American Mineralogist, Volume 73, pages 850–854, 1988

Solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$: New data and further discussion

E. Krause, V. A. Ettel
J. Roy Gordon Research Laboratory, INCO Limited, Mississauga, Ontario L5K 1Z9, Canada

Abstract

The solubility of crystalline samples of scorodite, synthetic and natural, was found to be about two orders of magnitude lower than those reported by earlier authors for apparently amorphous ferric arsenate. Congruent dissolution was observed between pH 1.0 and 2.4. Congruent dissolution data obtained with the synthetic sample were used to calculate the solubility product of scorodite at 23 °C as $K_{sp}(Fe^{3+}AsO_4^{3-}) = 10^{-24.41 \pm 0.15}$ and the free energy of formation as $\Delta G_f^0 = -1279.2$ kJ·mol^{-1}.

Introduction

The solubility of scorodite $FeAsO_4 \cdot 2H_2O$ was investigated in the past by Chukhlantsev (1956), Tozawa et al. (1977, 1978), Makhmetov et al. (1981), Dove and Rimstidt (1985, 1987), Rimstidt and Dove (1987), and most recently by Robins and Glastras, whose previously unpublished data are included in the recent discussion by Robins (1987) in this journal. The solubility products p$K_{sp}(Fe^{3+}AsO_4^{3-})$ calculated by these authors range from 19.9 to 22.2, and the derived values of the free energy of formation ΔG_f^0 range from −1243.0 (Sillen and Martell, 1964) to −1267.1 kJ·mol^{-1} (Robins, 1987).

Some of the measurements are biased toward higher solubilities, as the samples of scorodite used were prepared by methods we have found to lead to amorphous and more soluble precipitates (Krause and Ettel, 1985, 1987, 1988). In fact, Makhmetov et al. (1981) stated that their ferric arsenate precipitate was XRD amorphous.

Dove and Rimstidt (1985) used crystalline scorodite for their solubility study and observed lower As dissolutions than Chukhlantsev (1956) and the other investigators. Differences between their data and those of Chukhlantsev (1956) were interpreted in terms of particle-size effects. However, Dove and Rimstidt (1985) worked at pH values of about 6, where scorodite dissolves incongruently, which makes the calculations of solubility products less accurate, as is pointed out by Robins (1987) and by Nordstrom and Parks (1987).

In light of the importance of the solubility of scorodite for As disposal, we have conducted accurate measurements with well-defined crystalline samples of scorodite as part of our investigation of low-solubility As compounds suitable for safe disposal of As (Krause and Ettel, 1987, 1988).

Feed materials

A scorodite containing mineral specimen was obtained from the Royal Ontario Museum, Toronto. The scorodite phase was physically separated from the specimen.

The synthetic crystalline scorodite was prepared at CANMET, Ottawa (Dutrizac and Jambor, 1988), by combining 1.0 L of 0.3*M* $Fe(NO_3)_3$ with 25 g of As(V) (as As_2O_5) and heating to 160 °C for 24 h in an autoclave. After rapid cooling, the solids were filtered off, H_2O washed, and dried at 110 °C. Analysis of the synthetic scorodite (wt%) yielded 24.0 Fe, 30.0 As (33.4 reported by CANMET), <0.02 Ca, <0.05 Na, <0.5 SO_4, and 0.12 Cl. The particle size was 100% <5.5 μm (weighted average particle diameter = 2.5 μm). Analysis by XRD identified only scorodite with the lattice parameters $a = 10.33$ Å, $b = 10.02$ Å, $c = 8.94$ Å. In contrast to amorphous ferric arsenate precipitated at 80 °C, both scorodite samples showed sharp XRD patterns (Fig. 1).

