Solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$: Discussion

Robert G. Robins

Department of Mineral Processing and Extractive Metallurgy, University of New South Wales,
Kensington, N.S.W. 2033, Australia

Dove and Rimstidt (1985) reported solubility data for a synthetic scorodite prepared by mixing ferric chloride and sodium arsenate solutions and aging the resulting precipitate in the mother liquor at 95–105°C. The light tan–colored product gave a distinct X-ray diffraction pattern corresponding to scorodite.

The precipitated material was washed to remove electrolytes and excess arsenate and was used in a series of solubility experiments in which either HCl or NaOH was used to adjust pH. The various mixtures were held at 25 ± 0.5°C for periods up to eight weeks before analyzing the solutions for Fe and As and measuring pH.

The actual solubility product and free energy of formation reported by Dove and Rimstidt are based on the analysis of only four solution samples, all of which were in the pH range 5.53–6.36. They reported a solubility product $K_{so}(Fe^{3+} AsO_4^{3-}) = 10^{-21.7 \pm 0.5}$ and $\Delta G_f^0 = -1263.52$ kJ·mol^{-1}.

The solubility of ferric arsenate was determined by Chukhlantsev (1956) in solutions that were pH adjusted with both sulfuric acid and nitric acid. Chukhlantsev analyzed the solutions only for Fe^{3+}; the pH range of his experiments was 1.9–2.95, from which he reported a solubility product $K_{so}(Fe^{3+}AsO_4^{3-}) = 10^{-20.24 \pm 0.58}$. Dove and Rimstidt claimed this solubility product to be too high, probably owing to particle-size effects.

Nishimura and Tozawa (1978) reported a change in the solubility product of scorodite with pH in the range pH = 1–4, as is indicated in Table 1. The calculated solubility product was based on the analysis of both Fe and As in solutions taken from both precipitation and dissolution experiments. A plot of the log of Fe and As concentrations vs. pH (taken from Nishimura and Tozawa) is shown in Figure 1; an obvious divergence of the Fe and As levels occurs at about pH = 2. The reason for this divergence was later explained by Robins (1981) as being due to the instability of ferric arsenate above pH = 2, where ferric hydroxide becomes the stable solid phase. The solubility of scorodite can therefore be regarded as incongruent above pH = 2.

Robins (1982) has shown the solubility of ferric arsenate (and other metal arsenic compounds) in the form of solubility diagrams (log activity vs. pH) and has shown (unpub. work) the effect of ferric arsenate complexes such as $FeHAsO_4^+$ and $FeH_2AsO_4^{2+}$ on the solubility of ferric arsenate. Figure 2 is a solubility diagram for ferric arsenate calculated by a computer mass-balance modeling program and based on precipitation and dissolution ex-

periments that take into account the suggested complexes. The stability region for ferric hydroxide, as shown on this diagram, results from the use of a free energy for FeOOH (amorphous) of -459.49 kJ·mol^{-1}, which would be consistent with colloidal particles of about 5-nm diameter. The incongruent point above which ferric arsenate is unstable occurs here at pH = 4.8, which seems to be too high, as the divergence of the As and Fe concentrations in a solution in equilibrium with ferric arsenate (Fig. 1) indicates the incongruent point at pH = 2. This point at pH = 2 could be obtained on the solubility diagram by assuming more negative free energy of formation for amorphous FeOOH (i.e., larger particle size).

The solubility data obtained by Chukhlantsev (1956), Nishimura and Tozawa (1978), and Robins and Glastras (unpub.) are plotted on the solubility diagram in Figure 2. Dove and Rimstidt's results are also shown on the diagram.

It is obvious that Dove and Rimstidt's results were taken in a region where ferric arsenate exhibits incongruent solubility, despite their claim to the contrary. The scatter of their analyses on the four samples is considerable and is possibly due to the fact that ferric arsenate is not stable in this region. The tan color of their product is also indicative of incongruent origin, as ferric arsenate is off-white. However, their solubility product is fortuitously close to what might be considered as a reasonable value. Nishimura and Tozawa's single experiment at pH = 1.82 gives a solubility product of $10^{-21.1}$, which is more reliably based as it seems to have been obtained in the region where ferric arsenate is stable. Chukhlantsev's results in the region of pH = 2 could also be treated separately to obtain a more reliable solubility product.

