

Solubility and stability of scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$: Discussion

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Dove and Rimstidt (1985) have reported a solubility-product constant for the mineral scorodite that has prompted several questions regarding their investigation. Solubility studies at 25°C can be an excellent source of equilibrium-constant and free-energy data, but only if carefully conceived, planned, and executed. Some of the more important criteria for a successful study include (1) demonstrated reversibility of the reaction (i.e., approaching equilibrium from both undersaturation and supersaturation); (2) variation of one or more critical parameters over a large enough range to test the stoichiometry of the reaction (e.g., vary pH for the solubility of metal hydroxides, or vary CO_2 for the solubility of carbonate minerals); (3) identification of the major reactions and minimization of their number by appropriate choice of experimental conditions; (4) proper characterization of the solid phase before and after the experiment to check for purity, including the appearance of secondary phases forming during the experiment; (5) use of solid-liquid separation and analytical procedures appropriate to the investigation; and (6) appropriate choice of models for converting the raw data to thermodynamic functions.

Before applying these criteria to the study under discussion, a summary of previous investigations seems pertinent. At least seven independent studies have been undertaken on solubilities in the Fe_2O_3 - As_2O_5 - H_2O (or ferric arsenate-water) system, of which five studies set out to measure scorodite solubility. Hartshorne (1927) studied this system at 25°C and found that the approach to equilibrium was very sluggish. He formed an amorphous 1:1 ferric arsenate solid that was more hydrated than scorodite and a new acid salt that might be approximated by the formula $\text{Fe}_2(\text{H}_2\text{AsO}_4)_4(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. Vierhherz and Krachevskaya (1936), as cited by Linke and Seidell (1958), found that scorodite decomposed completely in basic solutions of NaOH. Takahashi and Sasaki (1950) studied this system at 30°C and produced a more hydrated form than scorodite, along with two other phases. Chukhlantsev (1956) determined the solubility-product constants of several metal arsenates under acid conditions at 25°C and published the first K_{sp} for scorodite ($10^{-20.24}$). Nishimura and Tozawa (1978, quoted in Robins, 1987) measured the solubility of scorodite from both oversaturation and undersaturation at low pH (1.8–3.1). They found dissolution of scorodite to be increasingly incongruent with increasing pH above pH = 2. The remaining two studies are the unpublished work of Robins and Glastras (Rob-

ins, 1987) and the study by Dove and Rimstidt (1985). The results from previous work would strongly suggest that this system reaches equilibrium with extreme difficulty, that the formation of additional complex solids and aqueous species is quite likely, and that the best chance of simple interpretable behavior would be under strong acid conditions.

An examination of the ASTM X-ray Search Files and accredited minerals by the International Mineralogical Association, as found in the *Glossary of Mineral Species* (Fleischer, 1987), resulted in four additional minerals and two compounds that might form in ferric arsenate solutions: pharmacosiderite, $\text{Fe}_3^+(\text{AsO}_4)_3(\text{OH})_3 \cdot 6\text{H}_2\text{O}$; kankite, $\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$; liskeardite, $(\text{Al}, \text{Fe}^{3+})_3(\text{AsO}_4)(\text{OH})_6 \cdot 5\text{H}_2\text{O}$; angelellite, $\text{Fe}_2(\text{AsO}_4)_2\text{O}_3$; $\text{Fe}(\text{H}_2\text{AsO}_4)_3 \cdot \text{H}_2\text{O}$; and $\text{Fe}(\text{H}_2\text{AsO}_4)_3 \cdot 5\text{H}_2\text{O}$. Of these, only kankite is a 1:1 compound like scorodite. As these phases have been characterized by X-ray diffraction and have been accepted as distinct phases by the mineralogical and chemical communities, then the possibility that they may form in these systems must be recognized. If formed, they would complicate the approach to equilibrium, as Hartshorne (1927) found.

