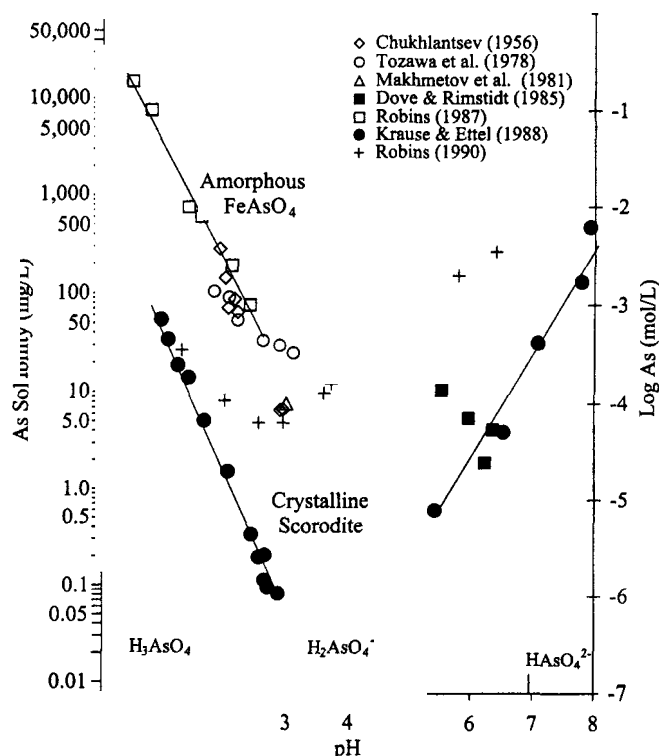


Fig. 1. Solubility of amorphous ferric arsenate and crystalline scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) as reported by various observers. Only solubility experiments in which the initial Fe/As molar ratio was near unity are shown. The solubility data of Robins (1990) is for a partially crystalline scorodite. See text.

(1985), and Robins (1987), are given in Table 1. The data from Tozawa et al. (1978), Krause and Ettel (1988), and Robins (1990) are listed in Table 2. Lines drawn through the data points in Fig. 1, which show the general behavior of AFA and scorodite(cr) as a function of pH, have no theoretical or statistical significance. As discussed below, the solubility data of Robins (1990), which lies between that for AFA and scorodite(cr) is apparently for a scorodite phase of intermediate crystallinity.

In their calculation of solubility products, Chukhlantsev (1956) and Krause and Ettel (1988) ignored ion activity coefficients. Chukhlantsev (1956) also did not consider important ferric hydroxide and ferric sulfate complexes. Except for Zhu and Merkel (2001), most researchers have also ignored ferric and other metal arsenate complexes. Dove and Rimstidt (1985) neglected ferric arsenate complexes and made their four solubility measurements from pH 5.53 to 6.36, where scorodite dissolves incongruently with precipitation of a ferric oxyhydroxide phase (cf. Nordstrom and Parks, 1987; Robins, 1987). The incongruity of their experiments is evident from the molar Fe/As ratios of their final solutions which are given in Table 1. We have chosen not to use solubility measurements obtained under incongruent conditions in our determination of the solubility product of scorodite.

A somewhat similar reevaluation of published ferric arsenate/scorodite solubility data to ours was performed by Zhu and Merkel (2001). However, these authors

Table 1

Experimental data measured at 20–25 °C and PHREEQC model-computed ion activity products of ferric arsenate and ferric hydroxide for the ferric arsenate/scorodite solubility results of Chukhlantsev (1956), Makhmetov et al. (1981), Dove and Rimstidt (1985) and Robins (1987)

pH	As (mg/L)	Fe (mg/L)	Fe/As molar	Ferric arsenate log IAP	Ferric hydroxide log IAP
Chukhlantsev (1956)					
1.90	280	209	1.00	-22.45	-41.27
2.00	144	107	1.00	-22.64	-41.14
2.05	70	52	1.00	-22.72	-40.57
2.15	86	64	1.00	-22.68	-40.85
2.20	64	48	1.00	-22.61	-40.25
2.95	6.6	4.9	1.00	-23.24	-39.47
Makhmetov et al. (1981)					
3.0	7.5	6.1	1.10	-23.08	-38.68
Dove and Rimstidt (1985)					
5.53	10.3	1.14	0.15	-23.59	-37.65
5.97	5.3	0.81	0.21	-23.75	-37.02
6.23	1.8	1.76	1.28	-23.56	-35.21
6.36	4.0	2.68	0.89	-23.27	-35.38
Robins (1987)					
0.5	15370	11457	1.00	-22.69	-42.74
0.8	7631	5688	1.00	-23.12	-43.34
1.4	754	562	1.00	-22.93	-42.02
1.6	599	446	1.00	-22.59	-41.47
2.1	189	141	1.00	-22.31	-40.32
2.4	75	56	1.00	-22.41	-39.73

The data of Robins (1987) was read from a graph by Krause and Ettel (1988), assuming congruent dissolution of ferric arsenate, which was also assumed by Chukhlantsev (1956). All results are from dissolution experiments.

Table 2

Experimental data and PHREEQC model-computed ion activity products of ferric arsenate and ferric hydroxide for the ferric arsenate and scorodite solubility results of Tozawa et al. (1978), Krause and Ettel (1988), Robins (1990), and Nishimura and Robins (1996)

PH	As (mg/L)	Fe (mg/L)	SO ₄ (mg/L)	Na (mg/L)	Fe/As molar	Ferric arsenate log IAP	Ferric hydroxide log IAP	PH	As (mg/L)	Fe (mg/L)	Na (mg/L)	NO ₃ (mg/L)	SO ₄ (mg/L)	Fe/As molar	Ferric arsenate log IAP	Ferric hydroxide log IAP	
Tozawa et al. (1978)								Robins (1990)									
1.82	130	73	1230		0.753	-23.11	-41.36	1.30	26.6	18.94	0.0	842		0.954	-24.78	-42.50	
2.06	91	20	577		0.295	-23.18	-41.24	2.00	8.04	2.08	0.0	154		0.346	-24.30	-41.33	
2.20	53	10	390		0.253	-23.33	-41.09	2.55	4.74	0.255	0.0	41.2		0.0723	-24.60	-41.17	
2.61	33	2.3	123		0.094	-23.57	-40.93	2.95	4.74	0.075	0.0	15.6		0.0213	-24.93	-41.22	
2.88	29	0.41	54.1		0.019	-24.19	-41.32	3.60	9.45	0.053	0.0	1.9		0.0075	-24.96	-40.97	
3.10	25	0.17	26.4		0.009	-24.52	-41.40	3.72	11.9	0.029	0.0	0.6		0.0033	-25.21	-41.21	
2.03	79	41	679		0.696	-23.01	-40.92	4.35	15.0	0.022	3.5	0.0		0.002	-25.31	-40.79	
2.32	45	12	287		0.358	-23.11	-40.69	4.85	59.6	0.028	18.1	0.0		0.0006	-25.20	-40.77	
2.68	37	2.2	97.8		0.080	-23.54	-40.91	5.80	150	0.885	49.0	0.0		0.0079	-23.70	-38.68	
3.08 ; ;	36	0.75	22.6		0.028	-23.87	-40.93	6.40	260	1.40	99.8	0.0		0.0072	-23.50	-38.01	
Nishimura and Robins (1996)								Krause and Ettel (1988)									
1.48	17,500	1.00		67.5	7.67E-05	-24.97	-45.57	0.97	54	58.6	0		10,900	1.44	-26.22	-44.34	
1.50	16,800	0.990		104	7.91E-05	-24.95	-45.52	1.08	34.2	41.3	0		8130	1.62	-26.17	-44.08	
1.53	15,000	0.500		105	4.47E-05	-25.20	-45.72	1.24	19.1	21.1	0		5280	1.48	-26.15	-43.79	
1.56	12,600	0.530		53.9	5.64E-05	-25.13	-45.57	1.41	14	13	0		3330	1.25	-25.90	-43.38	
1.60	11,300	0.300		89.1	3.56E-05	-25.33	-45.70	1.67	5.1	5.31	0		1640	1.39	-25.83	-42.82	
1.66	9440	0.340		119	4.83E-05	-25.19	-45.48	2.05	1.50	0.951	0		583	0.85	-25.84	-42.17	
1.68	9090	0.340		143	5.02E-05	-25.17	-45.43	2.43	0.33	0.26	0		215	1.06	-25.89	-41.36	
1.74	7680	0.070		168	1.22E-05	-25.78	-45.96	2.55	0.19	0.043	0		158	0.30	-26.54	-41.71	
1.81	5710	0.050		129	1.17E-05	-25.84	-45.87	2.64	0.11	0.053	0		126	0.65	-26.45	-41.31	
1.83	6370	0.070		230	1.47E-05	-25.68	-45.74	2.65	0.2	0.058	0		123	0.39	-26.15	-41.26	
1.94	3990	0.040		154	1.34E-05	-25.80	-45.63	2.69	0.093	0.035	0		111	0.50	-26.57	-41.33	
1.96	4250	0.035		211	1.10E-05	-25.84	-45.69	2.86	0.08	0.04	0		73.2	0.67	-26.21	-40.76	
2.05	3670	0.034		253	1.24E-05	-25.77	-45.51	5.42	0.59	0.013	0.093		0	0.03	-25.59	-38.55	
2.17	2170	0.030		155	1.85E-05	-25.71	-45.18	6.53	3.8	1.5	0.714		0	0.53	-23.50	-35.77	
2.18	2410	0.025		200	1.39E-05	-25.79	-45.29	7.08	31	7.8	10.1		0	0.34	-22.78	-35.26	
2.20	2660	0.025		256	1.26E-05	-25.77	-45.31	7.79	129	12	65.9		0	0.12	-22.60	-34.51	
2.34	2010	0.020		247	1.33E-05	-25.77	-45.11	7.92	463	52.1	234		0	0.15	-21.96	-34.07	
2.52	1570	0.013		253	1.11E-05	-25.84	-44.97										
2.64	1270	0.010		230	1.06E-05	-25.89	-44.85										
2.68	1110	0.010		205	1.21E-05	-25.88	-44.74										
2.79	934	0.010		188	1.44E-05	-25.83	-44.54										
3.29	704 ¹	0.030		187	5.72E-05	-25.24	-43.39										

Also given are concentrations of Na, NO₃, and/or SO₄ adjusted to attain charge balance in the modeling calculations. All the solubility data in the table are for dissolution experiments except for four precipitation experiments of Tozawa et al. (1978) for which the results have been italicized.

discounted the data of Krause and Ettel (1988) for crystalline scorodite, and did not consider the solubility studies of Robins (1990) or Nishimura and Robins (1996).