Solubility measurements

The solubility in water was determined at 23 ± 1 °C over the pH range 0.97 to 7.92. The scorodite (5 g) was added to 50 mL of H_2SO_4 or NaOH containing water (pH 0.9–12.36). The slurry was allowed to equilibrate for at least 14 d by continuous stirring. After measuring the equilibrium pH, the slurry was filtered through 0.2 μm membranes, the solution was stabilized and analyzed by DCP (≥0.5 mg/L) or by flameless AA (≤0.5 mg/L). Table 1 gives the observed Fe and As analyses as a function of the pH, together with estimated sulfate concentrations. In the pH range 0.97 to 2.43, log C_{As} and log C_{Fe} decreased linearly with increasing pH. Congruent dissolution of scorodite occurs in the above pH range according

0003–004X/88/0708–0850$02.00

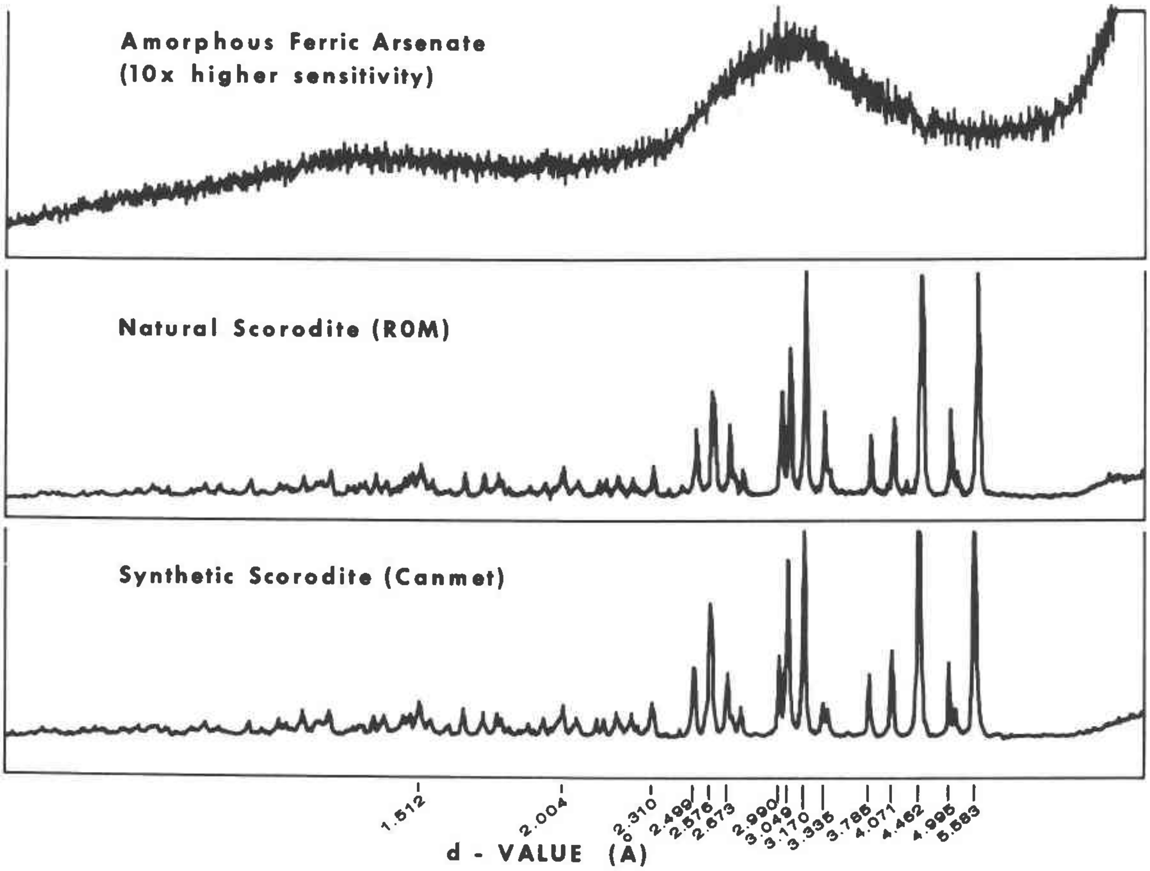

Fig. 1. XRD patterns of scorodite samples.

to the equilibrium reaction

$$FeAsO_4 \cdot 2H_2O_{scorodite} + 3H^+ = Fe^{3+} + H_3AsO_4 + 2H_2O. \quad (1)$$