The suggested criteria for a successful solubility study of scorodite have rarely been satisfied. For example, Dove and Rimstidt (1985) did not demonstrate reversibility, as all of their measurements were from undersaturation. In only four of 20 runs was dissolution considered congruent. The stoichiometry of the reaction suggests that ferric hydroxide was precipitating because the four samples were in a group in which the pH decreased with time, probably as a result of Reaction 4 in Dove and Rimstidt (1985): $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O} = \text{H}_2\text{AsO}_4^- + \text{Fe}(\text{OH})_{3(s)} + \text{H}^+$. The experimental conditions of the four samples included solutions with an initial pH of 5.6, which is likely to be outside the stability (or metastability) range of scorodite based on previous investigations and the additional arguments presented here. These particular four samples, however, showed a constant value of pH or a slight increase, which is inconsistent with the pH trend shown in Figure 3 of Dove and Rimstidt (1985). Although Fe hydrolysis would decrease the pH, As hydrolysis would increase the pH. The measured pH would reflect the relative rates and amounts of these hydrolysis reactions.

Dove and Rimstidt (1987) have argued correctly that congruent dissolution in four of their experiments might have occurred if metastability preserved scorodite while

slow nucleation prevented precipitation of other potential reaction products. Unfortunately, congruency is neither proven by their arguments, nor is it sufficient evidence that the particular reaction had reached equilibrium saturation. Many substances dissolve congruently long before they reach equilibrium saturation, and kinetic problems can keep them from saturation for long periods of time.

Incongruency should, as argued by both Dove and Rimstidt and by Robins, yield an Fe^{3+} "hydroxide" of some sort. We will use the shorthand, $\text{Fe}(\text{OH})_3$, to represent any appropriate solid, from amorphous, hydrous "hydroxides" through ferrihydrites and goethite. Dove and Rimstidt have argued that $\text{Fe}(\text{OH})_3$ did not precipitate in the four critical experiments, citing congruency and failure to observe $\text{Fe}(\text{OH})_3$ as evidence. We doubt this conclusion for several reasons.

1. The possibility of ferric hydroxide microparticles forming in Dove and Rimstidt's experiments was tested by performing equilibrium computations (using a PC-version of MINEQL) and comparing the resultant ion activity products (IAP) for $\text{Fe}(\text{OH})_3$ to known values of its K_{sp} from the literature. The results are shown in Table 1. The negative log of the ion activity product for $\text{Fe}(\text{OH})_3$, pIAP [$\text{Fe}(\text{OH})_3$], falls in the range 34.3–35.5. Dove and Rimstidt have admitted oversaturation, but have argued that $\text{Fe}(\text{OH})_3$ nucleation was sufficiently delayed on the grounds that they did not observe such a precipitate. In view of the results from other investigators, however, precipitation is likely. The most soluble pK_{sp} from the literature is about 36.4, but one of the most careful studies indicates that freshly precipitating amorphous $\text{Fe}(\text{OH})_3$ has a $pK_{sp} = 37.3$ (Langmuir and Whittemore, 1971), and most other studies (Bohn, 1967; Norvell and Lindsay, 1982; Hsu and Marion, 1985) agree with this value as an upper limit. Hence, Dove and Rimstidt's solutions are two to three orders of magnitude higher in the IAP for $\text{Fe}(\text{OH})_3$, than solutions that are known to precipitate ferric hydroxide. In view of this high degree of apparent supersaturation and the fast nucleation and precipitation kinetics that are well established (e.g., Bohn, 1967; Langmuir and Whittemore, 1971), we conclude that there was inadequate separation of colloidal ferric hydroxide from the truly aqueous Fe^{3+} species.

We also computed IAPs for Nishimura and Tozawa's results, using the same equilibrium constants in MINEQL, and found two or more orders of magnitude undersaturation with respect to amorphous $\text{Fe}(\text{OH})_3$, but close to saturation for ferrihydrite or microcrystalline goethite (Schwertmann and Taylor, 1977). However, as the incongruency of the dissolved As and Fe in Nishimura and Tozawa's experiments strongly suggests loss of Fe from solution, and the pIAP is fairly constant, it seems probable that microcrystalline goethite formed in their experiments.