In this study (see also Langmuir et al., 1999; Mahoney and Langmuir, 2002) we have focused on the solubilities of the most and least soluble ferric arsenate phases, amorphous ferric arsenate (AFA), and well-crystallized scorodite (scorodite(cr)), respectively. Published solubility data has been reevaluated using the geochemical code PHREEQC (Parkhurst and Appelo, 1999), and considering all of the above corrections, with a modified thermodynamic data base for aqueous arsenic species discussed in this paper, and separately for comparison using revised arsenic acid constants proposed by Nordstrom and Archer (2003). We also show the application of the solubility results to scorodite precipitation during the laboratory neutralization of arsenic-rich acid mill tailings raffinates, and to measured arsenic concentra-

tions in the pore waters of buried uranium mill tailings at the JEB tailings management facility at McClean Lake in northern Saskatchewan, Canada.

2. Scorodite solubility

2.1. Auxiliary thermodynamic data

Equilibrium constants for arsenic and arsenous acids and stability constants for metal arsenate complexes used in the PHREEQC calculations of chemical equilibria are given in Table 3. Discussion of the selection and derivation of these constants is presented in Appendix A.

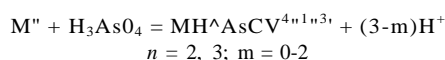
2.2. Studies considered in the revaluation

Because of the difficulty of making accurate activity coefficient corrections in solutions at ionic strengths above

Table 3

Equilibrium constants for As(III) and As(V) aqueous species and their reaction enthalpies used in PHREEQC calculations

Aqueous species	Reaction	Log <i>K</i>	$\Delta_r H^\circ$ (kJ • mol ⁻¹)	Source ^b
H ₂ AsO ₄ ⁻	H ₃ AsO ₄ = H ₂ AsO ₄ ⁻ + H ⁺	-2.24(-2.30) ^a	-7.11(-7.97)	(1)
HAsO ₄ ⁿ²	H ₃ AsO ₄ = HAsO ₄ ⁿ² + 2H ⁺	-9.20(-9.29)	-3.77(-4.95)	(1)
As<V ³	H ₃ AsO ₄ = AsO ₄ ⁻³ + 3H ⁺	-20.70(-21.09)	14.35(13.25)	(1)(3)
As(V)/As(III)	H ₃ AsO ₄ + 2H ⁺ + 2e ⁻ = H ₃ AsO ₃ + H ₂ O	18.90(19.35)	-125.6(-124.74)	(5)(2)
H ₂ AsO ₃ ⁿ	H ₃ AsO ₃ = H ₂ AsO ₃ ⁻ + H ⁺	-9.23(-9.17)	27.45(27.62)	(4)
HAs<V ²	H ₃ AsO ₃ = HAsO ₃ ⁻² + 2H ⁺	-21.33(-23.27?)	59.4	(5)(6)
AsO _j ⁿ³	H ₃ AsO ₃ = AsO ₃ ⁻³ + 3H ⁺	-34.74(-38.27?)	85.8	(5)(6)
HLAsCV	H ₃ AsO ₃ + H ⁺ = FLiAsO ₄ ⁻	-0.29		(4)



Aqueous species	Log <i>A</i>	Source ¹ⁿ	Aqueous species	Log *	Source ^b
CaH ₂ AsO ₄ ⁺	-1.18(-1.24)	(7)	MnAsO ₄ ~	-14.57C-14.96)	(7)
CaHAsO/	-6.51(-6.60)	(7)	NiH ₂ AsO ₄ ⁺	-0.72(-0.78)	(7)
CaAsO ₄ ~	-14.48(-14.87)	(7)	NiHAsO ₄ ^o	-6.30(-6.39)	(7)
MgH ₂ AsO ₄ ⁺	-0.72(-0.78)	(7)	NiAsO ₄ ⁿ	-14.36C-14.75)	(7)
MgHAsO ₄ ⁿ	-6.34(-6.43)	(7)	CuHAsO ₄ ^o	-5.52(-5.61)	(7)
MgAsO ₄ ~	-14.36(-14.75)	(7)	ZnHAsO ₄ ^o	-5.99(-6.08)	(7)
FeH ₂ AsO ₄ ⁺	1.8(1.74)	(8)	CdHAsO ₄ ^o	-5.49C-5.58)	(7)
FeHAsO ₄ ⁺	0.66(0.57)	(8)	PbH ₂ AsO ₄ ⁺	-0.71C-0.77)	(7)
FeAsO ₄ ^o	-1.8C-2.19)	(8)	PbHAsO ₄ ^o	-6.16(-6.25)	(7)
FeH ₂ AsO ₄ ⁺	0.44(0.38)	(7)	AlH ₂ AsO ₄ ⁺	0.83(0.77)	(7)
FeHAsO ₄ ^o	-5.66(-5.75)	(7)	AlHAsO ₄ ⁺	-1.91(-2.00)	(7)
FeAsO ₄ ⁻	-13.64(-14.03)	(7)	AlAsO ₄ ^o	-6.6(-6.99)	(7)
MnHAsO ₄	-5.45(-5.54)	(7)			

^a Parenthetic log *K* and $\Delta_r H^\circ$ values for the arsenic and arsenous acid dissociation reactions are from Nordstrom and Archer (2003). Parenthetic values for metal arsenate complexes have been computed using the listed arsenic acid values from Nordstrom and Archer (2003). Question marks indicate estimates.

^b Sources: (1) Smith and Martell (1976), Baes and Mesmer p. 370 (1976); (2) Bard et al. (1985); (3) Barin (1995); (4) Wagman et al. (1982); (5) Parkhurst (1995); (6) Naumov et al. (1974); (7) Whiting (1992); (8) Robins (1990).

0.1 M, we reviewed only solubility studies performed at lower ionic strengths. In our analysis, we also emphasized studies in which the pH, total dissolved As(V) and Fe(III) concentrations were known, ligand or charge balancing cation concentrations were known or could be estimated, and the studies made measurements either under conditions of congruent dissolution (pH < 3) or conditions that could be extrapolated to conditions of congruent dissolution of AFA or scorodite. Results of the solubility studies of Tozawa et al. (1978), Krause and Ettel (1988), Robins (1990), and Nishimura and Robins (1996) which satisfied these requirements are given in Table 2. Although we modeled the solubility data for AFA reported by Chukhlantsev (1956), Makhmetov et al. (1981), and Robins (1987), which were presumably obtained under congruent conditions, for several reasons these studies were not emphasized in the selection of a log *K_{sp}* value for AFA. Chukhlantsev (1956) only measured the Fe concentration in their equilibrium solutions, and assumed that dissolved mAs = mFe, which is usually not the case as noted below. The data of Robins (1987) was read by Krause and Ettel (1988) from a graph published by Robins (1987), and it was also assumed that mAs = mFe. Only a single solubility result measured at pH 3 was reported by Makhmetov et al. (1981), and the details of their experiments are unknown.

Among the studies we have chosen for detailed consideration, Tozawa et al. (1978) prepared amorphous ferric arse-

nate (AFA) by mixing 0.1 M Fe₂(SO₄)₃ and 0.2 M Na₂HAsO₄ solutions, and adding 0.5 M NaOH solution to maintain the pH at 1.7. The Fe/As ratio of the precipitate was 1.02. Dissolution experiments involved suspending 0.2 g of the AFA in 25 ml of water, with the pH adjusted with H₂SO₄ or NaOH solutions. Runs were kept at 25 °C, and were shaken for 24 h before filtration and analysis of the filtrate for pH, and Fe and As concentrations. Precipitation experiments, which involved the mixing of 0.005 M Na₂HAsO₄ and 0.0025 M Fe₂(SO₄)₃ solutions, were run for 1 h before filtration and solution analysis.

Robins (1990) precipitated AFA by refluxing a mixture of 0.1 M Fe₂(SO₄)₃ and 0.1 M H₃AsO₄ solutions at pH 1 for several days at low temperature. He rolled a slurry of the solid in deionized water for two years with the pH adjusted by adding either HNO₃ or NaOH before measuring equilibrium. TEM micrographs at equilibrium showed that the amorphous phase had formed crystals of scorodite. XRD measurements were not made to confirm the general extent of crystallinity. The solubility results discussed below indicate that the equilibrium phase was a partially crystalline scorodite.

The scorodite used in the experiments of Krause and Ettel (1988) was precipitated material that had been heated in an autoclave at 160 °C for 24 h. The XRD pattern gave sharp peaks indicating well-crystallized scorodite (scorodite(cr)). In the solubility experiments, which were run

between pH 0.97 and 7.92, 5 g of scorodite(cr) was added to 50 mL of H_2SO_4 , or to NaOH solution to increase the pH above 3. The slurry was stirred continuously for 14 days at $23 \pm 1^\circ\text{C}$ to attain equilibrium.