The As solubility passed through a minimum at a pH of about 4. Above pH 5, log C_{As} and log C_{Fe} increased nearly linearly with increasing pH. Scorodite dissolution above pH 2.43 exhibits incongruency because of the reactions

$$FeAsO_4 \cdot 2H_2O_{scorodite} + H_2O \rightarrow Fe(OH)_3 + (H_2AsO_4)^- + H^+ \quad (2)$$

or

$$FeAsO_4 \cdot 2H_2O_{scorodite} \rightarrow FeOOH + (H_2AsO_4)^- + H^+. \quad (3)$$

Our solubility measurements for crystalline scorodite are in good agreement with those of Dove and Rimstidt (1985). Additional measurements were conducted with a sample of natural scorodite. The As solubility at pH 5.4 was somewhat higher than that of the synthetic scorodite. This may have been due to small impurities contained in the natural scorodite sample. The two results are, however, in sharp contrast to high As solubilities observed with presumably amorphous ferric arsenate. Our own measurements for amorphous (1:1) $FeAsO_4$ precipitate indicate an As solubility of 160 mg/L at pH 5.0 (Krause and Ettel, 1987).

Figure 2 compares published As solubilities for crystalline and apparently amorphous "scorodite" in the tem-

TABLE 1. Solubility of crystalline scorodite at 23 °C

Original pH	Equilibrium pH	Analytical concentration (mg/L)		
		Fe	As	$(SO_4)^{2-}$*
		Congruent dissolution		
0.90	0.97	58	54	9295
1.04	1.08	41	34	6465
1.20	1.24	21	19	4475
1.38	1.41	13	14	2860
1.64	1.67	5.3	5.1	1630
2.08	2.05	0.95	1.5	612
2.85	2.43	0.26	0.33	101
		Incongruent reaction		
3.45	2.55	0.043	0.19	—
—	2.64	0.053	0.11	—
5.57	2.65	0.058	0.20	—
10	2.69	0.035	0.093	—
11.05	2.86	0.040	0.080	—
—	5.42	0.013	0.59	—
—	6.53	1.5	3.8	—
11.76	7.08	7.8	31.0	—
12.06	7.79	12	129	—
12.36	7.92	52	463	—

* Estimated from original sulfate concentration.

perature range 20–25 °C. As expected, there is greater scatter of experimental results in the region of incongruent dissolution. The data obtained for congruent dissolution fall between two distinct lines. Crystalline scorodite is approximately 100 times less soluble than the apparently amorphous form. Published thermodynamic calculations by Robins (1981, 1983, 1984, 1985, 1987) were based on ΔG_f^0 values estimated from solubility measurements of amorphous "scorodite."

TABLE 2. Equilibrium reactions and constants considered

	log *K*, 25 °C
Arsenate	
$HAsO_4^{2-} = AsO_4^{3-} + H^+$	−11.49*
$H_2AsO_4^- = HAsO_4^{2-} + H^+$	−6.86*
$H_3AsO_4 = H_2AsO_4^- + H^+$	−2.24*
Ferric ion	
$Fe^{3+} + H_2O = FeOH^{2+} + H^+$	−2.97**
$FeOH^{2+} + H_2O = Fe(OH)_2^+ + H^+$	−3.29**
$2FeOH^{2+} = Fe_2(OH)_2^{4+}$	3.18**
$Fe^{3+} + SO_4^{2-} = FeSO_4^+$	1.93**
$FeSO_4^+ + SO_4^{2-} = Fe(SO_4)_2^-$	0.18**
$Fe^{3+} + HSO_4^- = FeHSO_4^{2+}$	0.60**
$SO_4^{2-} + H^+ = HSO_4^-$	0.91**

* From Dove and Rimstidt (1985).
** From Zheng et al. (1986).