Whenever some type of ferric hydroxide has the potential to form, then the possibility must be considered that a surface coating of this phase on the scorodite grains

TABLE 1. Recalculated ion activity products from scorodite solubility experiments

Time (d)	Final pH	pIAP for scorodite (original values)	pIAP for scorodite (recalculated)	pIAP for $\text{Fe}(\text{OH})_3$
A. Results from Dove and Rimstidt's data				
5	5.97	21.88	21.84	35.20
8	6.36	21.71	21.50	34.29
25	6.23	22.14	22.00	34.60
57	5.53	21.32	21.37	35.48
B. Results from Nishimura and Tozawa's data				
	1.82	21.1	21.60	39.96
	2.06	21.3	21.62	39.73
	2.20	21.5	21.26	39.63
	2.61	21.6	21.85	39.22
	2.88	21.8	22.27	39.39
	3.10	22.2	22.46	39.33
	2.03	21.0	21.48	39.55
	2.32	21.3	21.65	39.23
	2.68	21.5	21.71	39.08
	3.08	21.4	21.78	38.73

Note: Recalculated using pK values of Baes and Mesmer (1976) and analytical data of Dove and Rimstidt (1985) or of Nishimura and Tozawa (1978) along with FeHAsO_4^{2+} and $\text{FeH}_2\text{AsO}_4^{2+}$ ion pairs of Robins (1987) and $p^*\beta_3 = 13.6$ for the stability constant of $\text{Fe}(\text{OH})_3$ (Ball et al., 1980).

slowed down the rate of dissolution. For example, the difference in degree of incongruency between the four selected samples of Dove and Rimstidt (1985) and the others that reached lower pH values may well be a kinetic effect. The samples of lower pH reacted to a greater extent, producing higher initial concentrations of Fe and As, of which the Fe largely precipitated or formed hydroxide particles of large enough grain size that they were not included in the analysis, whereas the four samples that were nearly congruent may have only slightly reacted because of the formation of a ferric hydroxide coating that kinetically inhibited further dissolution of scorodite. The resultant pIAP for scorodite on these four samples might be undersaturated because the scorodite never got a chance to fully dissolve.

2. Congruency cannot be regarded as proven by lack of solid reaction products because the methods used (observation of color, optical microscopy, and X-ray diffraction) are incapable of detecting small amounts of solid contaminants, especially if the solids are amorphous. Furthermore, because Fe^{3+} , like Al^{3+} (Smith and Hem, 1972), is notorious for production of unfilterable, uncentrifugable, colloidal or subcolloidal hydrolysis products en route to crystallization, any $\text{Fe}(\text{OH})_3$ produced by incongruent dissolution would not be recovered with the solid scorodite by simple centrifuging; thus it would not be detected by any method used for characterization of solids. Precipitation of $\text{Fe}(\text{OH})_3$ cannot be ignored because it represents incongruency; if analytical congruency is observed and $\text{Fe}(\text{OH})_3$ has precipitated, then some other process has removed As from solution as well.

3. Even if detectable $\text{Fe}(\text{OH})_3$ has not precipitated, congruency cannot be regarded as proven by apparent equality of total analytical concentrations of Fe and As in the

centrifugation supernatant, because colloidal $\text{Fe}(\text{OH})_3$ may have formed (scavenging some of the As; Pierce and Moore, 1982) and will not be removed by normal centrifugation; ultracentrifugation or ultrafiltration are required. If colloidal $\text{Fe}(\text{OH})_3$ does form during the experiment and does not centrifuge out with the scorodite, then analysis of the solution for total Fe will include both truly dissolved Fe and the colloidal material; thus the total Fe and total As concentrations will reflect apparent congruency. In fact, the concentration of dissolved Fe will be much less than analytical concentration, so a computed K_{sp} will be higher than it should be if colloidal $\text{Fe}(\text{OH})_3$ is not accounted for.