Nishimura and Robins (1996) mixed 0.1 M $\text{Fe}_2(\text{SO}_4)_3$ and 0.2 M H_3AsO_4 solutions at 25°C and pH 2 to precipitate ferric arsenate. The precipitate was washed until no sulfate was detected. The vacuum-dried precipitate had a molar Fe/As ratio of 1.01. Dissolution experiments involved adding precipitates to 100 mL bottles containing 25 mL of arsenic acid of variable concentrations. The bottles were shaken for 1-3 months at 25°C to attain equilibrium. X-ray diffraction and SEM analyses of the solids at equilibrium indicated they had become well-crystallized scorodite.

2.3. Formation of well-crystallized scorodite: the role of temperature and solution Fe/As ratio

In systems where the Fe/As molar ratio equals or exceeds unity, scorodite formed at ambient temperatures is more soluble (more amorphous) than that formed or aged at or above 100°C (cf. Welham et al., 2000). In their experiments, Dutrizac and Jambor (1988) found that completely crystalline scorodite was only formed at temperatures above 105°C . At lower temperatures some residual amorphous material remained which increased the apparent solubility of the scorodite. In the study of Demopoulos et al. (1995) the Fe/As molar ratio ranged from 1 to 4. By seeding their solutions with scorodite in a solution at low supersaturation, Demopoulos et al. (1995) precipitated crystalline scorodite at temperatures as low as 80°C . Such precipitation occurred in the absence of a seed only at or above 95°C .

In contrast, working in arsenic acid solutions with a molar Fe/As ratio ranging from 1×10^{-5} to 8×10^{-5} ($\text{Fe/As} < 1$), Nishimura and Robins (1996) formed well-crystallized scorodite at 25°C by shaking a ferric arsenate precipitate for 1-3 months in the continued presence of arsenic acid. X-ray diffraction showed that after that time the initially amorphous material had become scorodite(cr). The solubility results of Nishimura and Robins (1996) discussed below confirm that their scorodite was well-crystallized.

2.4. Incongruent dissolution: The Fe/As ratio

There is general agreement that the solubility product of scorodite should be computed from measurements at a pH low enough so that scorodite dissolution is congruent (i.e., no Fe(III) oxyhydroxide is precipitated). Incongruent dissolution of scorodite can take place at any pH, with the pH of incongruency depending on Fe and As concentrations, complexing, and the Fe/As ratio of the solution.

The empirical solubility data and modeled results in Table 2 indicate that with increasing pH, there are four possible solubility regions with respect to ferric arsenate and ferric oxyhydroxide (FO) solids. With increasing pH, starting in acid ferric arsenate solutions in which the molar

Fe/As ratio is initially equal to unity, these solubility regions are:

1. Undersaturated with respect to a ferric arsenate phase if that phase has completely dissolved before the solution can attain saturation.
2. At equilibrium with respect to a ferric arsenate phase which has a fixed K_{sp} . As and Fe concentrations decrease with increasing pH.
3. At equilibrium with respect to an FO phase which has a fixed K_{sp} , and with a ferric arsenate phase of decreasing then increasing apparent solubility.
4. In apparent equilibrium with a ferric arsenate phase and an increasingly amorphous FO phase. The solubilities and apparent K_{sp} values of both phases increase with increasing pH.

Of particular interest has been the pH of incongruent dissolution, which is the pH value that separates solubility regions 2 and 3. In solubility studies in which scorodite(cr) or AFA are dissolved in solutions that lack initial Fe(III) or As(V) concentrations, this pH is the pH above which the solution attains saturation with and begins to precipitate an FO phase and the Fe/As ratio of the solution drops below unity. Krause and Ettel (1988) assumed that congruent dissolution of crystalline scorodite took place in their experiments at pH 2.43 and below. Robins (1990), and Zhu and Merkel (2001) based on a literature survey, concluded that AFA dissolution is incongruent above about pH 2. Dove and Rimstidt (1985) argued that their four scorodite(cr) solubility measurements made between pH 5.53 and 6.36 were congruent. However, as shown in Table 1, the molar Fe/As ratios of their final solutions did not equal unity, and their solutions were generally supersaturated with respect to an amorphous FO phase, indicating that their solubility experiments were incongruent.

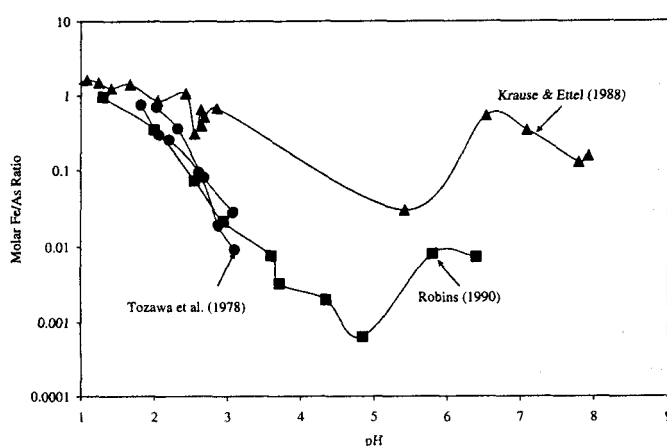


Fig. 2. Molar Fe/As(aq) ratio as a function of pH during dissolution/precipitation of ferric arsenate/scorodite in solutions initially free of dissolved As(V) and Fe(III) species. Data of Tozawa et al. (1978), Krause and Ettel (1988), and Robins (1990) are shown as solid circles, triangles, and squares, respectively.

Only Tozawa et al. (1978), Krause and Ettel (1988), and Robins (1990) (see Table 2) dissolved ferric arsenate or scorodite(cr) in solutions free of initial Fe(III) or As(V) species as a function of pH, and measured the aqueous concentrations of both Fe(III) and As(V) at equilibrium under conditions where a congruent solubility could be determined or estimated. Fig. 2 and Table 2 show that in the Tozawa et al. (1978) study of AFA solubility the Fe/As (aq) ratio decreases from 0.75 at pH 1.82 to 0.03 and below at pH 3.1 indicating incongruent dissolution throughout. Regression of their Fe/As versus pH data indicates that congruent dissolution of AFA in solutions without initial Fe(III) or As(V) (region 2) takes place below pH 1.82.

The ferric arsenate considered by Robins (1990) was partially crystalline. Table 2 and the Fe/As plot in Fig. 2 show that at his lowest pH of 1.30, Fe/As(aq) = 0.95, and the ratio decreased with increasing pH indicating incongruent dissolution.

In the dissolution experiments of Krause and Ettel (1988), the Fe/As ratio ranges from 1.25 to 1.62 between pH 0.97 and pH 1.67. The ratio drops to 1.06 and below 1.00 at pH 2.05 and above. Clearly, the authors' assertion that dissolution of scorodite was congruent for all runs between pH 0.97 and pH 2.43 is questionable. Based on their reported solubility, only about 0.3% or less of the scorodite in their runs would have been dissolved at equilibrium. The molar Fe/As ratio of their synthetic scorodite was 1.073 and dropped during dissolution, indicating the initial presence of an excess of dissolved Fe(III), which decreased with dissolution. This may explain why aqueous Fe/As ratios in their lowest pH runs exceeded unity.

Nishimura and Robins (1996) studied scorodite solubility in arsenic acid solutions in which the Fe/As ratio was near 10^{-5} . The plot of their Fe/As ratio versus pH in Fig. 3 shows rapidly decreasing ratios with pH below pH 1.74, constant ratios from pH 1.74 to 2.79, and an increased ratio at pH 3.29. Probable reasons for this behavior are discussed in Section 2.6.

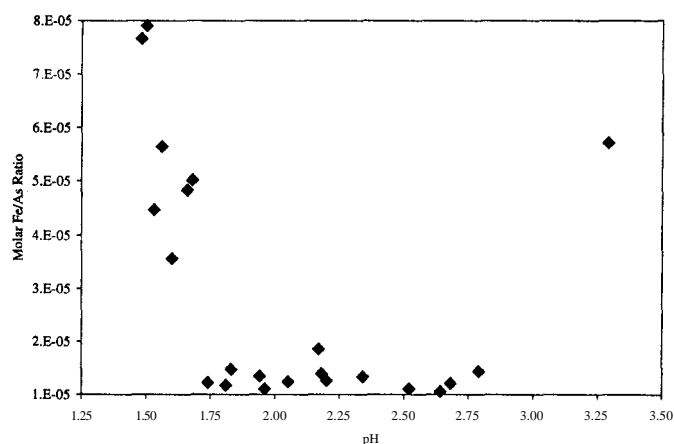


Fig. 3. Molar Fe/As(aq) ratio as a function of pH during the scorodite(cr) dissolution experiments of Nishimura and Robins (1996).

2.5. Stability of ferric oxyhydroxide phases

The ion activity product (IAP) of $[\text{Fe}^{3+}][\text{OH}]^f$ computed from the ferric arsenate/scorodite solubility runs of Tozawa et al. (1978), Krause and Ettel (1988), Robins (1990) and Nishimura and Robins (1996), is given in Table 2 and plotted versus pH in Fig. 4. At the lowest pH values of Krause and Ettel (1988) and Robins (1990) and in all of the experiments of Nishimura and Robins (1996), log IAP increases with increasing pH indicating undersaturated conditions with respect to FO.