TABLE 1. Solubility of $FeAsO_4 \cdot 2H_2O$ at 25°C in dissolution and precipitation (taken from Nishimura and Tozawa, 1978)

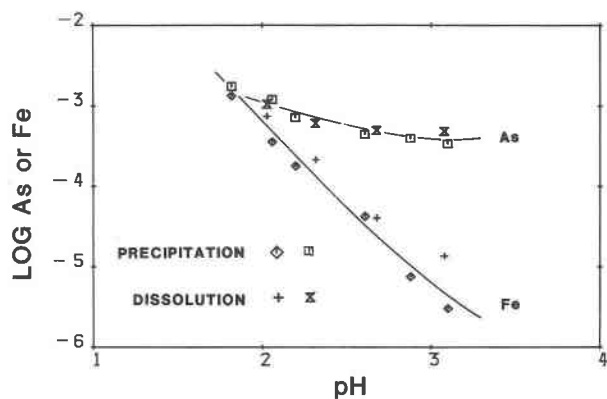| Type of experiment	Final pH	Fe (mg/L)	As (mg/L)	$-\log K_{so}$
Dissolution	1.82	73	130	21.1
	2.06	20	91	21.3
Fe:As mole ratio	2.20	10	53	21.5
	2.61	2.3	33	21.6
of $FeAsO_4$ = 1.02	2.88	0.41	29	21.8
	3.10	0.17	25	22.2
Precipitation	2.03	41	79	21.0
	2.32	12	45	21.3
Initial [Fe] = 0.005 M	2.68	2.2	37	21.5
Initial [As] = 0.005 M	3.08	0.75	36	21.4

Fig. 1. Fe and As concentrations associated with ferric arsenate in precipitation and dissolution; from Nishimura and Tozawa (1978) as in Table 1.

Robins and Glastras (unpub.) have obtained solubility data for ferric arsenate in the pH range 0–2, in the region of congruent solubility. This work was done in perchlorate, nitrate, and sulfate systems and takes into account complexing of Fe^{3+} and As^{5+}, as well as sulfate, nitrate, and perchlorate complexes, to give a free energy of formation for $FeAsO_4 \cdot 2H_2O$ of -1267.1 kJ·mol^{-1}. Dove and Rimstidt reported a free energy of formation for $FeAsO_4 \cdot 2H_2O$ of -1263.52 ± 0.28 kJ·mol^{-1}, assuming no complexing of Fe^{3+} and As^{5+}; however, such complexing is considerable. I would suggest that the free energies of formations hown in Table 2 better explain the solubility of scorodite (in perchlorate media). Dove and Rimstidt suggested that the solubility and free energy of formation given by them for ferric arsenate is more reliable than the data that can be obtained from the work of Chukhlantsev (1956). I would consider the data from both sources as inaccurate because of having been determined in the incongruent region.

Dove and Rimstidt also reported observations of As mineral parageneses and stated that there is a close spatial

TABLE 2. Free energies of formation for the various species considered in obtaining the stability diagram shown in Fig. 2

No.*	Species	$\Delta G^0_{f,298.15K}$ (kJ·mol^{-1})
1	Fe^{3+}	-16.99
2	$FeOH^{2+}$	-238.49
3	$Fe(OH)_2^+$	-459.19
4	$Fe(OH)_3^0$	-659.82
5	$Fe(OH)_4^-$	-830.06
6	$FeOOH(am)$	-459.49
7	$Fe_2(OH)_2^{4+}$	-489.95
8	$FeAsO_4(S)$	-792.87
9	$FeHAsO_4^+$	-788.27
10	$FeH_2AsO_4^{2+}$	-793.29
11	$H_3AsO_4^0$	-766.01
12	$H_2AsO_4^-$	-753.16
13	$HAsO_4^{2-}$	-714.59
14	AsO_4^{3-}	-678.39

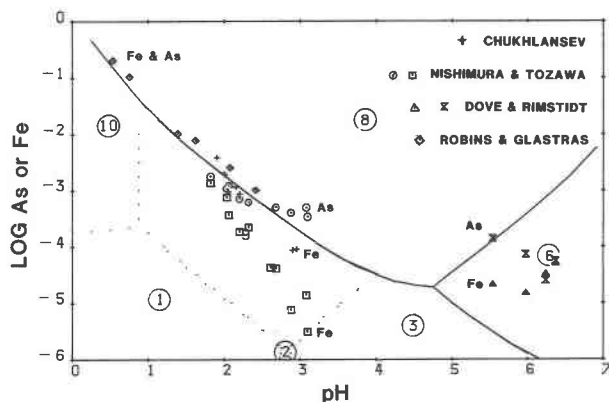* These numbers are used in Fig. 2 to denote the various species.