ESTIMATION OF THE SOLUBILITY PRODUCT

The solubility product, K_{sp} ($Fe^{3+}AsO_4^{3-}$), for scorodite is given by

$$K_{sp} = (a_{Fe^{3+}})(a_{AsO_4^{3-}}). \tag{4}$$

Published solubility products for scorodite vary considerably and not only as a result of differences in crystallinity. The calculation of $a_{Fe^{3+}}$ and $a_{AsO_4^{3-}}$ must take into account the various dissolved species of Fe(III) and As(V), e.g.,

$$C_{As(V)} = a_{AsO_4^{3-}} + a_{HAsO_4^{2-}} + a_{H_2AsO_4^-} + a_{H_3AsO_4}. \tag{5}$$

All prior authors have considered the four As species listed above and have used essentially the same equilibrium constants. However, the list of Fe(III) species considered varied widely between investigators. Chukhlantsev (1956), for example, measured only the total Fe concentration (the As concentration was presumed to be identical) and calculated the solubility product by assuming $C_{Fe(III)} = a_{Fe^{3+}} = C_{As(V)}$. This oversimplification resulted in a published solubility product being almost 10 times higher than that of Tozawa et al. (1978), who considered the following Fe species:

$$C_{Fe(III)} = a_{Fe^{3+}} + a_{FeOH^{2+}} + a_{Fe(OH)_2^+}. \tag{6}$$

TABLE 3. Comparison of published $FeAsO_4$ solubilities

Investigator(s)	Medium	pH	Temp. (°C)	Concentrations in mol·L⁻¹		
				−log $C_{Fe(III)}$	−log $C_{As(V)}$	pK_{sp}
Chukhlantsev (1956)	HNO_3	2.90	20	4.07	4.07*	20.64
		2.20	20	3.07	3.07*	20.44
		2.05	20	3.03	3.03*	20.66
	H_2SO_4	2.95	20	4.06	4.01*	20.52
		2.15	20	2.94	2.94*	20.18
		2.00	20	2.72	2.72*	20.19
		1.90	20	2.43	2.43*	19.86
Tozawa et al. (1978)	H_2SO_4	3.10	25	5.52	3.48	22.19
		2.88	25	5.13	3.41	21.76
		2.61	25	4.39	3.36	21.61
		2.20	25	3.75	3.15	21.49
		2.06	25	3.45	2.92	21.26
		1.82	25	2.88	2.76	21.08
Makhmetov et al. (1981)	HNO_3	3	25	3.96	4.00	20.46
Robins (1987)	$HClO_4$	0.5	25	0.7**	0.7**	
	HNO_3	0.8	25	1.0**	1.0**	
	H_2SO_4	1.4	25	2.0**	2.0**	
		1.6	25	2.1**	2.1**	
		2.1	25	2.6**	2.6**	
		2.4	25	3.0**	3.0**	
Dove and Rimstidt (1985)	HCl, NaOH	6.36	25	4.32	4.27	21.71
		6.23	25	4.50	4.61	22.14
		5.97	25	4.84	4.15	21.88
		5.53	25	4.69	3.86	21.32
Krause and Ettel (1987)	H_2SO_4	2.43	23	5.33	5.36	24.55
		2.05	23	4.77	4.70	24.34
		1.67	23	4.02	4.17	24.24
		1.41	23	3.63	3.73	24.26
		1.24	23	3.42	3.60	24.52
		1.08	23	3.14	3.34	24.53
		0.97	23	2.98	3.14	24.60

* Chukhlantsev measured only $C_{Fe(III)}$ and assumed that $C_{Fe(III)} = C_{As(V)}$.
** Estimated from Figure 2 (Robins, 1987).

Since H_2SO_4 was used in our study for the adjustment of pH, the following mass balance was considered to estimate the Fe^{3+} activity (Krause and Ettel, 1987, 1988):

$$C_{\mathrm{Fe(III)}} = a_{\mathrm{Fe^{3+}}} + a_{\mathrm{FeOH^{2+}}} + a_{\mathrm{Fe_2(OH)_2^{4+}}} + a_{\mathrm{Fe(OH)_2^+}} + a_{\mathrm{FeSO_4}} + a_{\mathrm{Fe(SO_4)_2^-}} + a_{\mathrm{FeHSO_4^{2+}}}. \quad (7)$$

Ferric arsenate complexes such as $FeHAsO_4^+$ and $FeH_2AsO_4^{2+}$ (proposed by Robins, 1987) were not considered since no reliable data are available.