At intermediate pHs, log IAP values for FO computed from the results of Tozawa et al. (1978), Robins (1990) and Krause and Ettel (1988) are relatively independent of pH. Thus, the average log IAP is -41.15 ± 0.25 for 22 experiments, which include the six dissolution and four precipitation experiments of Tozawa et al. (1978) between pH 1.82 and 3.08, the seven dissolution experiments of Robins (1990) between pH 2.00 and 4.85, and the five dissolution experiments of Krause and Ettel (1988) between pH 2.43 to 2.69. This average value is plotted as a dashed horizontal line in Fig. 4. It indicates that the FO phase precipitated between about pH 1.8 and 4.74 by incongruent dissolution of ferric arsenate solids is partially crystalline.

Above roughly pH 4.7 (the start of region 4), log IAP values for FO computed from the solubility data of Robins (1990) and Krause and Ettel (1988) lie on a line of decreasing stability (increasing solubility) with increasing pH in Fig. 4. According to Langmuir (1997) and others the log IAP of amorphous FO in systems low in arsenic (and sulfate) is -37. Larger values than this, which occur above pH 6 in Fig. 4, indicate supersaturated conditions with respect to amorphous FO. The precipitation of an FO phase under these conditions has probably been kinetically inhibited by the abundance of arsenate and/or sulfate in the experiments (Swash and Monhemius, 1994; Langmuir et al., 1999).

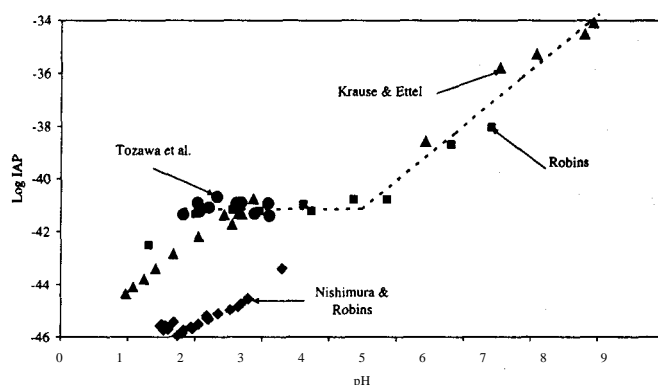


Fig. 4. Log IAP of ferric hydroxide in ferric arsenate/scorodite solubility studies of Tozawa et al. (1978)(circles), Krause and Ettel (1988)(triangles), Robins (1990)(squares), and Nishimura and Robins (1996) (diamonds). The dashed horizontal line is drawn at the average log IAP value of -41.2 between pH 1.8 and 4.7. The dashed sloping line is a linear regression of the 8 values at and above pH 4.7. See text.

2.6. Solubility of amorphous ferric arsenate and crystalline scorodite

If we wish to define the pH values that bound scorodite solubility regions 1-4, studying changes in the Fe/As (aq) ratio by itself is not as effective as also examining concurrent changes in the ion activity products of ferric hydroxide and ferric arsenate as a function of pH. Shown in Fig. 5 are log IAP values for $[\text{Fe}^{3+}][\text{AsO}_4^{3-}]$ plotted versus pH computed from the study results of Krause and Ettel (1988), Tozawa et al. (1978), and Robins (1990), along with vertical lines defining the four solubility regions introduced in section 2.4. The trend in log IAP values computed from the results of Krause and Ettel (1988) suggests that the three solubility runs between pH 0.97 and 1.24 were undersaturated with respect to crystalline scorodite and so are in region 1. The greater and constant log IAP values obtained between pH 1.41 and 2.43 represent equilibrium with respect to scorodite(cr) (region 2). The average and standard deviation of these four values is $\log \text{IAP} = -25.86 \pm 0.03$. When results of the same four runs are modeled using the stability constants for arsenic acid species and complexes based on Nordstrom and Archer (2003), the result for scorodite(cr) is $\log \text{IAP} = -26.22 \pm 0.03$. From pH 1.41 to 2.43 the dominant arsenate complex is H_2AsO_4^- , which comprises 93-96% of total arsenic. The dominant ferric complexes are $\text{Fe}(\text{SO}_4)_2^-$ and FeHAsO_4^+ , which comprise from 41-89% and 7-56% of total iron, respectively.

In region 3 of the study of Krause and Ettel (1988), the log IAP values for ferric arsenate are more negative than the average value in region 2, while the log IAP value for FO rises from -41.7 at pH 2.55 to -40.8 at pH 2.86, consistent with precipitation of increasingly amorphous FO in this pH range. Above pH ~ 4.7 (see Fig. 4) As(V) and Fe(III) concentrations rise, indicating increasing solubilities of scorodite and FO.

Log IAP values for ferric arsenate computed from the results of Tozawa et al. (1978) and Robins (1990), are also shown in Fig. 5, along with the suggested limits of the four

solubility regions for each study. In the amorphous ferric arsenate (AFA) dissolution experiments, of Tozawa et al. (1978), which were all run in solubility region 3, the log IAP for FO averages -41.08 ± 0.24 , and: the molar Fe/As(aq) ratio decreases from 0.75 to 0.009 between pH 1.82 and pH 3.1, respectively, indicating incongruent dissolution. In the same pH range, log IAP values for ferric arsenate decrease from -23.11 to -24.52. In four precipitation experiments from pH 2.03 to pH 3.08, these authors found Fe/As dropped from 0.70 to 0.03, and the ferric arsenate log IAP from -23.01 to -23.87, respectively. Assuming conditions for congruent dissolution exist below pH 1.82, where Fe/As = 1, and that only for such conditions can a reliable log K_{sp} value for AFA be obtained, we conclude that $\log \text{IAP}(\text{AFA})$ is greater than -23.01. In the absence of reliable solubility measurements for AFA, we will assume, somewhat arbitrarily, that the log K_{sp} for AFA is -23.0 ± 0.3 (-23.3 ± 0.3 if we assume the arsenic acid constants of Nordstrom and Archer, 2003). This compares favorably with average log K_{sp} values in Table 1 computed from the less reliable data of Chukhlantsev (1956), Robins (1987) and Makhmetov et al. (1981), which are -22.62 ± 0.10 , -22.67 ± 0.31 , and -23.08 , respectively. In the runs of Tozawa et al. (1978), the dominant aqueous complexes were H_2AsO_4^- , and secondarily FeHAsO_4^+ , which together comprised 84% or more of the iron and arsenic species in solution. FeSO_4^+ , equaled about 16% or less of the dissolved Fe(III) concentration.

The plot of log IAP values in Fig. 5 computed from the results of Robins (1990), shows that the log IAP of ferric arsenate increases from -24.8 at pH 1.30, where Fe/As = 0.95, to -24.3 at pH 2.00, where Fe/As = 0.35. Over the same pH range the log IAP for FO increases from -42.5 to -41.3. These values probably indicate undersaturated conditions with respect to ferric arsenate at pH 1.30 (region 1), and incongruent dissolution of ferric arsenate at pH 2.00 (region 3). If congruent dissolution of ferric arsenate was possible in these experiments, it would occur only in a narrow pH range near but above pH 1.3 and below pH 2.0. Assuming this assumption is correct, the log IAP (log K_{sp}) value of the ferric arsenate studied by Robins (1990) is between -24.3 and -24.8, suggesting that the phase is a partially crystalline scorodite. From pH 2.00 to pH 4.35 (in region 3) the log IAP value for ferric arsenate decreases from -24.3 to -25.3, respectively. Its value further increases at higher pH in region 4.

Nishimura and Robins (1996) measured the solubility of scorodite in 22 experiments between pH 1.48 and 3.29. Concentrations of dissolved As(V) greatly exceeded those of Fe(III) at equilibrium, with an Fe/As ratio in solution near 10^{-5} . The solubility data (including pH, and total dissolved As(V) and Fe(III) concentrations) were input into PHREEQC, using the arsenic acid constants of Smith and Martell (1976), and the stability constants for arsenate complexes consistent with these acid constants from Table 3. It was found that all solutions were deficient in cations, with an average charge balance error of -32%. The IAP for

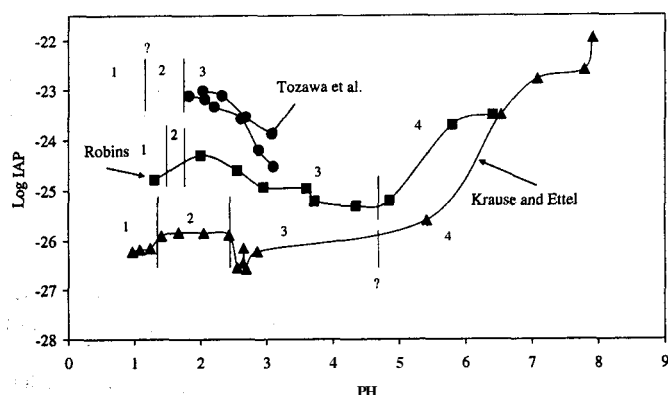


Fig. 5. Log IAP of ferric arsenate based on the solubility data of Tozawa et al. (1978), Krause and Ettel (1988), and Robins (1990). The lines have no statistical significance. Regions 1, 2, 3, and 4 for each data set are described in the text.