It seems very likely that either particulate or colloidal $\text{Fe}(\text{OH})_3$ has formed in even the near-congruent experiments of scorodite solubility reported by Dove and Rimstidt (1985). Accepting their argument that the color of their solid was appropriate for the pure scorodite, colloidal $\text{Fe}(\text{OH})_3$ seems to have been included in the total Fe analyses. If this is the case, then their estimate of the solubility-product constant is too high. The close similarity of their results to those of Nishimura and Tozawa (1978) should be considered fortuitous.

REFERENCES

- Baes, C.F., Jr., and Mesmer, R.E. (1976) The hydrolysis of cations. Wiley, New York, 489 p.
- Ball, J.W., Nordstrom, D.K., and Jenne, E.A. (1980) Additional and revised thermochemical data and computer code for WATEQ2—A computerized chemical model for trace and major element speciation and mineral equilibria of natural waters. U.S. Geological Survey Water-Resources Investigations Report 78-116, 109 p.
- Bohn, H.L. (1967) The $\text{Fe}(\text{OH})_3$ ion product in suspensions of acid soils. Soil Science Society of American Proceedings, 31, 641–644.
- Chukhlantsev, V.G. (1956) The solubility products of a series of arsenates. Journal of Analytical Chemistry (USSR), 11, 565–571.
- Dove, P.M., and Rimstidt, J.D. (1985) The solubility and stability of scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$. American Mineralogist, 70, 838–844.
- (1987) Solubility and stability of scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$: Reply. American Mineralogist, 72, 845–848.
- Fleischer, M. (1987) Glossary of mineral species, 5th edition. Mineralogical Record, Inc., Tucson, 227 p.
- Hartshorne, N.H. (1927) The system ferric oxide–arsenic acid–water at low concentrations of arsenic acid. Journal of the Chemical Society (London), 2, 1759–1768.
- Hsu, P.H., and Marion, G. (1985) The solubility product of goethite. Soil Science, 140, 344–351.
- Langmuir, D., and Whittemore, D.O. (1971) Variations in the stability of precipitated ferric oxyhydroxides. In J.D. Hem, Ed., Nonequilibrium systems in natural water chemistry, American Chemical Society Advances in Chemistry Series 106, 209–234.
- Linke, W.F., and Seidell, A. (1958) Solubilities: Inorganic and metal-organic compounds, A–I, vol. I, 1487 p. D. Van Nostrand Co., New York.
- Nishimura, T., and Tozawa, K. (1978) On the solubility products of ferric, calcium and magnesium arsenates. Bulletin of Research in the Institute of Mineral Dressing and Metallurgy (Tohoku University), 34, 20–26 (in Japanese).
- Norvell, W.A., and Lindsay, W.L. (1982) Estimation of the concentration of Fe^{3+} and the $\text{Fe}^{3+}(\text{OH})_3$ ion product from equilibria of EDTA in soil. Soil Science of American Journal, 46, 710–715.
- Pierce, M.L., and Moore, C.B. (1982) Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Research, 16, 1247–1253.
- Robins, R.G. (1987) The solubility and stability of scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$: Discussion. American Mineralogist, 72, 842–844.
- Schwertmann, U., and Taylor R.M. (1977) Iron oxides. In J.B. Dixon and S.B. Weed, Eds., Minerals in soil environments, p. 145–180. Soil Science Society of America, Madison, Wisconsin.
- Smith, R.W., and Hem, J.D. (1972) Effect of aging on aluminum hydroxide complexes in dilute aqueous solutions, chemistry of aluminum in natural waters, U.S. Geological Survey Water-Supply Paper 1827-D, 51 p.
- Takahashi, T., and Sasaki, K. (1950) Arsenates. V. Investigations into the three-component system: Ferric oxide–arsenic oxide–water. Journal of the Chemical Society (Japan), Industrial Chemistry Section, 53, 383–384.
- Vierhherz, I.S., and Krachevskaya, I.V. (1936) Zhurnal Prikladnoi Khimii, 9, 1909–1919.

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