Table 2 shows the equilibrium reactions and constants used. Equations 5 and 7 were solved to estimate the Fe^{3+} and AsO_4^{3-} activities in the pH range 0.97 to 2.43, and to calculate K_{sp} according to Equation 4. The activity coefficients were assumed to be 1. The solubility product for crystalline scorodite was found to vary between 2.53×10^{-25} and 5.80×10^{-25} ($\mathrm{mol^2 \cdot L^{-2}}$) in the above pH range (congruent dissolution). Thus, the mean value of K_{sp} for $FeAsO_4 \cdot 2H_2O$ is $(3.89 \pm 1.36) \times 10^{-25}$ at 23 ± 1 °C ($pK_{sp} = 24.41 \pm 0.15$). When the sulfate complexes of Fe(III) are considered for the estimation of $a_{\mathrm{Fe^{3+}}}$, K_{sp} is no longer a function of the pH in the congruent dissolution regime.

Some solubility measurements in the congruent dissolution regime were checked after more than 1 yr of contact between solids and solution. The value of pK_{sp} was found to be 24.7, demonstrating that the data in Table 1 were obtained under equilibrium conditions. After more than 1 yr of contact, the analysis of solids in equilibrium at pH 1.76 yielded (%) 23.5 Fe, 32.4 As, and 0.14 SO_4^{2-}. Analysis by XRD confirmed the presence of only scorodite. There was no indication of the formation of hydronium jarosite.

Table 3 shows a comparison of published $FeAsO_4$ solubilities. Measurements by Chukhlantsev (1956), Tozawa et al. (1978), Makhmetov et al. (1981), and those reported by Robins (1987) were conducted with apparently amorphous $FeAsO_4$ precipitates. Our recent studies (Krause and Ettel, 1987, 1988) show that crystalline scorodite is much less soluble than heretofore assumed on the basis of published solubilities of amorphous ferric arsenate.

The experimentally observed K_{sp} value was used to calculate the free energy of formation of scorodite. The value of ΔG_f^0 for $FeAsO_4 \cdot 2H_2O$ is computed as $-1279.2\ \mathrm{kJ \cdot mol^{-1}}$ by assuming $\Delta G^0_{f,\ \mathrm{Fe^{3+}}} = -16.99\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta G^0_{f,\ \mathrm{AsO_4^{3-}}} = -648.39\ \mathrm{kJ \cdot mol^{-1}}$ (Robins, 1985, 1987).

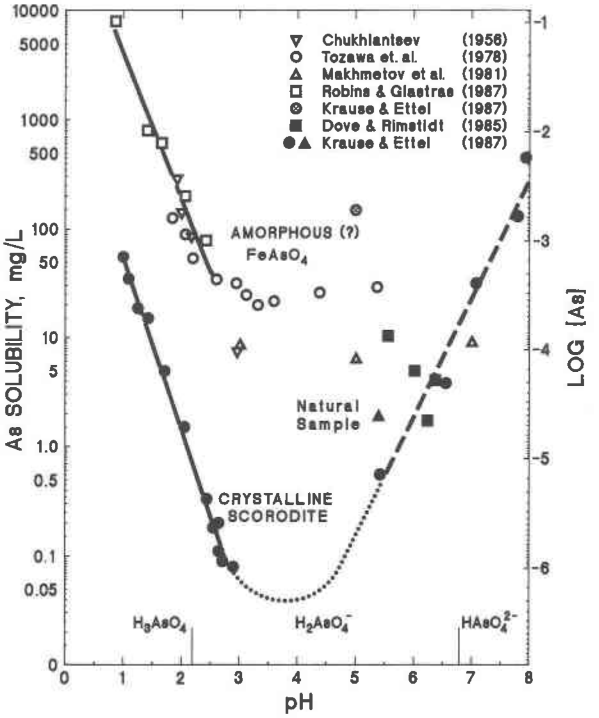

Fig. 2. Solubility of apparently amorphous $FeAsO_4$ precipitates and of scorodite, $FeAsO_4 \cdot 2H_2O$.