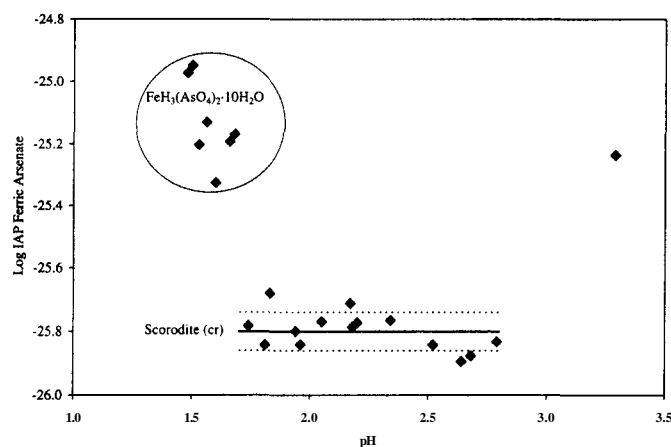


Fig. 6. Log IAP for ferric arsenate computed from the scorodite(cr) dissolution results of Nishimura and Robins (1996). Horizontal lines are drawn to show the average and ± 1 standard deviation of the average log IAP value for the 14 measurements of scorodite(cr) solubility. Circled points at low pH probably represent the solubility of $\text{FeH}_3(\text{AsO}_4)_2 \cdot 10\text{H}_2\text{O}$.

scorodite ($[\text{Fe}^{3+}][\text{AsO}_4^{3-}]$) was computed both ignoring this charge balance error, and introducing Na^+ to adjust the charge balance to zero. The log IAP computed with the corrected charge balance is plotted versus pH in Fig. 6. The figure shows relatively constant log IAP values for the 14 runs between pH 1.74 and 2.79, and larger log IAP values for runs below pH 1.74, and a run above pH 2.79. The higher solubility observed below pH 1.74 probably reflects equilibration with $\text{FeH}_3(\text{AsO}_4)_2 \cdot 10\text{H}_2\text{O}$, a phase identified by Nishimura and Robins (1996) in their experiments at slightly lower pHs. The increased log IAP value computed from the data at pH 3.29 corresponds to a further reduction in dissolved arsenic and an increase in iron concentrations with a resultant log IAP for FO of -43.4 which may indicate the precipitation of a relatively crystalline FO phase.

For the 14 data points between pH 1.74 and 2.79, which appear to be at equilibrium with respect to scorodite(cr), we obtain an average of $\log \text{IAP} = -25.80 \pm 0.06$ and $\log \text{IAP} = -25.79 \pm 0.06$, correcting and not correcting for the charge balance error, respectively. The low standard deviation of these averages provides confidence in the result. The same calculation performed using the arsenic acid constants of Nordstrom and Archer (2003) gives an average log IAP of -26.02 ± 0.05 for scorodite(cr) corrected for

charge balance. Solution speciation calculations indicate that in the 14 runs more than 99% of dissolved As(V) is present as $\text{H}_2\text{AsO}_4^{2-}$, and more than 99% of dissolved Fe(III) occurs as the FeHAsO_4^+ and $\text{FeH}_2\text{AsO}_4^{+2}$ complexes. This log A_p value for crystalline scorodite is in excellent agreement with $\log K_{sp} = -25.86 \pm 0.03$ obtained from our analysis of the data of Krause and Ettel (1988). The average of these values, which we adopt for crystalline scorodite, is $\log K_{sp} = -25.83 \pm 0.07$. If we use the arsenic acid constants of Nordstrom and Archer (2003), the average value for crystalline scorodite is instead -26.12 ± 0.06 . The recommended solubility products for ferric arsenate and scorodite determined in this study are listed in Table 4.

2.7. Phase relations of ferric arsenate and FO phases in $\text{FeAs} \sim 1$ systems

The relative thermodynamic stability of ferric arsenate and ferric hydroxide (FO) is obviously complicated by the fact that these phases vary widely in stability. Following discussion only applies to solubility studies in which the system Fe/As ratio is near unity, and focuses on explaining the data for scorodite(cr) as reported by Krause and Ettel (1988). The solid curves in Fig. 7 define As and Fe concentrations at equilibrium with scorodite(cr) and FO, computed with PHREEQC when we fix their $-\log A_p$ values at 25.83 and 41.2, respectively. Also plotted are measured As and Fe concentrations from Krause and Ettel (1988) (Table 2), and the pH ranges of regions 1-4.

As discussed above, scorodite solubility region 1 occupies a low pH range where the solution is undersaturated with respect to scorodite(cr). In region 2, the solution is at equilibrium with scorodite(cr). Regions 1 and 2 define pH conditions where scorodite(cr) should dissolve congruently.

If scorodite(cr) and the FO phase behaved as if they had the fixed solubilities assigned to them in Fig. 7, scorodite(cr) would dissolve incongruently above pH ~ 2.5 (above point B). Both phases would then coexist, but arsenic values would rise along the scorodite(cr) curve, while Fe(aq) values declined along the FO solubility curve. Although declining Fe(aq) values roughly follow the FO solubility curve drawn for a constant $-\log K_{sp}$ of 41.2, this is obviously not how the arsenic behaves. Above pH 2.5 in region 3, the solubility data of Krause and Ettel (1988) and

Table 4

Recommended solubility products of amorphous ferric arsenate, a partially crystalline scorodite, and scorodite(cr) computed assuming thermodynamic data for arsenic acid species and arsenate complexes based on this study, and based on Nordstrom and Archer (2003)

Phase	$\log A_{sp}$		Source of $\log A_{sp}$ value
	This study	Nordstrom and Archer	
Amorphous ferric arsenate	-23.0 ± 0.3	-23.3 ± 0.3	Extrapolated from the measurements of Tozawa et al. (1978)
Partially crystalline scorodite	-24.3 to -24.8	-24.6 to -25.1	Interpolated from the measurements of Robins (1990)
Crystalline scorodite	-25.83 ± 0.07	-26.12 ± 0.06	Average of average values computed from studies of Krause and Ettel (1988) and Nishimura and Robins (1996)

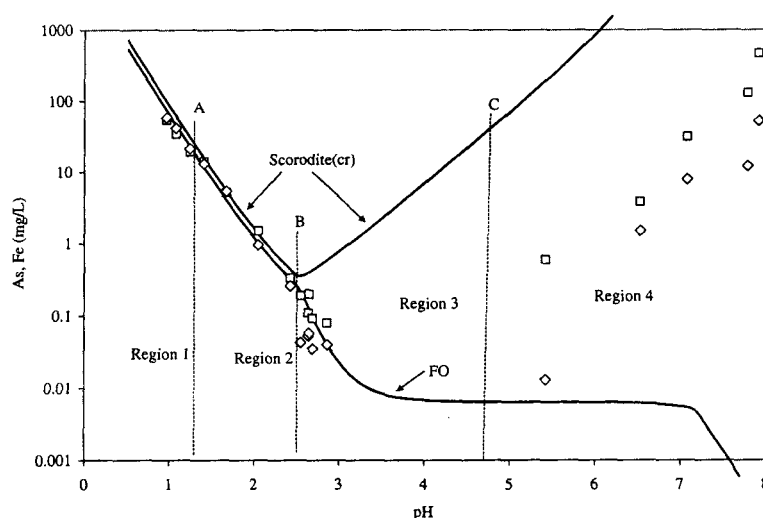


Fig. 7. The solubility of scorodite(cr) and FO in terms of As (upper solid line) and Fe (lower solid line) in the solutions of Krause and Ettel (1988) as computed by PHREEQC, assuming $-\log K_{sp}$ values of 25.83 and 41.2 for scorodite(cr) and FO, respectively. Also plotted is the solubility of scorodite(cr) as reported by Krause and Ettel (1988) with dissolved As and Fe concentrations shown as open squares and diamonds, respectively. Solubility regions and their boundaries are defined in the text.

Robins (1990) (Table 2 and Fig. 5), indicate that As(aq) and Fe(aq) concentrations continue to drop up to about pH 3 and pH 4.7, respectively.

The drop in As(aq) values to less than 0.1 mg/L near pH 3 corresponds to a decrease in the log IAP of scorodite (Table 2), but may partly reflect As(aq) adsorption by or coprecipitation with the FO phase. Above pH 4.7 (in region 4), As(aq) and Fe(aq) concentrations and $-\log$ IAP values for scorodite and FO decrease with pH. The $-\log$ IAP values for FO are as high as 34.07 at pH 7.92. That these values greatly exceed saturation with respect to amorphous FO which has a $-\log K_{sp}$ value of about 37 (Langmuir, 1997; Macalady et al., 1990) indicates that FO precipitation

was kinetically inhibited during the experiments of Krause and Ettel (1988), probably by the arsenic in the system.

Fig. 8 shows PHREEQC-computed solubility curves for coexisting ferric arsenate and ferric hydroxide and attempts to explain scorodite behavior in region 4. The plot indicates that when ferric arsenate and coexisting FO become more soluble with increasing pH (Table 2), the stability field of scorodite expands relative to that of FO from point B to successively higher pH values at points B', in good agreement with the As and Fe solubility data reported by Krause and Ettel (1988).

The pH value above which scorodite should dissolve incongruently and equilibrate with a precipitating FO

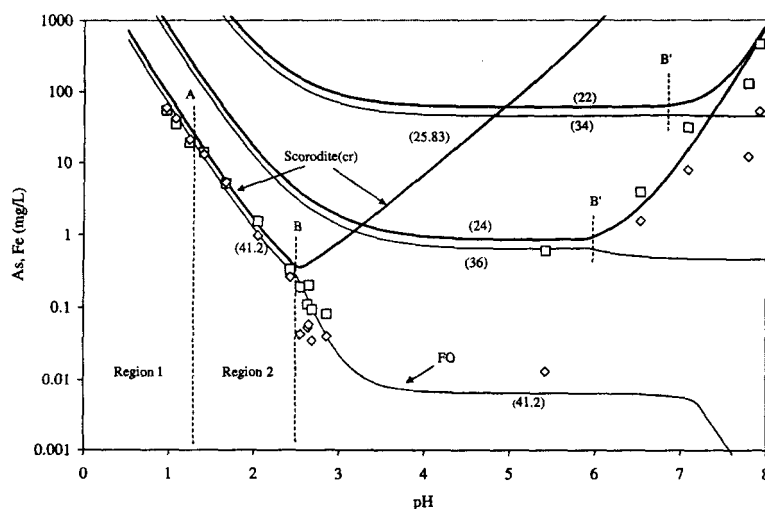


Fig. 8. The solubility of scorodite and FO in terms of As (heavy solid lines) and Fe (light solid lines) in the solutions of Krause and Ettel (1988) as computed by PHREEQC, assuming paired $-\log K_{sp}$ values of 25.83 and 41.2, 24.0 and 36.0, and 22.0 and 34.0, for scorodite and FO, respectively. Also plotted is the solubility of scorodite(cr) as reported by Krause and Ettel (1988) with dissolved As and Fe concentrations shown as open squares and diamonds, respectively. Solubility regions; and their boundaries are denned in the text.