Fig. 2. Computer stability diagram for ferric arsenate, calculated from the data in Table 2 and showing experimental data from Nishimura and Tozawa (1978), Chukhlantsev (1956), Robins and Glastras (unpub.), and Dove and Rimstidt (1985).

relationship between arsenopyrite and scorodite. They suggested that the reaction that forms scorodite is

$$FeAsS + 14Fe^{3+} + 10H_2O \rightarrow$$
$$14Fe^{2+} + SO_4^{2-} + FeAsO_4 \cdot 2H_2O + 16H^+.$$
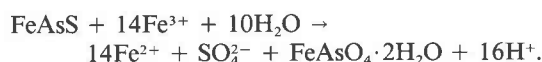
This equation may well represent a large part of an overall oxidation mechanism, but the oxidation of arsenopyrite is far more complex and dependent very closely on pH. Other minerals formed as part of this mechanism include orpiment and realgar (at low pH but in the region where scorodite is stable), but also pyrite, pyrrhotite, and loellingite. The mechanism for the oxidation of arsenopyrite needs some attention, as does the mechanism of its hydrothermal formation.

The stability of ferric arsenate is currently of particular concern in relation to its disposal as a residue from mineral-extraction operations. In many locations, ferric arsenate is dumped into tailings and residue-storage sites, on the assumption that it is stable and relatively insoluble. The conversion of ferric arsenate ($FeAsO_4 \cdot 2H_2O$) to ferric oxyhydroxide (α-FeOOH) does occur however, with the release of As to solution causing a potential environmental problem.

FURTHER DISCUSSION

The reply by Dove and Rimstidt (1987) to the above discussion of their 1985 paper suggests that although their scorodite solubility measurements were taken in the incongruent region where ferric hydroxide is the stable phase, the rate of decomposition of scorodite is slow enough to allow meaningful analysis of both As and Fe in solution. It has been my experience that if scorodite is placed into a solution with a pH greater than 3, there is the almost immediate formation of a surface layer of what seems to be a less-dense phase with a distinctly reddish-brown color. I have observed these changes using transmission electron microscopy, and I believe the surface layer to be ferric hydroxide.

The comments by Nordstrom and Parks (1987) on the Dove and Rimstidt (1985) paper suggest some aspects on which I can elaborate further.

Nordstrom and Parks (1987) agree that the region where scorodite will exhibit incongruent dissolution is where ferric hydroxide becomes the stable phase, and that region can be delineated with a pK_{so} for "ferric hydroxide." Literature values for pK_{so}, according to Flynn (1984), are in the range 37.1–39.0 for fresh to aged precipitate and, according to Langmuir and Whittemore (1971), depend on particle size. The literature values cited were originally obtained for precipitation of ferric hydroxide from pure solutions, not for a surface decomposition of one crystalline material (scorodite) to yield ferric hydroxide. Nordstrom and Parks (1987) also suggest that the decomposition of scorodite may occur with the formation of a surface coating of ferric hydroxide (I find this to be the case, as previously stated). Under these conditions, the apparent pK_{so} for ferric hydroxide is likely to be quite different from the values for a precipitate formed directly from solution, perhaps influenced by the particle size of the underlying scorodite.

In my laboratory, my coworkers and I have studied the formation and decomposition of scorodite fairly extensively. We find that when scorodite is precipitated at a pH just below the "incongruent point" (pH ≈ 1.8), it has a negative surface charge. If the pH is then raised, the surface potential becomes positive, and an examination of the precipitate by transmission electron microscopy (using a technique similar to that described by Green et al., 1974) would indicate that at this stage, the surface of the scorodite is coated with a separate phase, assumed to be ferric hydroxide. A separate investigation that involves the use of attenuated total-reflection Fourier-transform infrared spectroscopy also indicates the formation of surface ferric hydroxide. The comments by Nordstrom and Parks are certainly speculative, but I believe accurate.

We have also investigated the precipitation of ferric hydroxide onto scorodite particles as well as onto a variety of other crystalline materials. We find that the pH at which surface precipitation of ferric hydroxide occurs depends on the surface potential and particle size of the other phase and that in each case the ferric hydroxide can be characterized by a different "pK_{so}" value. In the case of ferric hydroxide on scorodite, "pK_{so}" = 39.5.

Nordstrom and Parks also comment on the use of free-energy values versus pK_{so} values. This really is a matter of consistency of data, and provided that the free energies of all of the species in the given system are quoted, then it is perhaps easier to manipulate free-energy data that relate to the individual components of the system. Many pK_{so} data have been calculated from free energies, as were those from Flynn (1984) quoted above. Dove and Rimstidt (1985) did not give all free energies in the system in specifying a free energy of formation for scorodite. My own preference for free energies is because the computer programs that we have developed for manipulating the data and plotting stability diagrams require an input of free energies of formation for the various species in the system. There is also, of course, the problem of correction for ionic strength (or correction to the molal infinite dilution standard state) which, in a system such as the Fe^{3+}-As^{5+}-H_2O system with the presence of various complex "ion pairs," becomes difficult.

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