ACKNOWLEDGMENTS

We thank Dr. J. A. Mandarino from the Royal Ontario Museum (ROM), Toronto, and Dr. J. E. Dutrizac from CANMET, Ottawa, for supplying samples for our measurements. We also thank the management of INCO Limited for supporting this study and for permission to publish it.

REFERENCES CITED

Chukhlantsev, V.G. (1956) The solubility products of a number of arsenates. Journal of Analytical Chemistry (USSR), 11, 565–571.

Dove, P.M., and Rimstidt, J.D. (1985) The solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$. American Mineralogist, 70, 838–844.

——— (1987) Solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$: Reply. American Mineralogist, 72, 845–848.

Dutrizac, J.E., and Jambor, J.L. (1988) The synthesis of crystalline scorodite, $FeAsO_4 \cdot 2H_2O$. Hydrometallurgy, 19, 377–384.

Krause, E., and Ettel, V.A. (1985) Ferric arsenate compounds: Are they environmentally safe? Solubilities of basic ferric arsenates. In A.J. Oliver, Ed., Impurity control & disposal. Proceedings, 15th Annual Hydrometallurgy Meeting CIM, Vancouver, Canada, August 18–22, 1985, paper 5.

——— (1987) Solubilities and stabilities of ferric arsenates. In G.L. Strathdee, M.O. Klein, and L.A. Melis, Eds., Crystallization and precipitation. Proceedings, ISCAP '87, Saskatoon, Canada, October 5–7, 1987, 195–210.

——— (1988) Solubilities and stabilities of ferric arsenates. Hydrometallurgy, in press.

Makhmetov, M.Z., Sagadieva, A.K., and Chuprakov, V.I. (1981) Solubility of iron arsenate. Journal of Applied Chemistry (USSR), 54, 823–824.

Nordstrom, D.K., and Parks, G.A. (1987) The solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$: Discussion. American Mineralogist, 72, 849–851.

Rimstidt, J.D., and Dove, P.M. (1987) Solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$: Reply. American Mineralogist, 72, 852–855.

Robins, R.G. (1981) The solubility of metal arsenates. Metallurgical Transactions B, March 1981, 103–109.

——— (1983) The stability of arsenic (V) and arsenic (III) compounds in aqueous metal extraction systems. In K. Osseo-Asare and J.D. Miller, Eds., Hydrometallurgy research development and plant practice. Proceedings, 3rd International Symposium on Hydrometallurgy, AIME, Atlanta, Georgia, March 6–10, 1983, 291–310.

——— (1984) The stability of arsenic in gold mine processing wastes. In V. Kudryk, D.A. Corrigan, and W.W. Liang, Eds., Precious metals: Mining, extraction, and processing. Proceedings, AIME/IMPI Meeting, Los Angeles, California, February 27–29, 1984, 241–249.

——— (1985) The aqueous chemistry of arsenic in relation to hydrometallurgical processes. In A.J. Oliver, Ed., Impurity control & disposal.

Proceedings, 15th Annual Hydrometallurgy Meeting CIM, Vancouver, Canada, August 18–22, 1985, paper 1.

——— (1987) Solubility and stability of scorodite $FeAsO_4 \cdot 2H_2O$: Discussion. American Mineralogist, 72, 842–844.

Sillen, L.G., and Martell, A.E. (1964) Stability constants of metal-ion complexes. The Chemical Society Special Publication no. 17, 305.

Tozawa, K., Nishimura, T., and Umetsu, Y. (1977) Removal of arsenic from aqueous solutions. 16th CIM Conference of Metallurgists, Vancouver, Canada, August 22–24, 1977.

Tozawa, K., Umetsu, Y., and Nishimura, T. (1978) Hydrometallurgical recovery or removal of arsenic from copper smelter by-products. 107th AIME Meeting, Denver, Colorado, February 27–March 2, 1978.

Zheng, C.Q., Allen, C.C., and Bautista, R.G. (1986) Kinetic study of the oxidation of pyrite in aqueous ferric sulfate. Industrial & Engineering Chemistry Process Design & Development, 25, 308–317.

Manuscript received August 17, 1987
Manuscript accepted February 29, 1988