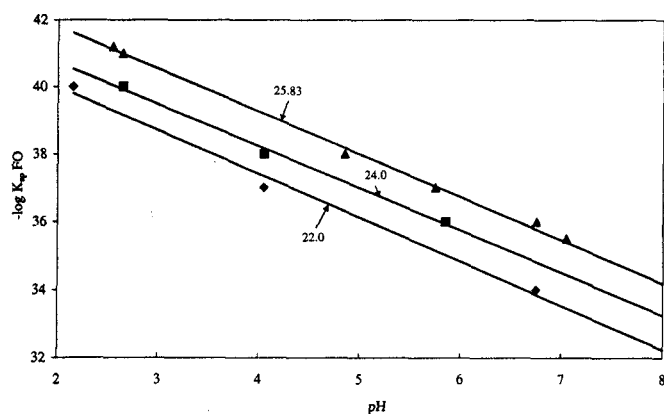


Fig. 9. The dependence of the pH at which ferric arsenate dissolves to precipitate an FO phase (points B and B' in Fig. 8) on the $-\log K_{sp}$ value of the FO phase, for ferric arsenate $-\log K_{sp}$ values of 22.0, 24.0, and 25.83.

phase (the pH of points B and B') is plotted in Fig. 9 as a function of the $-\log K_{sp}$ values for coexisting scorodite and FO. The figure shows that in the experimental solutions of Krause and Ettel (1988) scorodite coexists with an increasingly soluble FO phase at pH values that range from as low as 2.5 in acid solutions, to as high as 7 in near-neutral solutions where precipitation of the highly supersaturated FO phase is kinetically inhibited.

3. Application to arsenic behavior in buried mill tailings

3.1. Decrease in the apparent $\log K_{sp}$ ($\log IAP$) of ferric arsenates with increasing pH and increasing Fe/As ratio

In systems in which the Fe/As ratio equals 1, the apparent (computed) solubility product ($IAP = K_{sp}$) of the ferric arsenates decrease with pH up to pH 4-5 in Fig. 5. That the solubility product decreases and scorodite crystallinity increases may reflect a slowing rate of scorodite precipitation in the presence of lower concentrations of dissolved Fe(III) and As(V). Also, with increasing pH, relatively amorphous scorodite becomes undersaturated and would be expected to preferentially dissolve, leaving a more crystalline fraction behind. Any released arsenic may then reprecipitate as a more crystalline scorodite. It has been argued that the apparent decrease in the solubility of scorodite with increasing pH results from arsenate adsorption by the FO, however, insufficient iron is present in systems with Fe/As ~ 1 to explain the observed effect.

Numerous studies have shown that arsenic concentrations and the apparent $\log K_{sp}$ of scorodite (i.e., the $\log IAP$ of ferric arsenate) also decrease when the Fe/As ratio of the acid solution being neutralized is increased (cf. Fig. 10). For example, Vircikova et al. (1995) measured the solubility of ferric arsenate/FO mixtures as a function of the Fe/As ratio of the system. Our modeling of their solubility data at pH 2 shows that the apparent $\log K_{sp}$ for ferric arsenate is -23.89 for Fe/As = 1.6, -24.80 for Fe/As = 5.9, and -24.97 for Fe/As = 14.4.

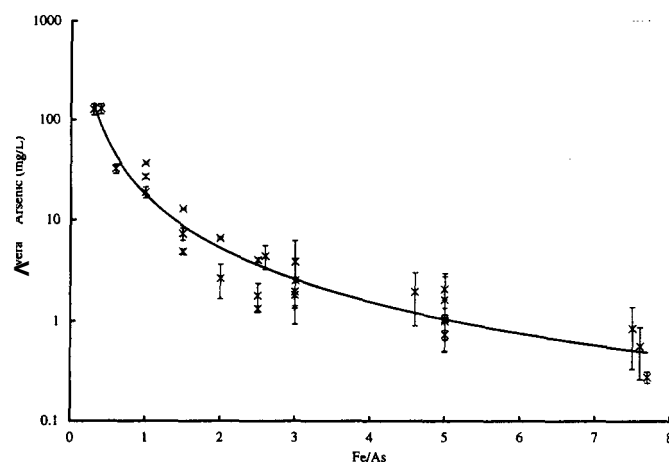


Fig. 10. Average arsenic concentrations in neutralized tailings solutions between pH 7-8 after 72 to 144 h aging tests at 25 °C as a function of the molar Fe/As ratio of the acid raffinate solutions before neutralization. From Langmuir et al. (1999).

3.2. Scorodite in raffinate neutralization experiments at the JEB Mill at McClean Lake

Neutralization of acid raffinates of uranium mill tailings produced at the JEB mill at McClean Lake in northern Saskatchewan, has been studied in laboratory experiments. In these experiments and in the mill, in a two-stage process, slaked lime [$\text{Ca}(\text{OH})_2$] is added to the acid raffinate which has a Fe/As molar ratio of 3. When the pH is held at pH 2-3 for a sufficient time during lime addition (~ 90 min. in the mill), poorly crystalline scorodite is formed. The pH is subsequently increased to a final pH of 7-8. The scorodite produced by this procedure has been identified by XRD, SEM, EM, and EXAFS analyses of the solids (cf. Langmuir et al., 1999; Jia et al., 2003; Cutler et al., 2003; and Jiang et al., 2004). Precipitates contain both poorly crystalline scorodite and a relatively amorphous FO phase in which small amounts of the arsenic are adsorbed or co-precipitated.

In example neutralization experiments, mill-produced acid raffinate solution with Fe/As = 3.6 was placed in six two-liter beakers on a multi-jar tester. Lime in increasing amounts was added to successive beakers while stirring, so that each beaker attained a predetermined pH value ranging from 2 to 8. All beakers were in the pH 2-4 range for 1 h or more during neutralization as in the mill, facilitating scorodite precipitation. After the beakers reached their target pH values, the slurries were filtered and the solutions and slurries analyzed. Chemical analyses of the acid raffinate solution and two neutralized solutions are given in Table 5.

Arsenic concentrations in the batch experiments as a function of pH are shown in Fig. 11. The plot indicates that As(aq) decreases from 686 mg/L in the raffinate to less than 1 mg/L after neutralization above pH 6. Fig. 12 gives $\log IAP$ values for ferric arsenate and ferric hydroxide as a function of pH computed with PHREEQC. Not shown are IAP values for the raffinate at pH 0.97, which are undersaturated

Table 5

Chemical analyses of the raffinate solution used in the batch neutralization tests and example neutralized raffinate solutions

Species or parameter	Raffinate	Neutralized sample pH 2.18	Neutralized sample pH 7.32
$r^{\circ}c$	25	25	25
pH	0.97	2.18	7.32
Pe	11.32	10.88	-3.19
As(3)	447	100	0.199
As(5)	221	48	0.17
Fe(2)	685	540	26
Fe(3)	1169	881	6.7
Al	200	803	0.01
Ca	589	512	612
Cl	13	16	18
Cu	19	16	0.01
K	357	394	477
Mg	229	1086	749
Na	23	83	59
Ni	515	502	13.1
Si	190	582	8
SO ₄	21,430	10,150	3020

Concentrations are in mg/L unless otherwise noted. Higher concentrations in neutralized samples than in the raffinate may result from concentrating solutions because of removal of water by the precipitation of gypsum [CaSO₄ · 2H₂O], or contaminants added in the lime used for neutralization.

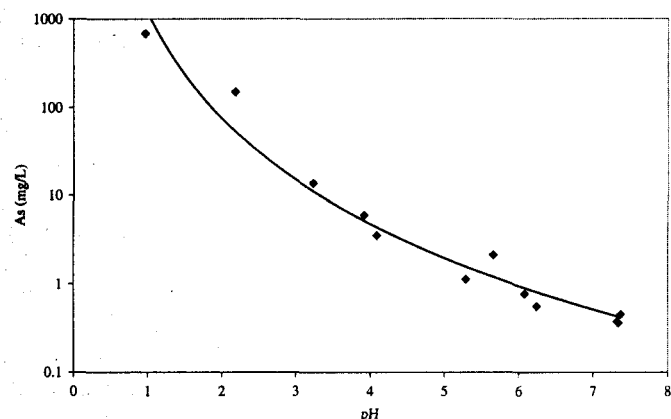


Fig. 11. Arsenic concentrations as a function of pH during batch neutralization of acid raffinate solution.

with respect to both solids. Log IAP values for ferric arsenate in Fig. 12 decrease from -22.80 at pH 2.18 indicating an AFA precipitate, to -24.67 at pH 7.37 indicating a more crystalline scorodite may be present at higher pH values.

Over the same pH range, the log IAP of FO increases from -39.49 to near -33.5. Log IAP values greater than -37, which is the log K_{sp} value for amorphous FO (Macalady et al., 1990; Langmuir, 1997) indicate a system in which the precipitation of a ferric hydroxide phase is kinetically inhibited, probably by the elevated arsenic and sulfate concentrations present (Langmuir et al., 1999). The high apparent solubility of the FO increases the stability field of scorodite to higher pH values relative to the stability field of the FO phase. The low solubility of scorodite at pH 7.37 is evident

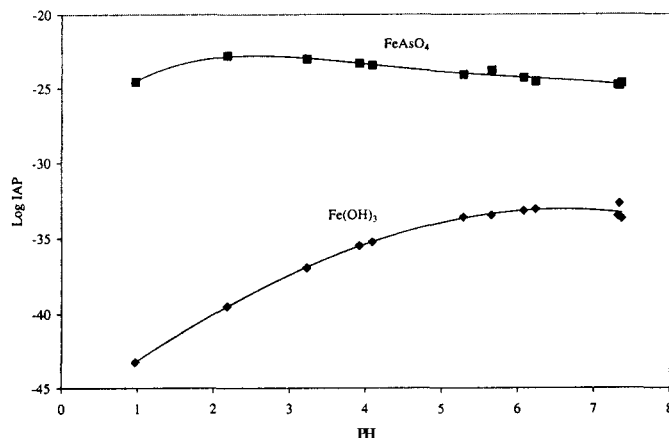
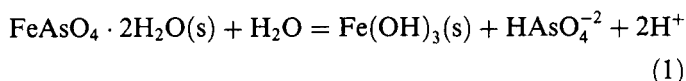


Fig. 12. Log IAP values for ferric arsenate and ferric hydroxide as a function of pH in the batch raffinate neutralization tests. Calculations made using measured Fe(III) and As(V) concentrations.

from calculations involving the ferric arsenate/ferric hydroxide equilibrium reaction, which may be written:



Assuming the apparent (computed) log K_{sp} values of -24.67 and -33.5 for ferric arsenate and ferric hydroxide respectively, the equilibrium constant of this reaction is:

$$K_r = 10^{-21.67} = [\text{HAsO}_4^{-2}][\text{H}^+]^2 \quad (2)$$

which gives an equilibrium HAsO_4^{-2} activity of 1.2×10^{-5} mol/L or 0.009 mg/L As at pH 7.37. This is less than the measured total As(aq) concentration of 0.45 mg/L because we have neglected activity coefficient corrections and other complexes in our simplified calculation. The result shows that at pH 7.37, ferric arsenate is more stable than the FO phase if As(aq) concentrations exceed this value, and that Reaction 1 should buffer As(aq) concentrations below 1 mg/L at pH 7.37.

Between pH 1 and 2, the ferric arsenate precipitated during lime neutralization removes more than 90% of As(aq) in the raffinate. Additional As(aq) removal with further pH increases in this system can be attributed to the apparent increase in scorodite crystallinity (decrease in the log IAP of ferric arsenate), or to arsenic adsorption and/or co-precipitation.

A simple modeling calculation suggests that As(V) adsorption by FO alone can explain the drop in arsenic concentrations with lime neutralization above pH 2-3. In this calculation, we use the diffuse layer model and parameters for As(V) sorption by FO from Dzombak and Morel (1990) given in PHREEQC, and assume a one-step adsorption process starting at pH 2.18 with As(V) adsorption to pH 7.37. Further assumptions include no back reaction of precipitated ferric arsenate, an initial As(V) concentration of 54.5 mg/L at pH 2.18, and 1440 mg/L of dissolved Fe at pH 2.18 which is precipitated as FO (as 'FeOOH' in the model), at pH 7.37. Sorbent FeOOH has an assigned

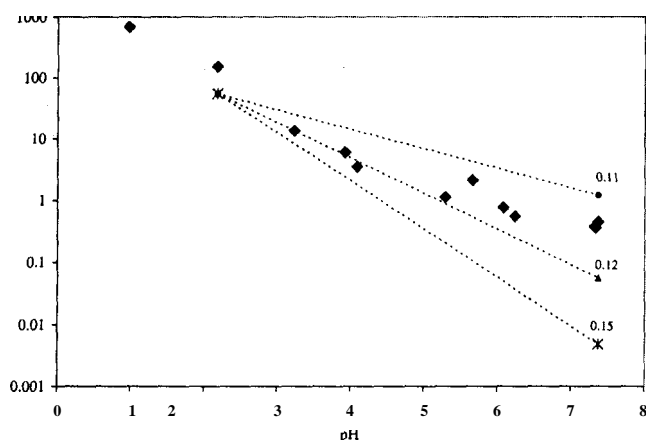


Fig. 13. Arsenic concentrations (solid diamonds) plotted as a function of pH during the batch neutralization tests. The dotted lines show trends in As(V) adsorption, predicted using the diffuse layer model (Dzombak and Morel, 1990), on ferrihydrite precipitated in a single step between pH 2.18 and 7.37. The model assumes initial precipitation of scorodite at pH 2.18. All remaining arsenic is then adsorbed by ferrihydrite. The dotted lines show As concentrations at a final pH of 7.37, assuming sorption site (Hfo_wOH) densities of 0.11, 0.12, and 0.15 mol of sites per mole of ferrihydrite precipitated. See text for further modeling details.

surface area of $600\text{m}^2/\text{g}$. Modeling results plotted in Fig. 13 show that a sorption density of 0.11 to 0.12 moles of As per mole of Fe in $FeOOH$ can explain the reduction in arsenic concentrations to less than 1 mg/L at pH 7.37.

There are important problems with this modeling exercise. Most importantly, the model assumes reversible As(V) adsorption by the FO precipitated from the raffinate, which is not observed. Mahoney et al. (2005) found that the As(V) readily released from neutralized tailings and raffinates to pore waters was only 0.2% of the total As present in the tailings. Whether precipitated as ferric arsenate, co-precipitated with an FO phase (cf. Waychunas et al., 1993) or adsorbed, most of the As(V) held by solids following neutralization to pH values near 7 is held irreversibly. This irreversibility apparently increases as the Fe/As ratio of raffinates is increased (cf. Harris and Krause, 1993).

5.5. Scorodite in the JEB tailings management facility

Starting in 1999, neutralized tailings slurry from the JEB mill at McClean Lake has been emplaced below the water table in the JEB open pit, or tailings management facility (TMF). In 2004, pore waters in the TMF were sampled from depths above mean sea level ranging from 364 m (oldest tailings) to 396 m (youngest tailings). Three example analyses of pore waters obtained from different depths are given in Table 6. Redox speciation of dissolved Fe and As in the pore waters was computed with PHREEQC from measured pH and Eh values and total Fe and As concentrations.

The average pore water pH is 7.76 ± 0.24 . There is no significant correlation between pH and pore water elevation. However, arsenic concentrations vary with elevation.

Table 6

Chemical analyses of some pore waters sampled at three different depths from the JEB tailings management facility in 2004

Parameter/analyte	Sample elevation (meters above mean sea level)		
	397.8	378.9	364.3
$T^\circ\text{C}$ (field)	12.2	NR ^a	10.7
pH (field)	7.54	7.45	7.70
Eh (mV) (field)	450	369	390
Specific Conductance (mS/Cm)	2460	2440	2480
DO (field)	6.8	8.2	9.0
Na	120	150	34
K	25	18	22
Mg	34	79	120
Ca	510	440	562
Sr	0.62	0.64	0.27
Ba	0.052	0.062	0.019
Mn (total)	1.75	5.97	1.6
Fe (total)	0.008	0.27	0.004
Ni	0.46	0.77	0.53
Al	<0.005	<0.005	<0.02
U	2.3	3.1	0.41
Cl	29	48	58
Si	4.1	9.3	4.6
SO_4	1600	1500	1900
HCO_3	55	179	44
$NH_3 + NH_4^+$ as N	7.3	10	NR
$N < V + NO_2^-$ as N	<0.01	0.23	0.07
COD	6	29	NR
As (III)	0.053	3.13	0.096
As(V)	0.257	1.17	0.384
Mo	7.22	7.14	4

Concentrations are in mg/L unless otherwise noted.

^a NR denotes not reported.

The average total As concentration at all depths is $4.1 \pm 3.6\text{ mg/L}$, with the highest values occurring at intermediate depths (between 375 and 392 m). Above and below these depths As concentrations in the youngest and oldest buried tailings, are less than $1\text{--}2\text{ mg/L}$. The increase in total As values at intermediate depths is as As(III)(aq), probably derived from the oxidation and dissolution of unreacted arsenide minerals in the residual tailings and As(III) desorption from tailings solids. This As(III)(aq) is subsequently oxidized to As(V) and precipitated in scorodite or adsorbed by FO solids in tailings at depths below 370 m.

There is no statistically significant trend in the log IAP values for ferric arsenate or ferric hydroxide with sample elevation. As in the laboratory study, computed log IAP values for ferric arsenate decrease with pH, while those for FO increase with pH. For the 35 pore waters between pH 7.18 and pH 8.28 $\log IAP(\text{ferric arsenate}) = -25.74 \pm 0.88$ and $\log IAP(\text{FO}) = -37.03 \pm 0.58$. This suggests that arsenic and iron concentrations in the TMF are limited by the solubility of a relatively crystalline scorodite phase and an amorphous FO phase, respectively. The apparent crystallinity of the scorodite and the amorphous character of the associated FO phase stabilizes scorodite relative to FO in the TMF. Both the neutralized

raffinates and TMF pore waters are at saturation with gypsum. The amorphous FO phase in the neutralization experiments and in the TMF is apparently prevented from crystallizing by the high amounts of arsenate and sulfate present in both of these systems.

X-ray diffraction analysis of core solids from the TMF was performed in 2001. Results suggested that scorodite averaged 0.7 ± 0.8 weight percent of the tailings in seven samples obtained over a depth range of 17 m. Detailed characterization of the scorodite was impossible because of its small relative amount in the tailings.

4. Conclusions

Published solubility data for amorphous ferric arsenate and for crystalline scorodite, was reevaluated using the geochemical code PHREEQC (Parkhurst and Appelo, 1999), taking into account ionic strength and ferric and arsenate aqueous complexes, and only considering studies where some measurements were made in acid solutions where congruent dissolution of the arsenate was possible, and the measured pH and concentrations of total As and Fe were reported. Computer modeling of the solubility data indicates that $\log K_{sp} = -23.0 \pm 0.3$ and -25.83 ± 0.07 for amorphous ferric arsenate and crystalline scorodite, respectively, at 1 bar pressure and 25 °C.

Laboratory experiments were performed in which arsenic-rich acid raffinate solutions from the JEB uranium mill at McClean Lake in northern Saskatchewan were neutralized to pH 2-8 with added $\text{Ca}(\text{OH})_2$. Poorly crystalline scorodite precipitated around pH 2, and relatively amorphous ferric oxyhydroxides (FO) began to precipitate between pH 2 and 3. Arsenic concentrations dropped from 686 mg/L at pH 0.97 to less than 1 mg/L at pH 7.37. At pH 7.37 the scorodite had an apparent $\log J_{sp}$ of -24.67 and so was partially crystalline, whereas the FO was highly amorphous and kinetically inhibited from precipitation. Arsenic removal during neutralization could also be explained by assuming precipitation of 90-98% of the As(V) in scorodite up to pH 2-3, and adsorption of the remaining As(V) by a precipitated FO phase between pH 2.18 and 7.37. Whatever the As(V) removal mechanism, it is largely irreversible.

A slurry of neutralized uranium mill tailings has been emplaced continuously in the JEB tailings management facility (TMF) at McClean Lake for five years, and as of 2004 occupied a thickness of about 32 m in the TMF. Pore waters sampled from the TMF in 2004 had an average pH 10.16 and an As(aq) concentration of 4.1 mg/L which decreased to 1-2 mg/L or less in the oldest tailings. The average $\log \text{IAP}$ values for ferric arsenate and FO were -25.74 and -37.03, respectively, indicating that well-crystallized scorodite and amorphous FO may control arsenic and ferric iron concentrations in TMF pore waters at near-neutral pH values.

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Associate editor: Liane G. Benning

Appendix A. Auxiliary thermodynamic data

A.1. Arsenic and arsenous acids

Cumulative dissociation constants for arsenic and arsenous acids used in the solubility modeling are given in Table 3. Of particular concern in this study, which involves oxidizing conditions, are the arsenic acid constants. In previous studies, Whiting (1992) and the authors (cf. Langmuir et al., 1999) have used the critically selected arsenic acid constants suggested by Smith and Martell (1976) and Baes and Mesmer (1976). More recently Nordstrom and Archer (2003) have reevaluated these constants and recommended the significantly different values given in Table 3. The consequences of using both sets on the stability of scorodite are considered in this study.

A.2. Metal arsenate complexes

Also important in the solubility calculations is consideration of metal arsenate complexes, which have been neglected by most previous researchers. Robins (1990) reported free energy values for the ferric arsenate complexes which have been used to compute the stability constants of these species listed in Table 3.

Lacking published stabilities of other metal arsenate complexes, Whiting (1992) estimated their stabilities. His approach involved using the Electronicity Principle of Brown and Sylva (1987a,b) (the BSEP model), and graphical methods. In both approaches a comparison is made between the measured and modeled association constants (Δ_{assoc} values) of metal phosphate complexes and corresponding arsenate complexes. This of course means that the accuracy of the association constant that we predict for a given metal arsenate complex will be limited by the accuracy with which we know the constant for the corresponding phosphate complex used in the prediction.

The BSEP model considers such factors as the hard and soft acid and base properties of the cation and ligand forming the complex, the charge and radius of the cation, whether the cation is a transition metal species, and the degree of ionicity or covalency of bonding in the complex. In his BSEP modeling effort, Whiting (1992) first compared the measured association constants of 23 metal phosphate complexes reported in the literature to value; predicted using the BSEP model. The ratio $\log [K_{\text{assoc}}(\text{measured})/\log K_{\text{assoc}}(\text{predicted})]$ (the 'correction factor') was then computed for each complex. The aver

age of the correction factors for all 23 phosphate complexes was 0.96 ± 0.33 , showing generally good agreement between measured and predicted values. The BSEP model was then used to predict the stabilities of the metal arsenate complexes. Assuming correction factors for the metal arsenate complexes would be the same as for the corresponding metal phosphate complexes, the predicted $\log K_{\text{assoc}}$ value for each metal arsenate complex was multiplied by the corresponding phosphate-derived correction factor. Some confidence in the results of this approach can be gained by comparing the BSEP model predicted and measured $\log K_{\text{assoc}}$ values for the $\text{FeH}_2\text{AsO}_4^{2+}$, FeHAsO_4^+ , and FeAsO_4 complexes. The predicted values are 4.06, 9.76, and 18.85, compared to the values measured by Robins (1990), which are 4.04, 9.86, and 18.9, respectively.

The stability of the metal arsenate complexes was also estimated graphically. This involved plotting measured $\log K_{\text{assoc}}$ values for arsenate complexes against measured values for corresponding phosphate complexes. The only published arsenate stability constants available for such plots are those for the arsenic acid species and the ferric arsenate complexes (Table 3).

A third point for each figure was obtained as follows. A plot of $\log K_{\text{assoc}}$ values for metal HPO_4^{2-} and H_2PO_4^- phosphate complexes versus the electronegativity (EN) of the metal cations in the complexes (see Fig. A1, Whiting, 1992, and Langmuir, 1997, p. 102) shows that as the EN of metal cations decreases, cation bonding with phosphate ligands (and presumably also with corresponding arsenate ligands) becomes more purely electrostatic, and $\log K_{\text{assoc}}$ values asymptotically approach constant values. These $\log K_{\text{assoc}}$ values should be equal for the same metal phosphate and arsenate complexes. For the metal $(\text{M}^{+2})\text{-H}_2\text{PO}_4^+$ and HPO_4^{2-} complexes the asymptotic $\log K_{\text{assoc}}$ values are 1.0 and 2.3, respectively. (See Fig. A1). The same extrapolation approach for the metal PO_4^{3-} complexes suggests an asymptotic $\log K_{\text{assoc}}$ value of about 5.2 for cation EN values below 0.4 (Whiting,

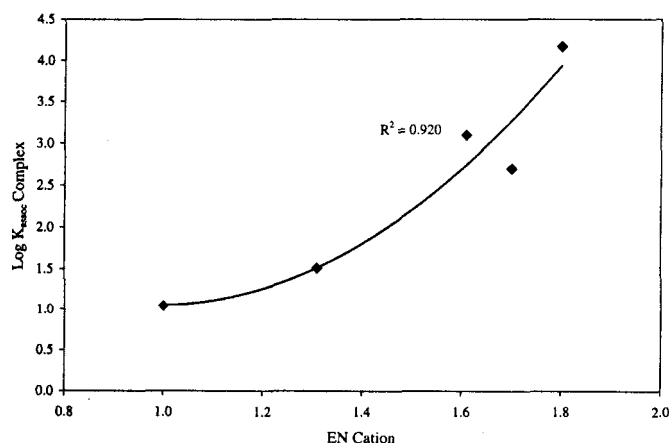


Fig. A1. Association constants of metal- H_2PO_4^- complexes plotted against the electronegativity of the metal cation.

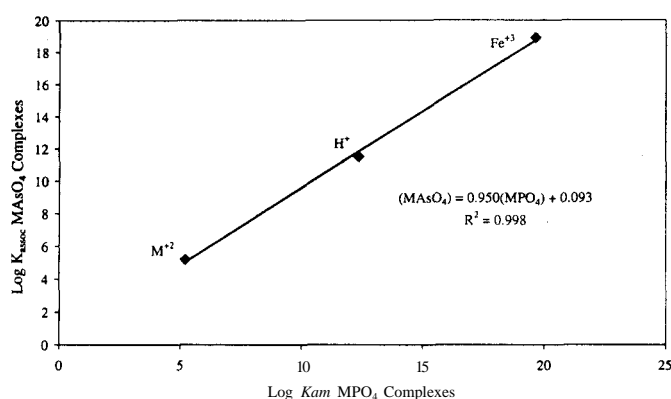


Fig. A2. Comparison of $\log K_{\text{assoc}}$ values of phosphate and corresponding arsenate complexes. Parentheses in the equation enclose the $\log K$ values of the association constants for the cation arsenate and phosphate complexes.

1992). That these are unrealistically low $\log K_{\text{assoc}}$ and EN values does not significantly affect the resultant equation of the line in Fig. A2, which is relatively insensitive to the value we choose for the third and lowest point on the plot where $\log/i_{\text{assoc}}(\text{MPCV}) = \log A_{\text{assoc}}(\text{MAsO}_4^-)$.

Regression of the three data points in each plot gives the equations:

$$(\text{MH}_2\text{AsO}_4) = 0.955(\text{MH}_2\text{PO}_4) + 0.10, \text{ with } R^2 = 0.998;$$

$$(\text{MHAsO}_4) = 0.987(\text{MHPO}_4) - 0.15, \text{ with } R^2 = 0.999; \text{ and}$$

$$(\text{MAsO}_4^-) = 0.950(\text{MPO}_4^{3-}) + 0.10, \text{ with } R^2 = 0.998.$$

In these equations the parenthetic terms represent the $\log K_{\text{assoc}}$ values for the metal complex (M) with the specified ligand. Agreement between $\log K_{\text{assoc}}$ values predicted for the arsenate complexes using the corrected BSEP model and the graphic approach are excellent. Thus the average ratio of these two values is 1.01 ± 0.02 . Association constants for the metal arsenate complexes given in Table 3 are averages of the values obtained with the corrected BSEP model and using the graphic approach.

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